**ELECTROCHEMICAL SUPERCAPACITORS** 

# MANGANESE DIOXIDE BASED COMPOSITE ELECTRODES FOR ELECTROCHEMICAL SUPERCAPACITORS

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### Abstract

Advanced electrodes based on  $MnO_2$  for the electrochemical supercapacitor (ES) application have been fabricated using electrochemical and chemical methods.

Electrosynthesis method has been utilized for the in-situ impregnation of manganese dioxide in commercial Ni plaque current collectors. Dipping-reduction, cathodic galvanostatic and reverse pulse electrosynthesis methods were investigated. The material loading was varied by the variation of the number of the dipping-reduction procedures in the chemical precipitation method or by the variation of charge passed in the electrochemical methods. The results obtained by different methods were compared. The dipping-reduction method offered the advantage of higher specific capacitances (SCs) at high scan rates, whereas other methods allowed higher material synthesis rate.

Cathodic electrolytic deposition (ELD) has been utilized for the fabrication of Ag-doped  $MnO_2$  films. The Ag-doped  $MnO_2$  films showed improved capacitive behavior and lower electrical resistance of 0.6 Ohm compared to pure  $MnO_2$  films. The highest SC of 770 F g<sup>-1</sup> was obtained at a scan rate of 2 mV s<sup>-1</sup> in the 0.5 M  $Na_2SO_4$  electrolyte.

Electrodes for ES application were fabricated by cathodic electrodeposition of MnO2

on CNTs, which were grown by chemical vapor deposition on stainless steel meshes. The MnO<sub>2</sub>-CNT nanocomposites showed excellent capacitive behavior and low electrical resistance of 0.5 Ohm.

Electrophoretic deposition (EPD) has been utilized for the deposition of composite  $MnO_2$ -multiwalled carbon nanotube (MWCNT) films for the ES application. Dopamine (DA), caffeic acid (CA), tyramine (TA), gallic acid (GA), polyacrylic acid (PAA) and pyrocatechol violet (PV) were shown to be effective and universal charging additives, which provide stabilization of  $MnO_2$  nanoparticles and MWCNTs in the suspensions. The influence of the structure of the organic molecules on their adsorption on the oxide nanoparticles has been investigated. We discovered that the number and site of OH group for dispersants were essential for the adsorption on oxide materials, and the number of aromatic ring was important for the adsorption on carbon materials. Pure CNT films were deposited using PV as a dispersant, which was the first time in literature to prepare pure CNT film using a dispersant. SCs decrease with increasing film thickness. SCs of composite  $MnO_2$ -MWCNT obtained using EPD were in the range of 350-650 F g<sup>-1</sup> depending on material loadings.

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## List of all Abbreviations and Symbols

AgNO <sub>3</sub> : silver nitrate	BA: benzoic acid
CA: caffeic acid	ChA: chromotropic acid
CNT: carbon nanotube	Co <sub>3</sub> O <sub>4</sub> : cobaltosic oxide
CV: cyclic voltammetry	CVD: chemical vapor deposition
DA: dopamine	DCA: 2,4-dihydroxycinnamic acid
DOPA: L-3,4-dihydroxyphenyl-alanine	DTA: differential thermal analysis
ELD: electrolytic deposition	EPD: electrophoretic deposition
ES: electrochemical supercapacitor FTIF	R: Fourier transform infrared spectroscopy
GA: gallic acid	IrO <sub>2</sub> : iridium dioxide
KCl: potassium chloride	KMnO <sub>4</sub> : potassium permanganate
mM: millimole per liter	MnO <sub>2</sub> : manganese dioxide
MoO: molybdenum oxide	MWCNT: multiwalled carbon nanotube
NaOH: sodium hydroxide	Na <sub>2</sub> SO <sub>4</sub> : sodium sulfate

NiO: nickel oxide	PAA: polyacrylic acid
PCA: p-coumaric acid	PV: pyrrocatechol violet
QCM: quartz crystal microbalance	RuO <sub>2</sub> : ruthenium dioxide
SC: specific capacitance	SEM: scanning electron microscopy
SnO <sub>2</sub> : tin dioxide	TA: tyramine
TCA: trans-cinnamic acid	TEM: transmission electron microscopy
TGA: thermogravimetric analysis	V <sub>2</sub> O <sub>5</sub> : vanadic oxide
XRD: X-ray diffraction	ZrO <sub>2</sub> : zirconium dioxide

ZrOCl<sub>2</sub> 8H<sub>2</sub>O: zirconium oxychloride

## **Declaration of Academic Achievement**

My supervisor Dr. Igor Zhitomirsky and I designed all the experiments and I fabricated, tested and analyzed all the samples for the ES application. Technician Wenhe Gong did the XRD test for my samples. Technician Steve Koprich helped me with the SEM test. Technician Fred Pearson did the TEM test. Technician Steve Kornic did the FTIR test. Technician Frank Gibbs did the TGA and DTA test. Prof. Xueliang Sun helped us grow CNT on stainless steel mesh by chemical vapor deposition.

## **Chapter 1 Introduction**

Recent years has witnessed considerable concerns in terms of climatic changes and rising depletion of fossil fuel, thus resulting in much concentration on the investigation and development of the alternative and renewable resources. Compared with other sustainable resources, i.e. sun, wind, water and etc., electrical energy storage systems have played a larger role in our daily lives due to their availability on demand. At the forefront of the electrical energy storage systems are electrochemical supercapacitors (ESs), which are capable of delivering a large amount of energy in a short response [1]. ESs have several advantages such as high power density, high cycle efficiency, fast charge/discharge response and long cycle life, compared with batteries. Thus, ESs have already been regarded as the solution to the mismatch between the fast growth for the power requirement of device and the disability of battery to discharge efficiently at high rates.

 $MnO_2$  has been considered as a promising electrode material for electrochemical ES because of its low cost and excellent capacitive performance in the aqueous electrolytes [2-4]. Impressive progress has been achieved in the fabrication of fine  $MnO_2$  powders with different types of manganese dioxides, including amorphous and nanocrystalline phases [2, 5, 6]. Thin  $MnO_2$  films [7] exhibited a specific capacitance (SC) of ~700 F g<sup>-1</sup>. However, the SC decreased with increasing film thickness due to

the low conductivity of  $MnO_2$ . The values of SC reported in the literature [8, 9] are usually in the range between 100 and 250 F g<sup>-1</sup>, which are far from the high theoretical SC (1380 F g<sup>-1</sup>) of  $MnO_2$  [4].

Recent studies highlighted the influence of the electrode porosity on the electrochemical performance [10-12]. The porous structure of  $MnO_2$  is beneficial for the ion access of the electrolyte to the surface of the material. Furthermore, many successful efforts have been made in the area of the fabrication of composite materials, where improved electronic conductivity has been achieved by the use of CNTs and other conductive additives [13-16]. Our ultimate goals are to synthesize new electrode materials such as nanostructured  $MnO_2$  particles, develop  $MnO_2$ -CNT composites, and then fabricate the advanced ES device for scientific and industrial applications.

## **Chapter 2 Literature Review**

#### **2.1 Fundamental aspects of energy storage**

Electrical energy can be reserved in two fundamentally different modes: (1) in batteries, as potentially available chemical energy that requiring Faradaic oxidation and reduction to release charges when both anode and cathode are present; and (2) in capacitors, as positive and negative electrical charges that residing on the interface between the electrodes and the electrolyte. This physical adsorption process is also known as non-Faradaic electrical energy storage [1]. For mode (1), chemical interconversion between the materials on the anode and cathode must take place. This irreversible process involving phase change of electrode materials will restrict the cycle life to one to several thousand charge and discharge cycles [1]. For mode (2), only an excess and a lack of electrical charges have to be stored on each plate of capacitors, and no chemical or phase changes are involved. Theoretically, electrical charges that are stored in this way can have an unlimited cyclability [1].

The major and characteristic difference between batteries and capacitors is that the charge and discharge processes of capacitors are nearly mirror image of each other, while those processes for batteries are rarely the same. As shown in Figure 2-1a, the rectangular-shaped CV of RuO<sub>2</sub> shows good reversibility and capacitance behaviors. The Pb/PbCl<sub>2</sub> battery electrode shows asymmetry image of current response in the



whole range of scanned potentials (Figure 2-1b).

Figure 2-1 (a) Symmetric CV for  $RuO_2$  in 1 M  $H_2SO_4$  solution, and (b) typical irreversible CV for Pb/PbCl<sub>2</sub> battery electrode [1].



Figure 2-2 Difference of charge and discharge relationship for batteries and capacitors [1].

Another characteristic feature that distinguishing batteries and capacitors is that, as shown in Figure 2-2, the potential difference of batteries is ideally constant throughout the whole charge and discharge processes, while the potential difference of capacitors linearly changes with the amount of stored charges. In a capacitor device being charged, every addition of charge has to do electrical work against the charges that have already stored in the capacitor, gradually increasing the potential difference between two electrodes. However, during the process of charging a battery, the potential difference, independent of the charges that added, remain constant as long as two electrode materials coexist.



Figure 2-3 Diagram illustrating the difference of energy stored by a capacitor and a battery [1].

Therefore, the significance of the energy density difference between capacitors and batteries can be understood by Figure 2-3. The line  $V_B$  is the constant voltage for a battery cell while full charge Q is stored; while the line  $V_C$  is the plot of voltage across a capacitor device which is being charged to the same charge Q. The integral VQ under line  $V_B$  and  $V_C$  corresponds to the energy for batteries and capacitors, respectively. From Figure 2-3, we can see that the energy of charging the capacitor to a terminal voltage  $V_B$  with charge Q is half of the energy of charging the battery to the

same terminal voltage  $V_B$  with the same charge Q. All in all, the maximal energy E that a battery can store is the product of charge Q and the potential difference V, i.e., E=QV. While the maximal energy stored by a capacitor should be 1/2 QV, which could also be expressed as 1/2  $CV^2$ , due to the equation Q=CV. Furthermore, the maximal power P of a capacitor device can provide is shown in the following:

$$P = \frac{V^2}{4ESR}$$
(2-1)

where ESR represents the equivalent series resistance (ESR) [17].

#### 2.2 Energy storage mechanisms

Due to different energy storage mechanisms, ESs could be classified into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors [1]. EDLCs could demonstrate 1 to 5 % pseudocapacitance out of its total capacitance due to the Faradaic reactivity of the surface functional groups, which are generated by the preparation or pretreatment process of the electrode materials such as carbon nanotube, activated carbon and carbon black. The pseudocapacitors usually show 5-10 % electrostatic double-layer capacitance, which is proportional to the electrochemically accessible interfacial area.

#### **2.2.1 Electrical double-layer capacitors**

An EDLC utilizes the non-Faradaic capacitance arising from the electrostatic charge

accumulation at the double-layer, and only an access or deficit of electrons have to be established on charge and the reverse on discharge. Virtually, no chemical phase or composition changes are involved in the charging and discharging processes of an EDLC, thus EDLCs are highly reversible and possess an almost unlimited cyclability, on the order of  $10^5$ - $10^6$  times without significant degradation.

The charging and discharging processes of an EDLC (taking the porous carbon electrode as an example) could be understood as the following [18]:

On the anode:

$$\mathbf{E}_{s} + \mathbf{B}^{-} \leftrightarrow \mathbf{E}_{s}^{+} / / \mathbf{B}^{-} + \mathbf{e}^{-}$$
(2-2)

On the cathode:

$$E_s + D^+ + e^- \leftrightarrow E_s // D^+$$
(2-3)

The overall reaction:

$$E_s + E_s + D^+B^- \leftrightarrow E_s^+ / / B^- + E_s^- / / D^+$$
(2-4)

where  $E_s$  designates the surface of the carbon electrode, // designates the double-layer where charges accommodate, and D<sup>+</sup> and B<sup>-</sup> are referred as the cations and anions of the electrolyte, respectively. During the charging process, as shown in the equations (2-2) and (2-3), electrons are transported from the anode to the cathode through the external circuit; at the meanwhile, anions move to anode and cations move to cathode. During the discharging process, electrons are transported from cathode to anode, and ions are released from the electrode surfaces to the bulk of the electrolyte. As shown in the overall reaction, the salt  $D^+B^-$  in the electrolyte is consumed during the charging process. In one word, only electrons would be transported to and from the electrode surfaces through the external circuit, and anions and cations of the electrolyte moved within the solution to the charged surfaces. Theoretically, no chemical or phase changes are involved or no charge transfer takes place on the interface of electrode and electrolyte [1]. This is the reason why the charging and discharging processes of an EDLC are highly reversible, leading to an almost unlimited cyclability.

The double-layer capacitance could be calculated by using the following equation [1]:

$$C = \frac{A\varepsilon}{4\pi d}$$
(2-5)

where A represents the surface area of the electrode, d represents the thickness of the double-layer, and  $\varepsilon$  represents the electrolyte dielectric constant. As shown in Figure 2-4, the charge accumulation is established across the double-layer, which is composed of a compact layer (Helmholtz layer) with the thickness about 0.5-0.6 nm, equivalent to the diameters of the solvent molecules and ions reside on it, and a wider region of diffuse layer with dimensions over 1 to 100 nm, depending on the concentration of the electrolyte. It is just owing to the small thickness of the compact molecular interfacial layer that a quite larger SC could arise for an EDLC, compared to that of a conventional capacitor, where the separation distance is within the micro meter range.



Figure 2-4 General representation of the structure of the double-layer [1].

#### 2.2.2 Pseudocapacitors

Pseudocapacitance is Faradaic in origin, involving charge transfer across the double-layer, which is the same as in the charging and discharging of batteries, but such capacitance originates due to some specific applied thermodynamic conditions, the electrode potential (V) is some continuous function of the charge (q) that passes through the electrode, so that a derivative dq/dV exists, which is tantamount to and measurable as the capacitance. The capacitance possessed by such systems is referred to as pseudocapacitance since it arises in a quite different way from that exhibited by an EDLC, where ideally no charge transfer takes place and capacitance originates in

an electrostatic way. The most studied material for the pseudocapacitor electrode is the ruthenium oxide. In contrast to the mechanism of an EDLC, Faradaic charge transfer takes place in the pseudocapacitor electrode.

The charging and discharging processes of the ruthenium oxide pseudocapacitor could be expressed in the following manner [18]:

On the anode:

$$HRuO_2 \leftrightarrow H_{1-\delta}RuO_2 + \delta H^+ + \delta e^-$$
(2-6)

On the cathode:

$$HRuO_2 + \delta H^+ + \delta e^- \leftrightarrow H_{1+\delta}RuO_2$$
(2-7)

The overall reaction:

$$HRuO_{2} + HRuO_{2} \leftrightarrow H_{1-\delta}RuO_{2} + H_{1+\delta}RuO_{2}$$
(2-8)

Here,  $0 < \delta < 1$ , while RuO<sub>2</sub> and H<sub>2</sub>RuO<sub>2</sub> designate the anode and the cathode in a full charged state, respectively. As shown in the equations (2-6) and (2-7), electrons moved through the external circuit during the charging and discharging processes. At the meanwhile, protons transported between two electrodes. However, there is no net ion exchange between the electrolyte and the electrode, and the concentration of the electrolyte does not change during charge-discharge cycle, which is opposite to that of an EDLC. The pseudocapacitance is usually much larger than the electrical double-layer capacitance, because there are more protons exchanged for pseudocapacitors than the ions involved in the accumulation for the capacitance process of an EDLC.

#### **2.2.3** Factors that influence the capacitance



Figure 2-5 Schematic diagram of the pore size network of an activated carbon [1].

For the conventional capacitors, the capacitance is usually tens of Faradays per gram of the electrode material due to the small surface area of the two-dimensional planar electrodes, and other problems such as diffusion or migration of ions could exist for such planar electrodes. The limitation of the two-dimensional planar electrodes could be greatly attenuated, if porous electrodes having high surface area and three-dimensional nature are employed.

The high surface area and three-dimensional porous electrodes could be achieved through the activation process. As shown in Figure 2-5, micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) are randomly produced in activated carbon [1]. According to the research of Conway et al. [1], it is the mesopore who makes the main contribution to the capacitance, while the micropore which dominates

most of the surface area (as shown in Figure 2-6) only makes a small contribution because the electrolyte ions could not penetrate, which means the smaller accessible surface area of electrodes.



Figure 2-6 Surface area distribution vs. pore width for two carbon preparations, M10 and M30 [1].

However, some scientists [19] claimed that there would be an anomalous increase in capacitance at pore size < 1 nm. As shown in Figure 2-7, when the pore size decreased from region I (more than twice the size of the solvated ions, Figure 2-7B) to region II (less than twice the size of the salvation ions, Figure 2-7C), the capacitance decreased because the compact layer was distorted and the effective surface area for the formation of double-layer was reduced. When the pore size continuously decreased to less than 1 nm (Figure 2-7D), corresponding to the size of the salvation shell, the salvation shells of ions were highly distorted so that ion center could approach closer to the electrode surface, leading to enhanced capacitance.



Figure 2-7 (A) Plot of normalized capacitance vs. average pore size for carbon. (B to D) Images of solvated ions residing in pores with distance between adjacent pore walls (B) greater than 2 nm, (C) between 1 and 2 nm, and (D) less than 1 nm [19].

### 2.3 Electrode materials for supercapacitors

As mentioned above, electrochemical properties and charging mechanisms of ESs strongly depended on the type of electrode materials used. Generally, the electrode materials for the ES applications were classified into three categories: (1) carbon materials with high specific surface area, for instance activated carbon [20], carbon nanotube [21] and graphene [22, 23], (2) conductive polymers, for example polypyrrole [24, 25], polyaniline [26-28] and polythiophene [29, 30], and (3) transition metal oxides such as RuO<sub>2</sub> [31, 32], MnO<sub>2</sub> [33, 34], NiO [35, 36], Co<sub>3</sub>O<sub>4</sub> [37], IrO<sub>2</sub> [38], SnO<sub>2</sub> [39], V<sub>2</sub>O<sub>5</sub> [40, 41] and MoO<sub>2</sub> [42, 43].

#### **2.3.1** Carbon materials

Carbon materials are considered as promising electrode materials for the ES industrial applications due to their advantages of low cost, high specific surface area, good electronic conductivity, abundance, non-toxicity, good chemical stability, high temperature stability and easy processing [44]. The charging mechanism of carbon materials-based ESs is the same as that of the conventional capacitors which utilized EDLC capacitance at the interface of the electrodes and the electrolyte. Therefore, EDLC capacitance predominately depended on the specific surface area of the electrodes. A host of techniques have been given to improve the specific surface area, including plasma surface treatment with  $NH_3$ , steam or  $CO_2$  activation, heat treatment and acid or alkaline treatment [10, 45-49].

It is supposed that the larger the specific surface area, the larger the SC. However, the SC of ESs does not increase with the increase of specific surface area. Since not all the specific surface area of ESs is electrochemically accessible to the electrolyte ions. Other than specific surface area, pore size is another important parameter that needs to be seriously considered for the selection of ES electrode materials. Largeot et al. [50] reported that both macro-pores and micro-pores had little or no contribution to the total capacitance of ES, and the pore size that can yield maximal capacitance was quite close to the size of solvated electrolyte ions. Nevertheless, the long-held axiom that the pore sizes smaller than the solvated electrolyte ions do not contribute to

charge storage has been challenged recently by Chmiola et al.[19]. They claimed that the solvation shell of the electrolyte ions could be highly distorted to allow closer approach of solvated electrolyte ions to the electrode surface and lead to enhanced capacitance, when the pore sizes were smaller than the sizes of solvated electrolyte ions (~1 nm).

Furthermore, surface functionalization has also been regarded as an effective way to enhance the SC of carbon-based ES [51-53]. It was shown that the surface functional groups or heteroatoms can improve the conductivity and increase the hydrophilicity and wettability of carbon materials, leading to fast electrolyte ions transport within electrode materials. It was believed that the existence of functional groups can also generate faradaic redox reaction, resulting in 5-10 % increase of the total capacitance [1].

#### 2.3.1.1 Activated carbon

Activated carbon is a popular and most extensively investigated material for the fabrication of EDLC electrodes due to its low cost, high electronic conductivity and high specific surface area. Its SCs can vary over a wide range of 40-220 F g<sup>-1</sup>, depending on the type of electrolyte used and how it is processed [54, 55]. Du et al. [55] investigated the effects of activated carbon structure and surface groups on the

electrochemical performance of ESs. It was noteworthy that the SC of activated carbon-based ESs significantly depended on the crystal orientation of their surfaces. Higher percentage of edge orientation than basal orientation could lead to higher EDLC capacitance and stronger bonding of functional groups on the surface. It was shown that two categories of surface functional groups, which had capacitor-like and battery-like behaviors, respectively, were revealed. The surface functional groups with capacitor-like behaviors could be included.

Xu et al. [56] fabricated activated carbon fiber cloth electrodes with high EDLC capacitance and good cycle stability using CO<sub>2</sub> activation. High SC of 168 F g<sup>-1</sup> for the electrode tested in 6 M KOH aqueous solution was obtained at a carbonization temperature of 900 °C. A relatively lower carbonization temperature treatment (600 °C) to the electrode could result in a higher SC of 208 F g<sup>-1</sup>.

#### 2.3.1.2 Carbon nanotubes

Owing to the good electronic conductivity, high mechanical strength and high specific surface area, considerable attention has been given to CNTs [57]. An's group [48, 49] investigated the key factors determining the performance of ES, fabricated using single-walled carbon nanotubes (SWCNTs). They obtained a maximum SC of 180 F  $g^{-1}$ , a power density of 20 kW kg<sup>-1</sup> and an energy density of 7 Wh kg<sup>-1</sup> in 7.5 M KOH
solution. It was demonstrated that heat treatment was necessary to increase the capacitance and reduce the resistance. Show et al. [58] prepared EDLC with polarizable electrodes containing CNTs. The EDLC demonstrated a low ESR of 2.5  $\Omega$ . The low resistance could be in favor of the preparation of capacitors with high powder density, according to equation (2-1).

### 2.3.1.3 Graphene

Graphene, a two-dimensional carbon material, has been considered as another good candidate for the ES application due to its excellent chemical stability, superior mechanical property and good electronic conductivity [23, 59]. Yan's group [23] fabricated high-performance EDLC based on graphene. It was shown that the wrinkling of the graphene can reduce the stacking and agglomeration, resulting in increased specific surface area. High SC of 349 F g<sup>-1</sup> was obtained for the electrode tested at a scan rate of 2 mV s<sup>-1</sup> in 6 M KOH solution. Moreover, after 5000 cycles the SC of the electrode had 8 % increase, demonstrating good electrochemical stability. Liu et al. [59] prepared graphene-based ESs with a specific energy density of 85.6 and 136 Wh kg<sup>-1</sup> at room temperature and 80 °C, respectively, at a current density of 1 A g<sup>-1</sup>, which were comparable to that of nickel metal hydride battery. It was shown that curved graphene can reduce restacking, thus make full utilization of the specific surface area and SC.

### **2.3.2 Conductive polymers**

Conductive polymer-based pseudocapacitors have attracted much attention due to the high conductivity in doped state, low cost, high charge storage capacity of the polymers and low environment impact [24-26]. The pseudocapacitance arises owing to the fast and reversible redox reactions related to the  $\pi$ -conjugated polymer chains [60, 61]. When oxidation occurred, ions moved to the polymer; while reduction took place, ions were released from the polymer into the electrolyte. These redox reactions existed in the entire bulk of the polymer, not only on the surface. Moreover, these redox reactions did not generate any structural modifications, such as phase changes, so these redox reactions were highly reversible.

### 2.3.2.1 Polypyrrole

Kim et al. [62] deposited thin polypyrrole layers with thickness of 5-10 nm on carbon fibers using an in situ chemical polymerization. The thickness of polypyrrole could be readily controlled by the variation of pyrrole concentration in solution. It was shown that the SCs of polypyrrole tested in 6 M KOH solution were 588 and 550 F g<sup>-1</sup> at scan rates of 30 and 200 mV s<sup>-1</sup>, respectively. Zhang et al. [63] prepared polypyrrole films on stainless steel substrate from 0.1 M pyrrole aqueous solution containing 0.5 M p-toluene sulphonic acid by pulse galvanostatic method. It was shown that high SCs of 403 and 281 F g<sup>-1</sup> were obtained in 1 M H<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> solution, respectively.

#### 2.3.2.2 Polyaniline

Li et al. [64] fabricated polyaniline films on stainless steel using electropolymerization method. High SC obtained from the polyaniline film was 608 F  $g^{-1}$ , which was 30 % of the theoretic SC (2000 F  $g^{-1}$ ). It was demonstrated that the significant difference between theoretic and experimental SC was due to the low utilization of polyaniline films.

#### 2.3.2.3 Other polymers

Conductive polymer poly(tris(4-(thiophen-2-yl)phenyl)amine) was utilized as an electrode material for the ES application [65]. Remarkably high SC of 990 F g<sup>-1</sup> was obtained at a scan rate of 50 mV s<sup>-1</sup> in 100 mM tetrabutylammonium tetrafluoroborate in acetonitrile. At a current density of 4 mA cm<sup>-2</sup>, the electrode presented an energy density of about 25 Wh kg<sup>-1</sup> and a power density of about 6 kW kg<sup>-1</sup>. Li et al. [66] prepared poly(3,4-ethylenedioxythiphene) by chemical oxidization using FeCl<sub>3</sub> and p-toluenesulfonic acid as oxidant and dopant, respectively. It was shown that the SC of poly(3,4-ethylenedioxythiphene) films could increase from 72 to 100 F g<sup>-1</sup> by ultrasonic irradiation.

#### 2.3.3 Transition metal oxides

Transition metal oxides are regarded as the next generation electrode materials for the ES applications due to their high specific capacitance, low cost, large voltage window and low ESR [1, 67]. In one word, transition metal oxide can provide higher energy density for ES than conventional capacitors and electrochemical stability than conductive polymers.

# 2.3.3.1 RuO<sub>2</sub>

Among the transition metal oxides,  $RuO_2$  is the most promising and extensively investigated material for the ES application due to its high SC, excellent rate capacity, high conductivity, long cycle life, large voltage window, as well as highly reversible redox reactions [31, 38, 68]. The charging mechanism for  $RuO_2$  in acidic condition is presented as the following [1]:

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x$$
(2-9)

According to equation (2-9), fast exchange between proton and cation is in favor of reversible redox reaction and high SC. Fu et al. [69] investigated the proton dynamics of hydrous  $RuO_2$  anneal at different temperatures. It was reported that the content of structural water is crucial for the hydrogen transfer in the bulk of hydrous ruthenium oxide, which could occur through hopping of alkaline ions and protons between H<sub>2</sub>O and OH<sup>-</sup> sites. Moreover, the SC of hydrous RuO<sub>2</sub> strongly depended on the content of

structural water. Long et al. [70] reported that  $RuO_2 \cdot 0.5H_2O$  had a high SC of 900 F g<sup>-1</sup>. However, when the structural water content decreased to  $RuO_2 \cdot 0.03H_2O$ , the SC reduced to 29 F g<sup>-1</sup>, and the SC of the anhydrous ruthenium oxide  $RuO_2$  was only 0.75 F g<sup>-1</sup>.

# 2.3.3.2 MnO<sub>2</sub>

As mentioned above, hydrous ruthenium oxide had remarkably high SC. However, its disadvantages of high cost, low abundance and toxicity limit its commercialization of ESs. Alternatively, researcher had spent considerable effort into discovering cheap and environmental friendly materials for the ES application. Since the initial report by Lee and Goodenough [71], MnO<sub>2</sub> has attracted enormous attention and been regarded as the next generation material for the ES application owing to its low cost, environmental friendliness, high SC and large voltage window [1, 72]. MnO<sub>2</sub> mainly utilized the charge-transfer pseudocapacitance arising from the reversible Faradaic reaction on the electrode surface. The proposed charging mechanism could be expressed as the following [2, 7]:

$$MnO_2 + D^+ + e^- \leftrightarrow MnO_2D \tag{2-10}$$

where  $D^+=Li^+$ ,  $Na^+$ ,  $K^+$  and  $H^+$ . The equation (2-10) indicates that high ionic and electronic conductivity of the active material is necessary in order to utilize the high theoretic SC of 1370 F g<sup>-1</sup> [4, 73].

Crystallinity and structural water content were believed to be two important factors that affect the electrochemical performance of MnO<sub>2</sub>. High crystallinity can give rise to higher conductivity, but reduction of specific surface area and limitation of protonation reaction could occur simultaneously. On the other hand, low crystallinity can result in the porous microstructure of MnO<sub>2</sub>, but electronic conductivity would be reduced. Therefore, the annealing technique could be an effective solution to the crystallinity dependent conductivity of MnO<sub>2</sub>. Good electrochemical behaviors were observed when MnO<sub>2</sub> was annealed at appropriate temperatures [74, 75]. Similar as ruthenium oxide, the structural water content of MnO<sub>2</sub> also play an important role for the transportation of electrolyte ions and electrochemical behaviors of ESs. Toupin et al. [73] reported that the annealing treatment up to 200 °C could lead to the removal of both physically and chemically adsorbed water, resulting in poor pseudocapacitance and ionic conductivity.

Another important factor that affects the electrochemical performance of  $MnO_2$  is the crystal structures. Extensive research [72, 76, 77] had unveiled that  $MnO_2$  had several typical crystal structures, such as  $\alpha$ -,  $\beta$ -, and  $\delta$ -MnO<sub>2</sub>. Particularly,  $\alpha$ - and  $\beta$ -MnO<sub>2</sub> had tunnel structures while  $\delta$ -MnO<sub>2</sub> had a layered structure as shown in Figure 2-8 by birnessite.



Figure 2-8 Structural transition of MnO<sub>2</sub> during material synthesis [77].

It was believed that different synthesis conditions could result in different crystal structures of MnO<sub>2</sub>, which had different conductivity and electrochemical behaviors. As shown in Figure 2-8, with the precursor acidity gradually increased, crystal structures of MnO<sub>2</sub> can result in a progression from layer structured  $\delta$ -MnO<sub>2</sub>, subsequently to tunnel structured  $\alpha$ - and  $\beta$ -MnO<sub>2</sub>. However,  $\delta$ -MnO<sub>2</sub> phase would predominate if alkaline solutions were used. Donne et al. [77] fabricated  $\delta$ -MnO<sub>2</sub> by a hydrothermal process, and they claimed that  $\delta$ -MnO<sub>2</sub> had a much higher SC than that of  $\alpha$ - and  $\beta$ -MnO<sub>2</sub>. Devaraj et al. [78] fabricated  $\delta$ -MnO<sub>2</sub> by a redox reaction between KMnO<sub>4</sub> and MnSO<sub>4</sub> in aqueous solution. High SC of 236 F g<sup>-1</sup> was obtained at a current density of 0.5 mA cm<sup>-2</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution.

#### 2.3.3.3 NiO

NiO is an alternative candidate for the ES applications in alkaline solution due to its low cost, low toxicity and high SC (theoretic SC of 3750 F  $g^{-1}$ ) [79, 80]. The charging mechanism of NiO in KOH electrolytes could be presented in the following [36]:

$$NiO + OH^{-} \leftrightarrow NiOOH + e^{-}$$
 (2-11)

It was reported that preparation process and annealing technique can significantly affect the electrochemical performance of NiO [36]. NiO synthesized by a chemical process [36] had a maximal SC of 167 F g<sup>-1</sup>, while porous NiO prepared by a sol-gel technique [81] had a maximal SC of 250 F g<sup>-1</sup>. While the SC of 696 F g<sup>-1</sup> could be obtained after being annealed at 250  $\degree$  [82].

#### 2.3.3.4 Co<sub>3</sub>O<sub>4</sub>

Another candidate of ES electrode material is  $Co_3O_4$  due to its excellent reversible redox behavior, high conductivity, large surface area and good chemical stability [37]. The charging mechanism of  $Co_3O_4$  as an electrode material of pseudocapacitors is as the following [83]:

$$Co_3O_4 + H_2O + OH^- \leftrightarrow 3CoCOOH + e^-$$
 (2-12)

Wang et al. [84] fabricated mesoporous  $Co_3O_4$  microspheres with a unique crater-like morphology using mesoporous silica material as a template. Small ESR of 0.4  $\Omega$  and SC of 102 F  $g^{-1}$  were obtained. Kandalkar et al. [37] prepared Co<sub>3</sub>O<sub>4</sub> film from the CoCl<sub>2</sub> precursor. High SC of 165 F  $g^{-1}$  was obtained in the 1 M aqueous KOH electrolyte at a scan rate of 10 mV s<sup>-1</sup>.

### 2.3.3.5 Other oxides

Many other materials, such as SnO<sub>2</sub>, IrO<sub>2</sub> and MoO<sub>2</sub>, have also been exploited and investigated as electrode materials for ES applications. For instance, hydrous IrO<sub>2</sub> demonstrated a SC of 550 F g<sup>-1</sup> [85]. However, its high cost, even higher RuO<sub>2</sub>, limited its ES applications. Rajeswari et al. [86] synthesized MoO<sub>2</sub> nanorods by thermal decomposition of tetrabutylammonium hexamolybdate in an inert atmosphere. SC of 140 F g<sup>-1</sup> was obtained in 1 M H<sub>2</sub>SO<sub>4</sub> solution.

### 2.3.4 Composites

### 2.3.4.1 Composites based on MnO<sub>2</sub>

In order to address the disadvantage of low electronic conductivity of  $MnO_2$ , conductive agents, such as activated carbon, CNTs and graphene are utilized extensively [87-89]. The addition of these conductive agents not only formed a three-dimensional porous conductive network for the fast transfer of electrons and ions, but also increased the active specific surface area of  $MnO_2$ , preventing its

agglomeration.

#### 2.3.4.1.1 MnO<sub>2</sub>-activated carbon

Lin et al. [88] synthesized  $MnO_2$  at different pH and temperatures and then deposited into activated carbon by chemical impregnation. Maximal SC of 460 F g<sup>-1</sup> was obtained in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 25 mV s<sup>-1</sup>.

#### 2.3.4.1.2 MnO<sub>2</sub>-carbon nanotube

Nam et al. [87] fabricated a three-dimensional nanostructure of MWCNTs and MnO<sub>2</sub> by electrodeposition of amorphous MnO<sub>2</sub> layers onto MWCNTs network. High SCs of 127 and 471 F g<sup>-1</sup> in a 1 M KCl solution were obtained for MnO<sub>2</sub> film and MnO<sub>2</sub>-MWCNTs composite, respectively, based on the mass of oxide. The difference of SC could be because the addition of MWCNTs increased the surface area and promoted the fast transfer of electrons and ions. Amade et al. [90] fabricated MnO<sub>2</sub>-MWCNTs composites for the ES application by anodic electrodeposition of MnO<sub>2</sub> on vertically aligned CNTs matrix. High SC of 642 F g<sup>-1</sup> was obtained in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup>. The electrode had a good rate capacity during the 800 cycles at a current density of 1 mA cm<sup>-2</sup>.

#### 2.3.4.1.3 MnO<sub>2</sub>-graphene

Chen et al. [91] fabricated  $MnO_2$ -graphene composites as an electrode material for the ES application by anodic electrodeposition on a graphene sheet. High SC of 328 F g<sup>-1</sup>, an energy density of 11.4 Wh kg<sup>-1</sup>, and a power density of 25.8 kW kg<sup>-1</sup> were obtained in a 1 M KCl solution at a current density of 1 mA cm<sup>-2</sup>. Fan et al. [92] fabricated asymmetric ES using  $MnO_2$ -graphene as the anode and activated carbon as the cathode. Wide voltage window of 1.8 V and high energy density of 51.1 Wh kg<sup>-1</sup> were obtained. The maximal SC of 113.5 F g<sup>-1</sup> was obtained at a scan rate of 1 mV s<sup>-1</sup> in an aqueous Na<sub>2</sub>SO<sub>4</sub> solution. Moreover, the ES exhibited excellent rate capacity with 97 % SC maintained after 1000 cycles.

# 2.3.4.2 Composites based on conductive polymers

It was believed that conductive polymers based composites could enhance the cycling stability, conductivity and mechanical stability [62]. The addition of carbon materials, especially CNTs, into conductive polymer, is believed to be an effective way to increase the specific surface area and SC.

### 2.3.4.2.1 Polypyrrole-carbon nanotube

For example, Hughes et al. [93, 94] fabricated polypyrrole-MWCNT composites using

electrodeposition from 0.5 M pyrrole solution containing MWCNTs. Porous microstructure of polypyrrole coated MWCNTs was obtained. The maximal SC of the composite was 192 F  $g^{-1}$ . The excellent electrochemical behavior could be attributed to the high conductivity, large surface area and easy access of electrolyte ions into the three-dimensional nanostructure.

#### 2.3.4.2.2 Polyaniline-carbon nanotube

A tube-covering-tube nanostructured polyaniline-CNT composites was fabricated using electrodeposition of polyaniline on the vertically aligned CNTs [95]. The composites had a porous structure, a large surface area and excellent conductivity. Superior electrochemical behaviors, such as high SC of 1030 F  $g^{-1}$  in 1 M H<sub>2</sub>SO<sub>4</sub> solution, excellent rate capability of 95 % capacity retention at 118 A  $g^{-1}$  and high stability of 5.5 % capacity loss after 5000 cycles were obtained.

#### 2.3.4.3 Other composites

Metal oxides are also good candidates to boost the electrochemical performance of conductive polymers. For example, a symmetric ES with two  $MnO_2$ -polypyrrole electrodes showed a high SC of about 180 F g<sup>-1</sup> and a good stability of 10 % loss after 4000 cycles, compared to the pure polypyrrole electrodes with 50 % loss in specific capacitance [96].

# 2.4 Fabrication methods

A number of methods, such as electrodeposition, sol-gel deposition and chemical in-situ precipitation, have been utilized for the fabrication of ES electrodes. In this chapter, electrodeposition will be presented and discussed.

### 2.4.1 Fundamental aspects



Figure 2-9 Schematic of electrophoretic deposition (EPD) and electrolytic deposition (ELD) [97].

The electrodeposition can be categorized into two techniques: electrolytic deposition (ELD) and electrophoretic deposition (EPD). Figure 2-9 demonstrates the difference between ELD and EPD. EPD utilizes the stable suspension of ceramic nanoparticles, while ELD uses the electrolysis of metal salts [97]. Due to the much higher deposition rate of EPD, much thicker films can be obtained by using EPD, while thin and nanostructured film can be anticipated if ELD is utilized, as shown in Figure 2-10.



Figure 2-10 Thickness of films deposited using ELD and EPD [97].



Figure 2-11 Schematic illustration of the internal energy as a function of separation distance between two particles in suspension [98].

Depending on the type of charged colloidal particles and starting salts, both anodic and cathodic deposition can be carried out for EPD and ELD, respectively. It should be noted that anodic electrodeposition offers the advantage of room-temperature processing. However, anodic electrodeposition on stainless steel and other low-cost metallic substrates presents difficulties, related to the anodic oxidation and dissolution of the substrates. Moreover, another factor that limits its wide application is regarding possible materials to be deposited by this method.

An important role in the electrodeposition process is played by the dispersion and stability of the suspension [99], which could be carefully manipulated by the interparticle forces, i.e. the van der Waals attraction and electrostatic repulsion. Since the van der Waals attraction for any given colloidal suspension is independent of almost any changes made to the suspension, the dispersion and stability of the suspension could be controlled by the modification of the electrostatic double-layer repulsion. A theoretic estimate of the relationship in terms of the separation distance between particles by using the combination of van der Waals attraction and electrostatic double-layer repulsion has been described by the classic DLVO theory which was established by Derjaguin and Landau and Verwey and Overbeek. According to this theory, the dispersion and stability of the suspension is controlled by the total internal energy of interaction  $(V_T)$ , which is determined by the simple sum of van der Waals attraction force (V<sub>A</sub>) when particles are approaching each other due to the Brownian motion they are undergoing and electrostatic double-layer repulsion  $(V_R)$ , which is exhibited as following:

$$\mathbf{V}_{\mathrm{T}} = \mathbf{V}_{\mathrm{A}} + \mathbf{V}_{\mathrm{R}} \tag{2-13}$$

The van der Waals attraction force  $(V_A)$  in the above equation could be expressed as the following:

$$V_{A} = \frac{-A}{12\pi D^{2}}$$
(2-14)

where A is the Hamaker constant and D is the particle separation. The repulsive potential  $V_R$  is a far more complex function, and it could be represented as the following:

$$V_{\rm R} = 2\pi\epsilon a\xi^2 e^{-\kappa D} \tag{2-15}$$

where a is the particle radius,  $\pi$  is the solvent permeability,  $\kappa$  is a function of the ionic composition and  $\xi$  is the zeta potential.

Figure 2-11 shows the schematic illustration of the internal energy as a function of separation distance between two particles in suspension. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together (Figure 2-11). But if the particles collide with sufficient energy due to the Brownian motion to overcome that energy barrier, the attractive force will be dominant to make particles adhere together. Therefore if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However, if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place.



Figure 2-12 Three main mechanisms of suspension stabilization [100].

In order to maintain the stability of the colloidal suspension, the repulsive force must be dominant. Basically speaking, there are three main mechanisms, electrostatic, steric and electrosteric stabilization, to make the suspension well-dispersed and stable, as shown in Figure 2-12. The three mechanisms are very essential when hydrophilic macromolecules are absorbed or bounded to the particle surface. The steric stabilization involves that polymers are added to the suspension, resulting in the adsorption of polymers onto the particle surface and prevention of the particle surfaces coming into close contact. If enough polymers are adsorbed, the coating is thick enough to keep particles separated by the steric repulsion between the polymer layers, while the van der Waals attraction forces are too weak to cause the particles to coagulate. The steric stabilization forces are commonly short-range force. The electrostatic stabilization is generally based on the mutual repulsion of like electrical charges. When combined with appropriate functionalities, some polymers can present both electrostatic and steric stabilization, commonly referred as electrosteric stabilization. Polymers, providing electrosteric stabilization, are usually called ionic polymeric dispersants. Such dispersants are very sensitive to the pH and the ionic strength of solutions [100].

Compared to the electrostatic stabilization, the steric stabilization is very simple, due to simple addition of a suitable polymer. However, sometimes it is very difficult to flocculate the suspension if it is required. In some cases, the polymer could be very expensive and will bring some undesired property to the suspension system. For example, when the ceramic material is fired or sintered, the polymer additive will be burned out, leading to shrinkage and defect in the finished cast.

Commonly, when a charged particle is placed in the suspension, a surface charge, either by ionization of surface groups or by adsorption of charged particles, will exist on the particle. The surface charges will modify the distribution of the surrounding ions, leading to the formation of two layers around the charged particles, i.e. double layers will form. One is very dense, called the stern layer; the other is relatively loose, called the diffuse layer, just as shown in Figure 2-4. If the particles move, for instance under the Brownian motion, these layers also move as a part of the particles. The boundary of this layer is defined as the slipping plane. The potential at the slipping plane is defined as the zeta potential, which is one of the main factors that mediate interparticle interactions. It is well-known that particles with high zeta potential of the same charge sign, either positive or negative charged, will repel each other. And it has

been demonstrated that high zeta potential is in favor of the stabilization of the suspension. For example, the Faraday gold sol made in the 1850's now is still a stable suspension due to its high zeta potential.

#### 2.4.2 Electrolytic deposition

Recently, ELD has aroused considerable interest for the fabrication of nanostructured thin oxide films for biomedical, electronic, electrochemical and catalytic applications [12, 97, 101]. This method has the advantages of low-temperature processing and easily controllable film composition by varying the bath content [102]. ELD generates colloidal particles from ceramic precursor solutions by redox reactions for subsequent deposition on the electrode-electrolyte interface [97, 102]. The deposit composition can be readily varied by the solvent, pH, additives, temperature, precursors and current density [103, 104]. Furthermore, ELD can strictly control the deposit composition, thickness, uniformity and deposition rate [97].



#### **2.4.2.1 Deposition kinetics and mechanisms**



Hydroxide

Oxide

Figure 2-13 ELD of ceramic films and powders [105].

Ion

As shown in Figure 2-13, ELD can be classified into two processes: the redox change process and the electrogenerated base process [105], which are also called anodic ELD and cathodic ELD, respectively. In the anodic ELD, at first the pH of the solution is adjusted so that the initial ceramic precursor with low oxidation state can be stable. Subsequently, when electrical current is passing between two electrodes the ceramic precursor is oxidized at the electrode surface. And we can anticipate the preparation of a metal ion or complex with a higher oxidation state, which is not stable and can be readily hydrolyzed into hydroxide film on anodic substrate. Oxide film is obtained by thermal dehydration of hydroxide film. While metal ions or complexes undergo hydrolysis by electrogenerated bases to form hydroxide films, which can be dehydrated into oxide film subsequently for the cathodic ELD process. A great number of electrochemical reactions are available for the electrogenerated base, some

of which are listed as the following [102, 105, 106]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (2-16)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (2-17)

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10OH^-$$
 (2-18)

$$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$$
(2-19)

$$ClO_4^- + 4H_2O + 8e^- \rightarrow Cl^- + 8OH^-$$
(2-20)

In the cathodic ELD, the hydrolysis reactions aforementioned in equation (2-16) can consume  $H_2O$  to generate OH<sup>-</sup> ions, resulting in a significant increase of pH and the coagulation of colloidal particles near the cathode [97]. Of particular importance for the deposition process is the generation rate of the OH<sup>-</sup> ions. While the generation rate of the OH<sup>-</sup> ions is higher than the consummation rate of the OH<sup>-</sup> ions, the extra OH<sup>-</sup> ions that are not consumed at the electrode surface will be transferred away through diffusion and electric field. Under this circumstance, high pH boundary moves away from the electrode surface, leading to low adhesion of the films on the substrate. A host of cations can undergo hydrolysis by an electrogenerated base to form colloidal particles of hydroxides, oxides and peroxides [107-109]. The deposition mechanism is the flocculation of particles by the electrolyte [110]. It is also noted that the pH changes, even at open circuit, will result in the deposit formation [110]. Furthermore, some other factors can also affect the deposit formation. For example, the flocculation of particles can be enhanced by the electrical field [110] and coulombic attraction [111].

#### 2.4.2.2 Anodic electrolytic deposition of MnO<sub>2</sub>

Owing to the advantage of room temperature processing, anodic ELD has attracted considerable attention for the preparation of  $MnO_2$  film for the application of ES [74, 112-115]. The  $MnO_2$  particles formation mechanism can be presented as the following [87]:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$$
 (2-21)

Hu et al. [113, 114] fabricated amorphous hydrous  $MnO_2$  films using anodic ELD on a graphite substrate, and systematically investigated the effect of manganese precursors on the deposition rate. It was shown [113] that, compared to  $MnSO_4$  5H<sub>2</sub>O,  $MnCl_2$  4H<sub>2</sub>O and  $Mn(NO_3)_2$  4H<sub>2</sub>O,  $Mn(CH_3COO)_2$  4H<sub>2</sub>O was a better precursor for the preparation of  $MnO_2$  film due to its high deposition rate at a relatively low deposition potential, as shown in Figure 2-14. SC decreased with increasing scan rate. High SC of about 300 F g<sup>-1</sup> was obtained at a scan rate of 5 mV s<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution for the amorphous hydrous  $MnO_2$  films.



Figure 2-14 Linear sweep voltammogram curves measured at 2 mV s<sup>-1</sup> in 0.1 M 1  $MnSO_4$  5H<sub>2</sub>O, 2  $MnCl_2$  4H<sub>2</sub>O, 3  $Mn(NO_3)_2$  4H<sub>2</sub>O and 4  $Mn(CH_3COO)_2$  4H<sub>2</sub>O [113].

Chang et al. [74, 112] reported that hydrous  $MnO_2$  with amorphous microstructures could be deposited using anodic ELD from  $Mn(CH_3COO)_2$  solution on a carbon substrate. It was shown that the crystallinity and microstructure of  $MnO_2$  could be influenced by the deposition potential [112]. SC decreased with increasing scan rate. The SC of 240 F g<sup>-1</sup> could be obtained at a scan rate of 5 mV s<sup>-1</sup> in 2 M KCl solution. In another study [74], it was demonstrated that cycle stability of  $MnO_2$  films could be enhanced with increasing annealing temperature.

Moreover, phase-controlled  $MnO_2$  nanoparticles with different types of crystal structures have been systematically investigated using anodic ELD [116]. Hexagonal  $\epsilon$ -MnO<sub>2</sub> nanoparticles were prepared from MnSO<sub>4</sub> solution using anodic ELD; defective rock salt MnO<sub>2</sub> nanoparticles were obtained from MnSO<sub>4</sub> solution containing ethylenediaminetetraacetic acid disodium salt using anodic ELD; and

defective antifluorite  $MnO_2$  nanoparticles were produced from  $MnSO_4$  solution including sodium citrate salt. It was demonstrated that crystal structure of  $MnO_2$ nanoparticles significantly influenced their capacitive behaviors. Furthermore, one anomalous trend that SC did not decrease with increasing scan rate was observed.

#### 2.4.2.3 Cathodic electrolytic deposition of MnO<sub>2</sub>

The problem related to anodic oxidation and dissolution of metallic current collectors can be avoided using the cathodic ELD [11, 12, 117]. In this method,  $MnO_2$  films were obtained by cathodic reduction of  $Mn^{7+}$  species from  $KMnO_4$  or  $NaMnO_4$  solutions, using the following reaction:

$$MnO_4 + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$
(2-22)

Wei et al. prepared MnO<sub>2</sub> films from 20 mM KMnO<sub>4</sub> solution using cathodic ELD at a constant current density of 2 mA cm<sup>-2</sup> [11]. The deposited MnO<sub>2</sub> mass could be readily varied by the variation of deposition time. High SC of 353 F g<sup>-1</sup> was obtained for a 45  $\mu$ g cm<sup>-2</sup> MnO<sub>2</sub> film tested in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solutions at a scan rate of 2 mV s<sup>-1</sup>. In another study [12], MnO<sub>2</sub> films were obtained using cathodic ELD from aqueous NaMnO<sub>4</sub> solution at a constant current density of 2 mA cm<sup>-2</sup>. The obtained films had typical pore sizes of ca. 100-200 nm and were crack-free. High SC of 220 F g<sup>-1</sup> was achieved for a 90  $\mu$ g cm<sup>-2</sup> film at a scan rate of 2 mV s<sup>-1</sup> on a Ni substrate.

The polymer assisted cathodic ELD [118, 119] was recently reported, and in this method polymer-metal complexes were utilized for the preparation of nanostructured  $Mn_3O_4$  deposits, which were electrochemically converted into  $MnO_2$  films. The polymer-metal complex was formed when metal ions ( $Mn^{2+}$ ) were added into an electrically neutral polymer polyethylenimine (PEI). Subsequently, cathodic ELD from solutions containing PEI- $Mn^{2+}$  complexes could lead to the preparation of cathodic deposits including  $Mn_3O_4$  nanoparticles and PEI. The addition of PEI as a binder enabled the formation of adherent  $MnO_2$  films and reduced film cracking after during. High SC of 425 F g<sup>-1</sup> was obtained at a scan rate of 10 mV s<sup>-1</sup>.

### 2.4.3 Electrophoretic deposition

Last decade has witnessed considerable interest in EPD for the processing of advanced ceramic materials and coatings with a wide range of novel applications for the electrochemical, electronic, catalytic and biomedical fields [120-122], not only in the research study but also in the industrial investigation due to its cost effectiveness requiring simple apparatus, fabrication of nanostructured and high purity deposits, and the feasibility to produce uniform deposition on the substrates with complex shape as well. It is well known that EPD is an excellent technique for the surface modification of materials and the deposition of polycrystalline patterned films with controlled crystalline texture, functionally graded composites and multi-component films [97,

123, 124]. EPD has been discovered in 1808 as the Russian scientist Ruess observed the phenomenon that an electric field could induce the movement of clay particles in water. Until 1933, EPD was first practically used to deposit thoria particles on the platinum substrate cathode as an emitter for the application of electron tube, which was patented in USA [98]. Hamaker [87, 125] was the first scientist who studied the EPD of ceramics, and only in the 1980 was the EPD method used in the advanced ceramics field.

EPD is achieved via the motion of charged particles in the suspensions to a certain electrode under an applied electric field, followed by the particle coagulation and deposition on the electrode surface. In order to effectively utilize this technique, it is imperative to prepare stable suspensions containing well-dispersed colloidal particles which are free to move once an electric field is applied. The electrostatic repulsion and high electrophoretic mobility of inorganic particles in the suspension are very critical for good dispersion. The repulsion should be reduced at the electrode surface, where the process of particle coagulation to form a deposit happens.



Figure 2-15 Schematic illustration of electrophoretic deposition process. (a) Cathodic EPD; (b) Anodic EPD [124].

Compared to other advanced techniques, EPD process is quite versatile because it could be easily modified for a specific application. For instance, any shape of substrates could be used for the EPD only if minor adjustment in terms of the electrode design and positioning is made. Especially, through control of the deposition time and applied voltage, the thickness and mass could be readily modified although EPD is a wet process. As shown in Figure 2-15, there are two types of EPD process depending on which electrode the deposition happens. When the particles are positively charged, under the applied electric field the deposition will happen on the cathode, which process is called the cathodic EPD (Figure 2-15a). The deposition of negatively charged particles on the anode is named the anodic EPD (Figure 2-15b). By proper modification of surface charge on the particle, we could realize two types of EPD. However, one problem related to the anodic oxidation and dissolution of the metallic substrate, which makes the measurement of deposit mass difficult, usually exists when the anodic EPD is used in aqueous suespensions. Therefore, cathodic EPD

is frequently used.

#### 2.4.3.1 Deposition kinetics and mechanism

The EPD technique has been successfully utilized in numerous applications, but the exact mechanism that could completely explain the phenomenon of the deposition on the electrode is not well understood [126]. Researchers have tried to explain the particle interaction, the kinetic deposition and deposition. Four fundamental mechanisms are: the flocculation by particle accumulation, the particle charge neutralization mechanism, the electrochemical particle coagulation mechanism and the electrical double layer (EDL) distortion and thinning mechanism [98, 123, 124, 126, 127]. For instance, Bouyer and Foissy [128] proposed that EPD was a two-step process which involved the migration of charged particle towards the oppositely charged electrode under an applied electric field and the particle accumulation and deposition on the electrode to form a dense deposit requiring that the particles lose their charges on the surface of the electrode.

Hamaker and Verway [87, 125] first pointed out that the stable suspension was the premise for the successful formation of the deposit by EPD and they observed that formation of the deposit by EPD was similar with the formation of the sediment through gravitation. In particular, for both types of process the pressure exerted by the

incoming particles makes the particles next to the deposit conquer the interparticle repulsion. Therefore, the fundamental effect of the applied electric field is to move the particles to electrode surface for the accumulation of the deposit. The mechanism is called flocculation by particle accumulation.

Grillon et al. [129] proposed the particle charge neutralization mechanism, which presented that the charged particles would be neutralized when they reached the electrode and then became static. However, this mechanism is only plausible for the deposition of single particle and monolayers. This mechanism could not explain the deposition requiring longer deposition time or the process where the electrode-particle contact is prevented, such as the deposition occurring on the semi-permeable membrane between two electrodes.

The electrochemical particle coagulation mechanism suggested that the reduction of repulsion between particles was due to the increase of the electrolyte concentration in the vicinity of the electrode surface, leading to the decrease of the zeta potential and flocculation of particles to form a deposit. This mechanism is only valid when OH<sup>-</sup> ions are generated near the electrode surface such as in the suspension containing water or alcohols [124].

Based on the idea of distortion and thinning of electrical double-layer, Sarkar et al. [98]

proposed the electrical double layer (EDL) distortion and thinning mechanism, which explained the invalidation of the electrochemical particle coagulation mechanism when there is no increase of electrolyte concentration near the electrode surface. Figure 2-16 demonstrates the schematic representation of the deposition mechanism due to the electrical double-layer distortion and thinning. With the movement of the double-layer system, the fluid flow and the applied electric field will distort the double-layer system to make it thinner ahead and wider behind the particles. Moreover, the cations in the liquid also move along with the positively charged particle to the cathode. The counter ions in the extended 'tail' will tend to react with these accompanying cations. As a result of this chemical reaction, the double layer around the 'tail' of the particle will be thin so that the next incoming particle can approach close enough and induce deposition.



Figure 2-16 Schematic representation of the deposition mechanism due to the electrical double-layer distortion and thinning [98].

#### 2.4.3.2 Dispersion and electrophoretic deposition of MnO<sub>2</sub>

 $MnO_2$  films were prepared by EPD using sodium alginate as a dispersant [33, 130], which ensured the stabilization of aqueous solutions containing  $MnO_2$  nanoparticles. It was shown that crack-free  $MnO_2$  films were prepared due to the binding property of sodium alginate. Moreover, sodium alginate offered pH dependent charges to the  $MnO_2$  nanoparticles and facilitated the EPD through the formation of electrically neutral alginic acid on the electrode surface. The thickness of deposits could be readily controlled by the variation of deposition time and voltages. The composition of deposits could be varied by changing the concentrations of  $MnO_2$  nanoparticles or sodium alginate in aqueous solution. High SC of about 150 F g<sup>-1</sup> was obtained for a film tested in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 2 mV s<sup>-1</sup>.

Chen et al. fabricated  $MnO_2$  films by EPD after  $MnO_2$  nanoparticles were dispersed in ethanol solution containing several drops of  $H_2SO_4$  [131] or stabilized in ethyl alcohol solution containing several drops of sulfuric acid [132]. High SCs of 236-275 F g<sup>-1</sup> were obtained in 1 M Na<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 25 mV s<sup>-1</sup>. High cycle efficiency of 85 % after 300 cycles was obtained.

#### 2.4.3.3 Dispersion and electrophoretic deposition of carbon nanotubes

Chemical oxidation in acids at high temperatures was used in order to functionalize

CNTs with carboxylic groups and other oxygen-containing groups. These acidic groups can electrostatically stabilize CNTs by developing negative charges on the surface of CNTs [133, 134]. However, after acid treatment, structural defects were introduced, leading to the reduction of electrical and mechanical properties. Alternatively, the physical adsorption of polymers is widely used to overcome the van der Waals attraction and to stabilize CNTs in solutions. For instance, micelles of cross-linked copolymer polystyrene-block polyacrylic acid (PS-b-PAA) can encase CNTs and disperse them by the steric stabilization [135, 136]. Salts, such as  $Mg(NO_3)_2$   $\cdot 6H_2O$  [137] and Ni(NO<sub>3</sub>)<sub>2</sub>  $\cdot 6H_2O$  [138], were also used to prepare stabilized CNTs suspensions. However, impurities were introduced into the CNTs films during deposition. CNTs can also be dispersed when coated by ionic surfactants. For example, anionic sodium dodecyl sulfate (SDS) is widely used to decrease CNT agglomeration in water [136, 139]. The hydrophobic tail of SDS can adsorb on CNT surface through hydrophilic interaction, and the hydrophilic head of SDS can enable CNTs to be negatively charged [139]. Therefore, CNTs with adsorbed SDS can be dispersed through electrostatic stabilization. However, the control of the amount of SDS in the CNT suspension will present difficulties at concentrated CNT suspension due to the phase separation controlled by the competition between the dispersion entropy and the depletion attraction [140].

### 2.4.3.4 Electrophoretic deposition of MnO<sub>2</sub>-carbon nanotube composites

Chun et al. [141] prepared MnO<sub>2</sub>-MWCNTs nanocomposites on Ni substrate from isopropyl alcohol containing hydrochloric acid by EPD. The as-received MWCNTs were modified in nitric acid first to be functionalized with carboxylic groups. Subsequently, the MWCNTs were added into a KMnO<sub>4</sub> solution containing MnSO<sub>4</sub>, resulting in the preparation of MnO<sub>2</sub>-MWCNTs nanocomposites [141]. It was shown that the nanocomposites had a SC of about 470 F g<sup>-1</sup> at the scan rate of 100 mV s<sup>-1</sup> and can preserve about 86 % of the original SC after 6000 charge discharge processes. Moreover, the SC increased and the charge transfer resistance decreased with the increase of annealing temperature, due to the increase of MnO<sub>2</sub>/Mn<sub>3</sub>O<sub>4</sub> ratio. In another study [142], a similar procedure for the preparation of MnO<sub>2</sub>-MWCNTs nanocomposites was presented. At first, MWCNTs were purified in acid and deposited on stainless steel in aqueous solution by EPD. Subsequently, the stainless steel substrate with deposited MWCNTs was dipped into KMnO<sub>4</sub> solution containing  $\rm H_2SO_4$  for the preparation of MnO\_2-MWCNTs nanocomposites. High SC of 870 F  $\rm g^{-1}$ was obtained. However, such specific capacitance value might not accurate due to the oxidation of MWCNTs by KMnO<sub>4</sub> and difficulties for the calculation of deposit mass.

### 2.4.4 Electropolymerization



Figure 2-17 Electropolymerization mechanism of polypyrrole [24].

Polypyrrole with different microstructures, such as nanobelts, nanobricks and nanosheets, was fabricated from pyrrole aqueous solution containing KNO<sub>3</sub> using electropolymerization for the application of ES [24]. KNO<sub>3</sub> was added in order to control the size of polypyrrole nanostructure [143]. The mechanism of polypyrrole was presented in Figure 2-17. The neutral pyrrole was oxidized into a cation followed by the aromatization and oxidation of dimer, which could be reoxidized to the cation [25]. High SC of about 590 F g<sup>-1</sup> was obtained for polypyrrole multilayer nanosheets tested in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 2 mV s<sup>-1</sup>. The high SC can be due to the higher Brunauer-Emmett-Teller (BET) surface area of 37.1 m<sup>2</sup> g<sup>-1</sup> for polypyrrole nanosheet than polypyrrole nanobelts and nanobricks.

Vertically aligned polyaniline nanotubes with diameters around 200 nm were electropolymerized on titanium nanotube templates [26]. The morphology and nanostructures of polyaniline strongly depended on the scan rates during the electropolymerization. High SC of 740 F  $g^{-1}$  was obtained and only 13 % of SC was lost after 1100 cycles.

### 2.4.5 Other methods

Sol-gel process [75, 144-146], chemical precipitation [147-149] and hydrothermal process [150-152] were also utilized for the preparation of electrodes for the ES application. Lin et al. [75] fabricated MnO<sub>2</sub> electrode on graphite substrates by sol-gel process. The MnO<sub>2</sub> precursor sols were prepared at room temperature by adding manganese acetate into a citric acid solution containing n-propyl alcohol. Subsequently, ammonium hydroxide was added into the solution to modify the pH of the solution. Until a transparent sol was formed, the graphite substrate was dipped into sols and dried. MnO<sub>2</sub> films, consisting of Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> phases, could be obtained after the annealing process. High SC of 230 F g<sup>-1</sup> was obtained.

Li et al. [147] produced  $MnO_2$  nanorods by chemical precipitation from a mixture of  $KMnO_4$  and  $Mn(CH_3COO)_2$  aqueous solution containing the hexadecyl trimethyl ammonium bromide as the structure-directing agent. Subsequently, as-prepared  $MnO_2$  nanorods were annealed in order to get good crystallinity. SC of 166 F g<sup>-1</sup> was obtained.

Yan et al. [150] fabricated porous  $MnO_2$  films on nickel foam substrates by hydrothermal process from KMnO<sub>4</sub> aqueous solution containing SDS. High SC of 240 F g<sup>-1</sup> for a 1 mg cm<sup>-2</sup> film tested in a 1 M Na<sub>2</sub>SO<sub>4</sub> solution was obtained at a current density of 1 A g<sup>-1</sup>. The prepared MnO<sub>2</sub> films had a good reversibility and cycling stability.

# 2.5 Application of ESs

Due to their high power density and long cycle life, ESs have been widely used in different kinds of applications, such as telecommunication, automotive, transportation, etc., serving as the power back-up, alternating power source, power assistant and regenerative braking.

### **2.5.1** Power tools

Recently, a cordless capacitor powered screwdriver, capable of being charged in 90 s, was brought into the market. The screwdriver, as shown in Figure 2-18, consists of 6 2.7 V, 100 F ES cells, totally possessing about 1.5 kJ stored energy. Although the high rate lithium ion battery with the same dimension as the ES could provide almost 20 times more energy, it generally has limited charging-discharging cycles and only a fraction of its stored energy could be used effectively. The capacitor powered screwdriver, as shown in Figure 2-18, is aimed at the home "do-it-yourself" market.
Due to the infrequent use nature, the home used screwdriver is always in a state of partial charge or fully discharge. The first step is to charge the screwdriver, which could take 10 minutes or even longer for the one with a battery. However, the capacitor powered screwdriver could be fully charged in 90 s, or even shorter if only temporary use is needed.



Figure 2-18 Capacitor powered screwdriver that is fully charged in 90 s [153].

Another tool that utilizes the high power density of ES is a power tube cutter produced by the Superior Tool Co. [153]. The power cutter has ESs parallel connected with the rechargeable battery to boost its efficiency, which makes it possible to cut as much as possible tubes on each battery charge.

#### 2.5.2 Energy conservation application

At major seaports, the wide utilization of capacitor system in the rubbery-tired gantry crane proves that the capacitor system is cost-effective. One primary function of capacitor system in this application is to preserve energy that would be otherwise wasted in the repetitious up and down movement of the crane. The second function of the capacitor system is to replace the large size of diesel engine, allowing a size reduction. As shown in Figure 2-19, during the loading and unloading container of the crane, the capacitor system as pointed in Figure 2-19 preserves energy in the loading lowering that is then used to raise the next load, resulting in improved efficiency and greatly reduce the gas emission.



Figure 2-19 Hybrid diesel electric rubbery tired gantry seaport crane with a supercapacitor energy storage system [153].

## **Chapter 3 Objectives**

The objectives in my research could be expressed in the following:

- (i) To prepare nanosized and well-dispersed  $MnO_2$  through the reduction of  $KMnO_4$  by using different reducing agents, and investigate the formation mechanism of the nanostructured  $MnO_2$  with different phases (i.e. birnessite, cryptomelane, amorphous);
- (ii) To develop new methods for the fabrication of composite  $MnO_2$ -MWCNT with the improved dispersion of MWCNTs in the  $MnO_2$  matrix;
- (iii) To develop new methods for the surface modification of current collectors with reduced interface resistance and for the impregnation of porous current collectors with active materials;
- (iv) Investigation and optimization of microstructure and composition of composite electrodes.
- (v) Investigation of capacitive behavior of composite electrodes.

## **Chapter 4 Experimental Procedures**

## 4.1 Starting Materials

Dopamine hydrochloride (DA), tyramine hydrochloride (TA), gallic acid (GA), benzoic acid (BA), caffeic acid (CA), chromotropic acid disodium salt dihydrate, polyacrylic acid (PAA, MW = 1,250,000), NaOH, ZrOCl<sub>2</sub> 8H<sub>2</sub>O, trans-cinnamic acid (TCA), p-coumaric acid (PCA), and 2,4-dihydroxycinnamic acid (DCA), <sub>L</sub>-3,4-dihydroxyphenyl-alanine (DOPA), submicrometer NiO, AgNO<sub>3</sub>, pyrrocatechol violet (PV) and KMnO<sub>4</sub> were purchased from the Aldrich-Sigma Corporation. Thin films of MnO<sub>2</sub> and Ag-doped MnO<sub>2</sub> were prepared by cathodic electrodeposition method [12] from the aqueous 20 mM KMnO<sub>4</sub> solutions containing 0-2 mM AgNO<sub>3</sub> on stainless steel foil substrates ( $30 \times 45 \times 0.1 \text{ mm}^3$ ) at a current density of 1 mA cm<sup>-2</sup>. MWCNTs were supplied by Arkema Co. The average diameter and length of MWCNTs were ~15nm and ~0.5 µm, respectively. Commercial Ni foams and plaques were supplied by Vale Canada.

## 4.2 Materials synthesis

# 4.2.1 Chemical precipitation of MnO<sub>2</sub> nanoparticles by using ethanol or isopropanol

MnO<sub>2</sub> nanoparticles with an average particle size of 30 nm were prepared by the

reduction of aqueous  $KMnO_4$  solutions using the method described in a previous investigation [130]. The prepared nanopowders contained Mn with oxidation state of 3.6, K with Mn/K ratio of 3.1 and adsorbed water [130].

The addition of 100 mL of isopropanol to 100 mL of aqueous 0.1M KMnO<sub>4</sub> solutions resulted in the formation of dark-brown precipitate. The precipitate was filtered, washed with isopropanol-water mixture (50 vol. % of water) and dried in the air. The investigation of the precipitate showed that isopropanol can be used as a reducing agent for the fabrication of manganese dioxide from KMnO<sub>4</sub> solutions. This approach has been further utilized for the reduction of KMnO<sub>4</sub> solutions in similar conditions in pores of Ni plaques and fabrication of electrodes by chemical impregnation of Ni plaques.

# 4.2.2 In-situ precipitation of MnO<sub>2</sub> nanoparticles by using dipping method

The addition of 100 mL of isopropanol to 100 mL of aqueous 0.1M KMnO<sub>4</sub> solutions resulted in the formation of dark-brown precipitate. The precipitate was filtered, washed with isopropanol-water mixture (50 vol. % of water) and dried in the air. The investigation of the precipitate showed that isopropanol can be used as a reducing agent for the fabrication of manganese dioxide from KMnO<sub>4</sub> solutions.

#### 4.2.3 Electrolytic deposition of MnO<sub>2</sub> nanoparticles

Electrolytic deposition was performed from 20 mM KMnO<sub>4</sub> solutions galvanostatically at a cathodic current density of 5 mA cm<sup>-2</sup> or in reverse pulse regime at a cathodic current density of 5 mA cm<sup>-2</sup> for 2 min and then an anodic current density of 2 mA cm<sup>-2</sup> for 1 min.

# 4.2.4 Electrophoretic deposition of MnO<sub>2</sub> films and MnO<sub>2</sub>-MWCNTs nanocomposites

Electrophoretic deposits were obtained on stainless steel substrates from the suspension of  $MnO_2$  and MWCNTs in ethanol at constant voltages of 10-50 V. The distance between the substrates and platinum counter electrodes was 15 mm. The deposition time was varied in the range of 0-10 min.

Electrodeposition was performed from aqueous 0.5-2 g  $L^{-1}$  PAA solutions containing 0-0.2 g  $L^{-1}$  MWCNTs, and 0-4 g  $L^{-1}$  of oxide powders. The pH of the solutions was adjusted to 8 by NaOH. The deposition voltage was 3-5 V, and the deposition time was varied in the range of 1-10 min. The films were obtained on 304 stainless steel and platinized silicon wafer substrates and dried in air for 48 h. Deposition yield was studied for the films deposited on stainless steel substrates. A minimum of three samples were prepared in each deposition experiment. All the deposits were obtained

using fresh solutions. The deposition yield measurements were repeatable, and the error was less than 5 %.

## 4.3 Materials characterization

#### **4.3.1** Crystallinity study

The X-ray diffraction (XRD) studies were performed using a powder diffractometer (Nicolet I2, monochromatized Cu K<sub>a</sub> radiation) at a scanning rate of 0.5  $^{\circ}$ min<sup>-1</sup>.

#### 4.3.2 Morphology study

The microstructure and composition of the films were investigated using the JEOL JSM-7000 F scanning electron microscope (SEM), equipped with energy dispersive X-ray spectroscopy (EDS) and a JEOL 2010F transmission electron microscope (TEM).

#### 4.3.3 Adsorption study

The adsorption of the organic molecules on  $MnO_2$  has been monitored using a quartz crystal microbalance (QCM 922, Princeton Applied Research) controlled by a computer. The mass  $\Delta m$  of adsorbed material was calculated using Sauerbrey's

equation:

$$-\Delta F = \frac{2F_o^2}{A\sqrt{\rho_q\mu_q}} \times \Delta m$$
(4-1)

where  $\Delta F$  is frequency decrease of the QCM,  $F_0$  is the parent frequency of QCM (9 MHz), A is the area of gold electrode (0.2 cm<sup>2</sup>),  $\rho_q$  is the density of the quartz and  $\mu_q$  is the shear modulus of quartz.

#### 4.3.4 Surface chemistry study

Fourier transform infrared spectroscopy (FTIR) studies were performed using Bio-Rad FTS-40 instrument.

#### **4.3.5** Composition study

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) investigations were carried out in air at a heating rate of 5  $\,^{\circ}$ C min<sup>-1</sup> using thermoanalyzer (Netzsch STA-409). The deposits were removed from the substrates for the TGA and DTA studies. Chemical analysis was performed using inductively coupled plasma (ICP) optical emission spectroscopy (OES) (Vista-PRO, Varian). The mean oxidation state (MS) of manganese was investigated using the iodometric method [154].

## 4.4 Electrode fabrication

#### **4.4.1 Electrode prepared by electrochemical methods**

Electrochemical deposits were obtained from suspensions of manganese dioxide and MWCNTs at constant voltages of 10-50 V on  $3 \times 6$  cm<sup>2</sup> or  $6 \times 6$  cm<sup>2</sup> stainless steel foils, which were rinsed with weak acid and deionized water and then dried in air at room temperature before use. After deposition, samples were dried in air for 24 h before mass measurement and testing.

#### 4.4.2 Electrode prepared by dipping method

Commercial Ni plaques were cut into  $1 \times 1.5$  cm<sup>2</sup> area and rinsed in acetone, ethanol and deionized water for 1 h, respectively. Subsequently, clean and dry Ni plaques were put into aqueous 0.1M KMnO<sub>4</sub> solution during 15 min. Reduction was performed in the isopropanol-water mixture (50 vol. % water) during 30 min, and the plaques were dried in the air. The procedures were repeated, and mass gain was investigated as a function of the number of the dipping-reduction procedures.

### **4.5 Testing of electrodes**

#### 4.5.1 Cyclic voltammetry study

Capacitive behavior of the films was studied using a potentiostat (PARSTAT 2273, Princeton Applied Research) controlled by a computer using a Power Suite electrochemical software.

Electrochemical studies were performed using a standard three-electrode cell containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution, degassed with the purified nitrogen gas. Surface area of the working electrode was 1 cm<sup>2</sup>. The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE). The electrodeposition cell included a substrate centered between two Pt counter electrodes. The distance between the substrate and counter electrodes was 15 mm. CV studies were performed within a potential range of 0-0.9 V versus SCE at scan rates of 2-100 mV s<sup>-1</sup>. The SC was calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the film mass (m) and the width of the potential window ( $\Delta$  V):

$$C = \frac{Q}{m\Delta V}$$
(4-2)

The standard deviation of the SC value was less than 4 %.

### 4.5.2 Impedance spectroscopy study

Impedance spectroscopy investigations were performed in the frequency range of 0.1 Hz-100 kHz at a voltage of 5 mV. Simulations of the impedance behavior were performed on the basis of the equivalent-circuit models using ZsimpWin version 3.10.

## **Chapter 5 Experimental Results and Discussion**

## 5.1 Electrolytic deposition

#### 5.1.1 Electrolytic deposition of MnO<sub>2</sub> on MWCNT network

Recent studies highlighted the influence of the electrode porosity on the electrochemical performance [10-12]. The porous structure of  $MnO_2$  is beneficial for the ion access to the surface of this material. Furthermore, many successful efforts have been made in the area of the fabrication of composite materials, where improved electronic conductivity has been achieved by the use of CNTs and other conductive additives [13-16].

#### 5.1.1.1 Morphology study

Significant interest has been generated in application of electrochemical methods for the fabrication of  $MnO_2$ -CNT composite electrodes. The microstructure of CNTs formed on the current collectors is important for the fabrication of  $MnO_2$ -CNT electrodes. According to the Ref. [155] the electrodeposition of  $MnO_2$  on the dense arrays of parallel CNTs, formed on the flat Ta foil substrates, presented difficulties, due to the limited ion access to the CNT surface and electrical shielding effect of the dense arrays of conductive CNTs. The authors reported nanoflower microstructure of the  $MnO_2$  particles formed only at the junctions of the individual CNTs [155].





(c)

Figure 5-1 (a and b) SEM images at different magnifications of CNTs on stainless steel gauze and (c) and TEM image of individual CNTs.

In the previous investigations [54, 156], it was shown that relatively low density CNT arrays can be formed by CVD. As an extension of the previous investigations, the CVD method was utilized for the CNTs growth on stainless steel gauzes and the formation of porous CNT microstructures. The CNTs formation on thin wires of the stainless steel gauzes offered additional benefits. In this case, the growth of parallel CNT arrays can be avoided. Moreover, the high surface area of the meshes was beneficial for the ion access during electrodeposition of MnO<sub>2</sub> and for the

electrochemical performance of the MnO<sub>2</sub>-CNT electrodes fabricated by this method.

Figure 5-1 shows typical SEM images of CNTs grown on the stainless steel gauze substrates. The SEM images at different magnifications (Figures 5-1a and b) indicated that CNTs were randomly oriented and formed a porous network. The CNTs totally cover the wires of the meshes and have a length of about 10  $\mu$ m. TEM studies (Figure 5-1c) showed that the diameter of MWCNTs is about 70-80 nm.





(a)

(b)



(c)

Figure 5-2 SEM images at different magnifications (a, b and c) of MnO<sub>2</sub>-CNT nanocomposites.

The use of gauzes as substrates and porous microstructure of the randomly oriented CNTs offered the advantage of improved access of  $MnO_4^-$  ions to the CNT surface, compared to the dense arrays of vertically-aligned parallel CNTs [155] formed on the foil substrates. The deposition mechanism, kinetics of deposition, structure and composition of the  $MnO_2$  formed by cathodic electrosynthesis were described in the previous investigations [11, 12, 117]. Figure 5-2 shows the SEM images of the electrodes after cathodic electrodeposition. Similar to the literature data [155] on anodic electrodeposition, we observed enhanced deposition at the CNT junctions (Figure 5-2a). However, SEM images indicated that  $MnO_2$  particles were also deposited on individual CNTs and CNT bundles (Figure 5-2b). The SEM image at higher magnification showed that particle size of  $MnO_2$  was in the range of 30-50 nm. This is in a good agreement with the results of the previous investigations [11, 12], which showed the formation of nanostructured  $MnO_2$  by the cathodic electrodeposition method.

#### **5.1.1.2 Cyclic voltammetry study**

Figure 5-3a shows CVs for  $MnO_2$ -CNT nanocomposites at different scan rates. The box-shape CVs at different scan rates showed good capacitive behavior. It was suggested that porous structure of the  $MnO_2$ -CNT electrodes (Figure 5-2) was beneficial for the electrolyte access to the active material, whereas CNTs provided

improved electronic conductivity. Turning again to equation (2-10), it should be noted that the improved electrolyte access to the active material and good electronic conductivity of the CNT support enabled relatively high SC. The SCs calculated from CVs at different scan rates are shown in Figure 5-3b. The MnO<sub>2</sub>-CNT nanocomposite with the film mass of 120  $\mu$ m cm<sup>-2</sup> exhibited a SC of 356 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup> and a SC of 230 F g<sup>-1</sup> at a scan rate of 100 mV s<sup>-1</sup>.



Figure 5-3 (a) CVs at scan rates of 20 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup> and 100 mV s<sup>-1</sup> for the  $MnO_2$ -CNT nanocomposites on stainless steel mesh and (b) SC versus scan rate for the  $MnO_2$ -CNT nanocomposites.

In a previous investigation [11], it was found that the 45  $\mu$ g cm<sup>-2</sup> film prepared by cathodic electrodeposition on stainless steel foil substrates exhibited a SC of 353 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. However, at a scan rate of 100 mV s<sup>-1</sup> the SC was only 135 F g<sup>-1</sup>. The increase in film's mass resulted in significant reduction in SC. The SC of a 100  $\mu$ g cm<sup>-2</sup> film on a stainless steel foil was 263 and 86 F g<sup>-1</sup> for scan rates of 2 and 100 F g<sup>-1</sup>, respectively [11]. The results of our investigation indicate that the use of CNT-modified stainless steel gauze substrates allowed a higher SC, especially at high

scan rates. The improved capacitive behavior of the  $MnO_2$ -CNT nanocomposites can be attributed to their lower electrical resistance.

#### 5.1.1.3 Impedance spectroscopy study

Figure 5-4a shows complex impedance data of the  $MnO_2$ -CNT nanocomposites. Good agreement of simulated and measured impedance data (Figure 5-4a) was found for the equivalent circuit containing a transmission line with 3 RC (or RQ) elements. The high frequency value of the real part of complex impedance has been used from the estimation of equivalent series resistance which was found to be ~0.4 Ohm.



Figure 5-4 Nyquist plot of the complex impedance  $Z^*=Z'-iZ''$  for (a) the MnO<sub>2</sub>-CNT nanocomposites and (b) MnO<sub>2</sub> with MnO<sub>2</sub> film mass of 120 µg cm<sup>-2</sup> on a stainless steel gauze. The variability in data between samples prepared under similar conditions was in the range of ±5 %.

In order to investigate the influence of CNTs on the resistance of the electrode material, manganese dioxide films were deposited on stainless steel gauze. Figures

5-4a and b compared the impedance data in the frequency range of 0.1 Hz-100 kHz for the manganese dioxide films of the same mass deposited on gauze substrates with and without CNTs. The results indicated that the samples, containing CNTs, showed significantly lower resistance compared to the sample without CNTs. Moreover, the MnO<sub>2</sub>-CNT composites prepared by the combined electrodeposition-CVD method on the gauze substrates showed lower resistance and higher capacitance compared to the MnO<sub>2</sub>-CNT films prepared by electrophoretic deposition on the stainless steel foils [157]. Electrochemical deposition offers the advantage of smaller particle size and agglomeration-free processing of nanomaterials [97]. Another advantage of the method developed in this investigation compared to Ref. [157] is related to the cathodic processing of manganese dioxide. The SC of 200 F g<sup>-1</sup> for the composite MnO<sub>2</sub>-CNT films deposited by anodic electrophoretic deposition [157] was much lower, compared to the SC of 356 F g<sup>-1</sup> obtained in this investigation for the films of similar mass.

#### 5.1.2 Electrolytic deposition of Ag doped MnO<sub>2</sub> film

As mentioned before, the SC of  $MnO_2$  films decreased with increasing film mass due to the low conductivity of  $MnO_2$ . This problem was addressed by the fabrication of composite materials containing conductive additives [15, 158] or by electrodeposition of Mo-doped  $MnO_2$  films [42]. Recent investigations showed that 1-8 wt.% Ag addition to lithium manganese dioxide electrode can significantly improve battery performance due to the increase in conductivity [159]. In another investigation the increase in conductivity of Ag-doped RuO<sub>2</sub> compared to pure RuO<sub>2</sub> was reported [160]. As a result, Ag-doped RuO<sub>2</sub> showed much higher SC compared to the SC of undoped RuO<sub>2</sub>. Therefore, it is important to fabricate and investigate the Ag-doped MnO<sub>2</sub> films.

 $MnO_2$  films for application in ES can be prepared by anodic or cathodic electrodeposition from aqueous solutions. However, anodic electrolytic deposition of  $MnO_2$  on metallic current collectors presents difficulties related to the anodic oxidation and dissolution of metals. In contrast, cathodic electrodeposition can be performed on various metallic substrates. It should be noted that cathodic electrodeposition is an important industrial technique for the deposition of metals. Therefore, cathodic electrodeposition is a promising method for the co-deposition of oxides and metals and the fabrication of doped films and composites.

In a previous investigation [12], it was demonstrated that nanostructured  $MnO_2$  films can be obtained by the cathodic reduction of  $Mn^{7+}$  species from KMnO<sub>4</sub> solution using the equation (2-22). Moreover, Ag can be deposited by cathodic reduction of Ag<sup>+</sup> species from AgNO<sub>3</sub> solutions [161]. These results pave the way for the fabrication of Ag-doped MnO<sub>2</sub> films. The goal of this investigation was the fabrication of Ag-doped  $MnO_2$  films by cathodic electrolytic deposition from the KMnO<sub>4</sub> aqueous solution containing AgNO<sub>3</sub>. The results presented below indicated that Ag-doped MnO<sub>2</sub> films showed improved capacitive behavior.

#### 5.1.2.1 Morphology study



Figure 5-5 SEM image of a film prepared from 20 mM KMnO<sub>4</sub> solution containing 2 mM AgNO<sub>3</sub>.

Figure 5-5 shows a typical SEM image of a film prepared from the KMnO<sub>4</sub> solution containing AgNO<sub>3</sub>. The cathodic electrodeposition resulted in the formation of nanostructured films, which were continuous and crack-free. Numerous EDS analyses showed that the Ag content in the films was  $5\pm0.6$  at.%.

#### 5.1.2.2 Cyclic voltammetry study



Figure 5-6 CVs at a scan rate of 100 mV s<sup>-1</sup> for 50 µg cm<sup>-2</sup> films prepared from 20 mM KMnO<sub>4</sub> solution : (a) containing 2 mM AgNO<sub>3</sub> and (b) without AgNO<sub>3</sub>.

The electrochemical performance of the Ag-doped MnO<sub>2</sub> and pure MnO<sub>2</sub> films was compared using cyclic voltammetry. The films showed capacitive behavior in a voltage window of 0-0.9 V versus SCE. The typical box-shape CVs for the films are presented in Figure 5-6. The larger area of CV for Ag-doped MnO<sub>2</sub> film indicates a higher SC.

The SCs calculated from the CV data at different scan rates are shown in Figure 5-7. The SCs decreased with the increase in mass loadings and scan rates in the range of 2-100 mV s<sup>-1</sup>. The MnO<sub>2</sub> film with a mass loading of 50  $\mu$ g cm<sup>-2</sup> showed a SC of 400 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. The SC was much lower, compared to the theoretical SC of 1370 F g<sup>-1</sup> [162]. Literature data indicates that SC of 1370 F g<sup>-1</sup> can be achieved in very thin films with mass of ~5  $\mu$ g cm<sup>-2</sup> [4]. However, the SC decreased with increasing film mass due to the low electronic conductivity of MnO<sub>2</sub>. The SCs of

400-450 F g<sup>-1</sup> were reported for mass loading of 25-75  $\mu$ g cm<sup>-2</sup> [163]. In another investigation the SC decreased from 330 to 150 F g<sup>-1</sup> with increasing mass loading in the range of 18-116  $\mu$ g cm<sup>-2</sup> [8].



Figure 5-7 SC versus scan rate for films prepared from 20 mM KMnO<sub>4</sub> solution: (A) without AgNO<sub>3</sub> and (B) containing 2 mM AgNO<sub>3</sub> for different film mass: (a) 50, (b) 100 and (c) 160  $\mu$ g cm<sup>-2</sup>.

The results presented in Figure 5-7A are in good agreement with the literature data. The SC at a scan rate of 2 mV s<sup>-1</sup> decreased from 400 to 105 F g<sup>-1</sup> with the increase of film mass from 50 to 160  $\mu$ g cm<sup>-2</sup> (Figure 5-7A). However, the Ag-doped MnO<sub>2</sub> films with similar film mass exhibited higher SCs in the same scan rate range. The Ag-doped MnO<sub>2</sub> film with a film mass of 50  $\mu$ g cm<sup>-2</sup> showed a SC of 770 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. The SCs decreased from 770 to 225 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. The SCs decreased from 770 to 225 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup> with the increase of film mass from 50 to 160  $\mu$ g cm<sup>-2</sup> (Figure 5-7B). The difference in the capacitive behavior of the Ag-doped MnO<sub>2</sub> films and pure MnO<sub>2</sub> films was especially evident at higher scan rates. The SCs for 160  $\mu$ g cm<sup>-2</sup> films at a scan rate of 100 mV s<sup>-1</sup> were 147 and 8 F g<sup>-1</sup> for Ag-doped MnO<sub>2</sub> and pure MnO<sub>2</sub>

films, respectively. The improved capacitive behavior of the Ag-doped  $MnO_2$  films can be attributed to their lower electrical resistance. This is in good agreement with the results of impedance spectroscopy presented in Figure 5-8.



Figure 5-8 Nyquist plots of the complex impedance  $Z^*=Z'-iZ''$  for films prepared from the 20 mM KMnO<sub>4</sub> solution: (a) without AgNO<sub>3</sub> and (b) containing 2 mM AgNO<sub>3</sub> for the film mass of 50 µg cm<sup>-2</sup>. The inset shows the high frequency range of the impedance spectra.

#### 5.1.2.3 Impedance spectroscopy study

The Nyquist plot of the complex impedance  $Z^*=Z'-iZ''$  (Figure 5-8) compares the data for Ag-doped MnO<sub>2</sub> and pure MnO<sub>2</sub> films with the same mass of 50 µg cm<sup>-2</sup> in the frequency range of 0.1 Hz-100 kHz. In the high frequency range, both spectra showed semi-circles, which corresponded to the charge transfer resistance [1]. The diameter of the semi-circle showed the magnitude of the charge transfer resistance [1]. The results indicated that the Ag-doped MnO<sub>2</sub> electrodes showed significantly lower charge transfer resistance compared to the pure MnO<sub>2</sub> electrodes. It should be noted that lower resistance of films can improve the electrochemical performance of electrodes, which is in good agreement with the CV testing results. The comparison of  $Z''=1/\omega C$  data at the same frequencies indicated lower Z'' for Ag-doped MnO<sub>2</sub> compared to pure MnO<sub>2</sub>, which is in good agreement with corresponding SC data. It is important to note that Ag is not a capacitive material. Therefore, the Ag content in the composite films must be optimized.

The results presented in this investigation indicated that Ag-doped  $MnO_2$  films have been successfully prepared by the cathodic electrolytic deposition from the KMnO<sub>4</sub> aqueous solution containing AgNO<sub>3</sub>. The deposition method resulted in the formation of nanostructured films, which were continuous and crack-free. Ag-doped MnO<sub>2</sub> films showed lower resistance and improved capacitive behavior compared to pure MnO<sub>2</sub> film. The highest SC of 770 F g<sup>-1</sup> was achieved at a scan rate of 2 mV s<sup>-1</sup>. The Ag-doped MnO<sub>2</sub> films prepared by the cathodic electrolytic deposition on low-cost stainless steel substrates can be considered as possible electrode materials for ES.

### 5.2 Electrophoretic deposition

#### 5.2.1 Dispersion and deposition using dopamine

#### 5.2.1.1 Effect of additive concentration and time

EPD method has been developed for the deposition of composite manganese dioxide-

MWCNT films using DA as a dispersing agent in ethanol solution. The suspensions of manganese dioxide in ethanol were unstable and showed relatively fast sedimentation when ultrasonic treatment was interrupted. The cathodic deposits obtained from such suspensions were highly agglomerated and non-uniform. In contrast, relatively uniform deposits were obtained from well dispersed and stable suspensions of manganese dioxide containing DA as a dispersant. Figure 5-9 shows typical dependences of the deposition yield versus DA concentration. The deposition rate increased with increasing DA concentration (Figure 5-9). The mass of the deposited materials increased with increasing deposition time, indicating the formation of films of different thickness (Figure 5-10).



Figure 5-9 Film mass versus DA concentration in the 4 g  $L^{-1}$  manganese dioxide suspension at the deposition voltage of 20 V and deposition time of (a) 1 min and (b) 2 min.

It is known that colloidal particles in suspensions exhibit a charge, which can be modified by the use of additives [97]. The formation of cathodic deposits indicated that manganese dioxide particles were positively charged in ethanol suspensions. It is in this regard that alcohols behave as proton donors [164]. Pure alcohols can ionize in the following way:

$$\mathrm{RCH}_{2}\mathrm{OH} + \mathrm{RCH}_{2}\mathrm{OH} \rightarrow \mathrm{RCH}_{2}\mathrm{O}^{-} + \mathrm{RCH}_{2}\mathrm{OH}_{2}^{+}$$
(5-1)



Figure 5-10 Film mass versus deposition time for (a) 4 g  $L^{-1}$  and (b) 9 g  $L^{-1}$  manganese dioxide suspensions containing 15 mg  $L^{-1}$  dopamine at a deposition voltage of 20 V.

Damodaran and Moudgil [164] have proposed a mechanism of particle charging, in which the adsorbed alcohol ionized into a protonated alcohol and an alkoxide ion, followed by the dissociation of the protonated alcohol. The dissociated alcohol and alkoxide ion desorbed into the solution, leaving a proton on the particle surface. This resulted in the formation of positively charged particles in the suspensions.

#### 5.2.1.2 Proposed adsorption mechanism



Figure 5-11 Adsorption of protonated DA on MnO<sub>2</sub>.

It is suggested that the addition of dopamine hydrochloride to the suspensions resulted in the adsorption of the protonated DA on the MnO<sub>2</sub> surface. The adsorbed protonated DA (Figure 5-11) improved particle stability and increased particle charge. The deprotonation of the amino groups of DA in the high pH region at the electrode surface [97] promoted deposit formation. As a result, the increase in the deposition yield was observed with increased DA concentration (Figure 5-11).

#### 5.2.1.3 Surface chemistry study

The adsorption of DA has been investigated using FTIR method. Figure 5-12 shows FTIR spectra for as-prepared  $MnO_2$ , a deposit obtained from the  $MnO_2$  suspension containing DA and as-received dopamine hydrochloride. The FTIR spectrum of as-prepared  $MnO_2$  exhibited a very broad peak centered at 3400 cm<sup>-1</sup> associated with the stretching vibration of OH groups of adsorbed water molecules [165, 166]. The

bands at 1625, 1538 and 1412 cm<sup>-1</sup> represented the vibrations related to interactions of Mn with OH and other surface groups [165, 167, 168]. The broad peak below 750 cm<sup>-1</sup> can be attributed to the vibrations of the Mn-O bonds [165-169]. After the surface modification with DA, new band at 1088 cm<sup>-1</sup> appeared, which can be attributed to the aryl-oxygen stretching vibrations [170, 171]. However, the bending vibrations of OH groups of DA [172] at 1365 cm<sup>-1</sup> were not observed in the FTIR spectrum of MnO<sub>2</sub> modified with DA. This is in good agreement with proposed mechanism of DA adsorption on oxide particles, which involves chelation of surface metal ions [173].



Figure 5-12 FTIR spectra for (a) as-prepared MnO<sub>2</sub>, (b) MnO<sub>2</sub> deposited from the 4 g L<sup>-1</sup> MnO<sub>2</sub> suspension, containing 26 mg L<sup>-1</sup> DA and (c) as-received dopamine hydrochloride.

#### 5.2.1.4 Adsorption study

QCM studies of DA adsorption were performed using  $MnO_2$  thin film with mass of 1  $\mu g$  on a gold electrode of a quartz crystal. The film was deposited by EPD from  $MnO_2$ 

suspension without DA. Figure 5-13 shows the mass gain of the electrode after the injection of the 100 mg  $L^{-1}$  DA into the ethanol solution. The increase in the electrode mass indicated DA adsorption on MnO<sub>2</sub> in agreement with FTIR data.



Figure 5-13 QCM data for the mass of adsorbed DA on the 1  $\mu$ g MnO<sub>2</sub> film (film area 0.2 cm<sup>2</sup>) from the 100 mg L<sup>-1</sup> DA solution versus time.

#### 5.2.1.5 Composition studies

DA has been also used for the stabilization of MWCNT suspensions. As pointed out above, the stabilization mechanism, discussed in the literature, involved  $\pi$ - $\pi$ interactions of DA and MWCNTs. EPD from the suspensions containing MWCNTs and DA resulted in the deposition of MWCNTs on the cathode. Moreover, codeposition of MnO<sub>2</sub> and MWCNTs was achieved using DA as a common charging and stabilizing additive.

Obtained deposits were studied using TGA and DTA (Figure 5-14). The deposit

prepared from the suspension without MWCNTs showed mass loss, which can be mainly attributed to dehydration. A small mass gain at ~460  $\C$  and a corresponding small exotherm in the DTA data could be attributed to oxidation of non-stoichiometric MnO<sub>2</sub>. The total mass loss at 900  $\C$  was found to be 15 mass%. The deposit, prepared from the suspension containing MWCNTs, showed an additional step in the mass loss in the range of 450-500  $\C$  and an exotherm in the corresponding DTA data at ~450  $\C$ . The total mass loss at 900  $\C$  was found to be 33 mass%. The additional mass loss could be attributed to burning out of MWCNTs and indicated the formation of composite MnO<sub>2</sub>-MWCNT deposits.



Figure 5-14 TGA (a,b) and DTA (c,d) data for deposits obtained from (a and c) the 4 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 8 mg  $L^{-1}$  DA and (b,d) the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 15 mg  $L^{-1}$  DA and 0.6 g  $L^{-1}$  MWCNT, deposition voltage 20 V.

#### **5.2.1.6 Morphology study**

The SEM images of the deposits are shown in Figure 5-15. SEM studies of the films prepared from the MnO<sub>2</sub> suspensions containing DA showed that film thickness can be varied in the range of 0-5  $\mu$ m; however cracking was observed when film thickness exceeded ~2  $\mu$ m (Figure 5-15a). The film cracking can be attributed to drying shrinkage. It is suggested that the deposition of thicker films requires the use of binders [97], which can prevent film cracking. SEM investigations of the films of similar thickness prepared from MnO<sub>2</sub> suspensions containing MWCNTs and DA showed reduced cracking and increased porosity. The analysis of SEM images (Figure 5-15) of such films indicated that MWCNTs with high aspect ratio can provide microstructure reinforcement and reduce cracking. It is also suggested that increased porosity of the films containing MWCNTs can result in reduced cracking due to crack-tip blunting mechanism [174]. SEM studies also showed the incorporation of MWCNTs into the MnO<sub>2</sub> film resulted in the reduced agglomeration of the MnO<sub>2</sub> particles (Figures 5-15b and d).





Figure 5-15 SEM images at different magnifications of the films prepared from (a,b) the 4 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 8 mg  $L^{-1}$  DA and (c,d) the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 15 mg  $L^{-1}$  DA and 0.6 g  $L^{-1}$  MWCNTs, at a deposition voltage of 20 V.



Figure 5-16 CVs at a scan rate of 5 mV s<sup>-1</sup> for the films prepared from (a) the 4 g L<sup>-1</sup> MnO<sub>2</sub> suspension containing 8 mg L<sup>-1</sup> DA and (b) the 9 g L<sup>-1</sup> manganese dioxide suspension containing 15 mg L<sup>-1</sup> DA and 0.6 g L<sup>-1</sup> MWCNTs, deposition voltage 20 V, film mass 0.17 mg cm<sup>-2</sup>.

#### 5.2.1.7 Cyclic voltammetry study

The incorporation of MWCNTs into  $MnO_2$  films and microstructure changes resulted in improved electrochemical performance of the composite films. Figure 5-16 shows CV data for the films. The CVs presented in Figure 5-16 indicated capacitive behavior with a larger area of the CV for the film containing MWCNTs compared to the film of the same mass without MWCNTs. The difference can be attributed to the higher SC of the film containing MWCNTs. The SCs calculated from the CV data at different scan rates are shown in Figure 5-17. The MnO<sub>2</sub> film showed a SC of 340 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. The SC decreased with an increase in scan rate in the range of 2-100 mV s<sup>-1</sup> (Figure 5-17). The MnO<sub>2</sub> film containing MWCNTs exhibited a higher SC in the same scan rate range with the highest SC of 650 F g<sup>-1</sup> at 2 mV s<sup>-1</sup>.



Figure 5-17 SC versus scan rate for films prepared from (a) the 4 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 8 mg  $L^{-1}$  DA and (b) the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 15 mg  $L^{-1}$  DA and 0.6 g  $L^{-1}$  MWCNTs, at a deposition voltage 20 V with a film mass of 0.17 mg cm<sup>-2</sup>.

A complicating factor in the application of MnO<sub>2</sub> for ES is low electronic and ionic

conductivity of this material. Thin MnO<sub>2</sub> films (~ 1  $\mu$ g cm<sup>-2</sup>) exhibited ideal capacitive behavior [7] in a voltage window of 0-0.9 V and showed a SC of ~700 F g<sup>-1</sup>. Previous investigations [119] showed that the capacitance decreases from 400 F g<sup>-1</sup> to 177 F g<sup>-1</sup> when the film mass increases from 50  $\mu$ g cm<sup>-2</sup> to 200  $\mu$ g cm<sup>-2</sup>. Obtained SC values are much lower than the theoretical SC [162] of 1370 F g<sup>-1</sup>.

The development of ES requires the use of porous active materials with small particles size and high surface area. The small size and high surface area of MnO<sub>2</sub> nanoparticles and film porosity are important for the ion access to the active material. The incorporation of MWCNTs into the MnO<sub>2</sub> matrix [175, 176] can improve the electronic conductivity of the composite materials. Porous microstructure and reduced agglomeration of particles was beneficial for the capacitive behavior of the composite MnO<sub>2</sub>-MWCNT films prepared by EPD using DA as a dispersant and charging agent.



Figure 5-18 Nyquist plot of the complex impedance  $Z^*=Z'-iZ''$  for the film, prepared from the 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension containing 15 mg L<sup>-1</sup> DA and 0.6 g L<sup>-1</sup> MWCNTs, deposition voltage 20 V, film mass 0.17 mg cm<sup>-2</sup>, electrode area 1 cm<sup>-2</sup>.

#### **5.2.1.8 Impedance spectroscopy study**

Figure 5-18 shows complex impedance data of the composite MnO<sub>2</sub>-MWCNT film. The equivalent circuit of ES was discussed in several investigations [17, 177-179] and included RC transmission line [177], describing the porous electrode, and Warburg impedance W [17], representing the diffusion resistance of electrolyte inside the pores. C<sub>n</sub> elements represented double layer capacitance and pseudo capacitance, whereas R<sub>n</sub> elements represented electrolyte resistance in pores, faradaic resistance and equivalent series resistance of the electrodes. Conway and Pell [177] described the impedance of porous electrode using 5 element (n=5) circuit. A constant phase element (CPE) Q, rather than a pure capacitance C, was used in another investigation [180]. The CPE element describes a 'leaking' capacitor with microscopic roughness of the surface and capacitance dispersion of interfacial origin [180]. Solutions resistance R<sub>S</sub> is usually combined in series with the RC transmission line [181]. The equivalent circuits should allow an optimum representation of the measured spectra with a minimum set of model parameters. Good agreement of simulated and measured voltage data (Figure 5-18) was found for the equivalent circuit containing a transmission line with three RC (or RQ) elements.

The results of our investigation showed that cathodic EPD can be used for the fabrication of porous films of nanostructured  $MnO_2$  for application in ES. The formation of composite materials by EPD requires the use of similar charging

additives for all individual components [97]. It is suggested that the chelating mechanism of DA adsorption and positive charge of DA can be beneficial for the cathodic EPD of composite materials, containing nanoparticles of other oxides. Moreover, our results showed that DA is an effective dispersant for the EPD of CNTs. Other methods of CNT charging for EPD, such as functionalization or chemical treatment, can result in the CNT degradation and usually reduce the electronic conductivity of CNTs. Porous composites for application in ES were obtained because of the use of DA as a dispersant and charging agent for MnO<sub>2</sub> and MWCNTs. The investigation of the electrochemical properties of the composites showed that SCs were significantly higher, compared to the results of previous investigations [118, 119]. It is suggested that high SCs were obtained by the use of DA, which provided good dispersion of MnO<sub>2</sub> nanoparticles and MWCNTs in the suspension.

#### 5.2.2 Dispersion and deposition using caffeic acid

Advances in electrophoretic nanotechnology are inevitably reliant on the development of charging and dispersing methods. The goal of this investigation was the use of caffeic acid as a charging and dispersing agent for EPD of inorganic nanoparticles. This research is motivated by recent advances in the investigation of the mechanism of mussel adhesion to metal and mineral surfaces in water, which showed that strong adhesion is attributed to the chelation of catecholic amino acid,
L-3,4-dihydroxyphenylalanine (DOPA) [182-184]. The chemical structure of caffeic acid is similar to that of DOPA. Therefore, the bio-inspired chemistry of caffeic acid adhesion to inorganic nanoparticles was in the focus of this investigation. The results presented below indicated that caffeic acid is a promising charging and dispersing agent for EPD of inorganic materials and composites. It was found that the adsorption of caffeic acid on inorganic particles and deposition efficiency are influenced by surface chemistry of the inorganic particles. The experimental data obtained for caffeic acid and other molecules with similar structures were compared. These results provide an insight into the chemical mechanism of caffeic acid adsorption.

### 5.2.2.1 Structures of DOPA, CA, TCA, PCA and DCA



Figure 5-19 Chemical structures of (a) DOPA, (b) CA, (c) TCA, (d) PCA and (e) DCA.

Figure 5-19 compares chemical structures of DOPA, CA, TCA, PCA and DCA. The

chemical structure of DOPA (Figure 5-19a) includes two OH groups bonded to adjacent carbon atoms of the aromatic ring, carboxylic and amino groups. The total charge of zwitterionic DOPA molecules is governed by ionization of the different functional groups [185]. The functional groups of DOPA are protonated at low pH. Therefore, the positive charge of DOPA at low pH is attributed to the protonated amino group  $(NH_3^+)$  [185]. The pH increase leads to deprotonation of carboxylic, phenolic and amino groups. As a result, DOPA possesses a negative charge at high pH. It was found [185] that the amino group was protonated below pH=10 and it reduced the total negative charge of the anionic groups. As pointed out above, the EPD of zwitterionic molecules and their application as charging agents presents difficulties due to charge reversal. Therefore, CA molecule (Figure 5-19b), containing only anionic groups, offers advantages for application in EPD. The anionic groups can be deprotonated in the bulk of solutions and neutralized at low pH at the electrode surface. The charge neutralization is beneficial for anodic deposition of particles, containing adsorbed CA.

The adsorption of CA on inorganic particles is governed by the phenolic and carboxylic bonding sites. Similar to DOPA, the structure of CA contains two OH groups bonded to adjacent carbon atoms of the aromatic ring. Turning again to the investigation of molluscs adhesion in aqueous environment, it should be noted that excellent adhesion of molluscs to different surfaces is attributed to proteins, containing DOPA [186]. The adsorption of the molluscs to hard surfaces is very fast and strong, because sea waves can damage the molluscs approaching the surface [186].

Such adsorption is especially attractive for application in electrophoretic nanotechnology. The adsorption is critical for the efficient dispersion of nanoparticles. Moreover, as pointed out above, non-adsorbed dispersant is detrimental for dispersion and deposition.

The DOPA adhesion to metals and oxides in aqueous solutions is attributed to catecholate type of bonding, involving metal atoms of the adsorbent and adjacent OH groups of DOPA. A similar mechanism can be suggested for CA adsorption. Indeed, DOPA and CA belong to the catechol family of materials. In order to analyze the CA adsorption mechanism, TCA, PCA and DCA molecules were investigated (Figures 5-19c, d and e). The structures of TCA, PCA and DCA are similar to the structure of CA. However, TCA does not have OH groups bonded to the aromatic ring (Figure 5-19c), whereas PCA has only one phenolic OH group (Figure 5-19d). The structure of DCA includes two phenolic OH groups; however, in contrast to CA, they are bonded to non-adjacent carbon atoms of the aromatic ring (Figure 5-19e). All the organic molecules contained a COOH group.



#### 5.2.2.2 Proposed adsorption mechanisms

Figure 5-20 Suggested adsorption mechanisms of CA: (a) bidentate chelating bonding, (b) bidentate bridging bonding (inner sphere), (c) bidentate bridging bonding (outer sphere) of catechol group, (d) chelating of carboxylic group.

Figure 5-20 shows possible mechanisms of CA adsorption on metal oxide surfaces. The basic adsorption mechanisms were identical to those proposed in other investigations of aromatic molecules, containing OH and COOH groups [187-189]. It is known that the catechol group is a powerful complexing agent, despite of its extremely high pKa values [190]. It is able to coordinate metal atoms at acidic or basic pH conditions with complete deprotonation of the OH groups [187, 190, 191]. However, the mechanism of adsorption is not clear at present. It was suggested [187, 190, 191] that it involves the replacement of OH groups on oxide surface by the deprotonated ligand. Bidentate chelating bonding (Figure 5-20a) and bidentate bridging bonding (Figure 5-20b) mechanisms were proposed [192, 193]. Investigation

showed the possibilities of inner sphere (Figure 5-20b) or outer sphere bonding (Figure 5-20c), depending on the nature of the adsorbent material [194]. The following reaction stoichiometry [195, 196] was proposed for bidentate chelating bonding, involving metal atoms (M) and catechol ( $L^2$ - $H_2^+$ ):

$$M-2OH + L^{2} + 2H^{+} \rightarrow ML + 2H_{2}O$$
(5-2)

The bidentate bridging inner-sphere bonding is based on the reaction [195, 197]:

$$2M-OH + L^{2-} + 2H^{+} \to M_{2}L + 2H_{2}O$$
(5-3)

The outer sphere bonding is formed as follows [197, 198]:

$$2M-OH + L^{2-} + 2H^{+} \rightarrow (M-OH_{2}^{+})_{2} - L^{2-}$$
(5-4)

Other mechanisms included monodentate bonding, involving one OH group, or mixed monodentate-bidentate bonding [193, 199].

From the preceding discussion of the CA structure, it is evident that CA has catechol and carboxylic adsorption sites in competition. The adsorption behavior of organic ligands possessing carboxylic acid groups has been extensively studied in the literature. The mechanism of adsorption, involving a carboxylic group [188, 200] is shown in Figure 5-20d. The investigation of benzoic and phthalic acids [188, 201], which do not have OH groups bonded to the aromatic ring, provided evidence that carboxylic groups were involved in adsorption of the acids on zirconium, titanium and iron oxides. Therefore, similar adsorption mechanism can be suggested for the adsorption of CA. Studies of the interactions of CA with different ions in aqueous solutions showed that the bonding mechanism depended on the nature of metal ions [202]. Among the two possible coordination sites, the carboxylate group of CA showed greater complexing power toward Pb(II). However, Al(III) preferentially coordinated the catechol group of CA [202].

The adsorption of DOPA and other materials from catechol family on various oxides was mainly investigated in aqueous suspensions. However, organic solvents, such as ethanol, offer advantages for EPD [97, 123, 126]. Relatively high electric fields can be applied to non-aqueous suspensions and high deposition yields can be achieved. The application of an electric field to aqueous suspensions can result in significant gas evolution at electrodes, due to the electrochemical decomposition of water [97]. EPD in aqueous suspensions is usually performed at lower electric fields in order to reduce gas evolution. This results in lower deposition rates. Therefore, in order to achieve high deposition rates, EPD was performed using ethanol solvent. It is important to note that the adsorption of CA on oxide particles can be influenced by the nature of solvent used. The dispersion of materials in aqueous suspensions involves the dissociation of the dispersant and adsorption of formed anions or cations on the particle surface. In non-aqueous solvents these steps can be reversed. The dispersing agent can be adsorbed on the particle surface and then dissociate, releasing ions to the solution [203].



# 5.2.2.3 Effects of CA concentration and time on MnO<sub>2</sub> deposition

Figure 5-21 Film mass ( $\blacktriangle$  - anodic, •-cathodic) as a function of (A,B) CA concentration and (C) deposition time for 9 g L<sup>-1</sup> MnO<sub>2</sub> suspensions in ethanol at deposition voltages of (A,C) 20 V and (B) 50 V, deposition time (A,B) 2 min and CA concentration (C) 0.4 g L<sup>-1</sup>.

EPD from  $MnO_2$  suspensions in ethanol allowed for the formation of cathodic deposits. Therefore,  $MnO_2$  particles were positively charged in the suspensions. As mentioned before, pure alcohols can ionize in the following way shown in equation (5-2). The dissociated alcohol and alkoxide ion desorbed into the solution [164], leaving a proton on the particle surface. This resulted in the formation of positively charged particles in the suspensions. Such mechanism can also explain the positive charge of  $MnO_2$  particles in ethanol suspensions. Figures 5-21A and B compare deposition yield data for  $MnO_2$  suspensions in ethanol at deposition voltages of 20 V and 50 V. The addition of CA to the suspensions resulted in decreasing cathodic deposition yield. No deposition, either cathodic or anodic, was observed at CA concentration of 0.05 g  $L^{-1}$ . At higher CA concentrations, anodic deposition was observed. The anodic deposition yield increased with increasing CA concentration. The increase in the deposition voltage resulted in increasing deposition yield (Figures 5-21A and B). The formation of anodic deposits indicated that MnO<sub>2</sub> particles were negatively charged at CA concentration above 0.05 g L<sup>-1</sup>. The film mass increased with increasing deposition time (Figure 5-21C). Therefore, films of different mass can be obtained and deposition yield can be controlled. The addition of TCA, PCA and DCA to MnO<sub>2</sub> suspensions resulted in decreasing deposition yields, however no deposition, either cathodic or anodic, was observed at TCA, PCA and DCA concentrations above 0.05 g  $L^{-1}$ . The MnO<sub>2</sub> suspensions, containing TCA, PCA and DCA were unstable and showed rapid sedimentation immediately after ultrasonic agitation. In contrast, MnO<sub>2</sub> suspensions containing 0.2-0.5 g  $L^{-1}$  CA were stable for more than 7 days. The results indicated that the adsorption of anionic CA, TCA, PCA and DCA on the positively charged MnO<sub>2</sub> particles resulted in charge compensation and reduction of the deposition yield at concentrations of the anionic molecules below  $0.05 \text{ g L}^{-1}$ . The electrostatic attraction of the anionic molecules and positively charged MnO<sub>2</sub> promoted adsorption of the molecules on the particle surfaces. It was suggested that strong chemical adsorption of CA on the MnO<sub>2</sub> particles resulted in charge reversal at higher CA concentrations. The adsorbed CA molecules allowed for improved suspension stability. However, the adsorption of TCA, PCA and DCA on  $MnO_2$  nanoparticles was weak. As a result, no charge reversal was observed and the suspensions were unstable. Turning again to the structures of CA, TCA, PCA and DCA, as shown in Figure 5-19, it can be concluded that strong adsorption of CA is attributed to catecholate type of bonding, involving two adjacent OH groups, bonded to the aromatic ring. It is in this regard that all the molecules have COOH groups. PCA has one OH group, whereas DCA has two OH groups bonded to non-adjacent carbon atoms. The dissociation of the organic molecules resulted in the formation of corresponding anions and H<sup>+</sup>. Therefore, a competitive adsorption of the anions and H<sup>+</sup> on the MnO<sub>2</sub> particles can be expected. However, only anionic CA, which belongs to the catechol family, showed strong adsorption to the MnO<sub>2</sub> particles, which resulted in charge reversal.

# 5.2.2.4 Effects of CA concentration and time on ZrO<sub>2</sub> deposition

Further understanding of the adsorption mechanism of CA was achieved using  $ZrO_2$  as a model ceramic material. The results presented below showed that surface chemistry, rather than the crystal structure and composition, determined the adsorption behavior of CA. The comparison of the experimental data for different phases of MnO<sub>2</sub> and ZrO<sub>2</sub> provided an important insight into the mechanism of CA adsorption and particle dispersion. It was found that particle agglomeration can be reduced if particle synthesis is performed in the presence of CA. Moreover, these studies showed that composite materials can be obtained using CA as a charging and dispersing agent for different components. Moreover,  $ZrO_2$  was used as an electrode material for the ES application [204].

Zirconia particles were prepared by chemical precipitation at pH=8 from 0.1M ZrOCl<sub>2</sub> solution without CA (zirconia I) and containing 4 g  $L^{-1}$  CA (zirconia II). The suspensions of zirconia I in ethanol were unstable. No deposition was observed from such suspensions. The addition of CA resulted in improved suspension stability. Moreover, the addition of CA allowed for the formation of anodic films. The film mass increased with increasing CA concentration, and increasing deposition time (Figures 5-22A and B). However, no deposition was achieved from the zirconia I suspensions, containing TCA, PCA and DCA. The results indicated that catechol group of CA allowed for strong adsorption on zirconia I. Therefore, the addition of CA to the zirconia I suspensions resulted in negatively charged particles, which were deposited by anodic EPD. In contrast, anodic EPD was achieved from zirconia II suspensions without CA additive. Figure 5-22C shows that film mass increased with increasing deposition time at a constant deposition voltage. The deposition yield for zirconia II was comparable with that for zirconia I deposited in the presence of CA additive in the suspension. It is suggested that CA was adsorbed on zirconia II during synthesis of this material from ZrOCl<sub>2</sub> solution and remained adsorbed during washing of the precipitated powder. It should be noted that synthesis of  $MnO_2$  cannot be performed in the presence of CA, because redox reaction of  $KMnO_4$  and CA results in CA decomposition.



Figure 5-22 Film mass for anodic deposits versus (A) CA concentration in 9 g  $L^{-1}$  zirconia I suspensions at a deposition time of 2 min and versus (B,C) deposition time for (B) 9 g  $L^{-1}$  zirconia I suspension, containing 0.4 g  $L^{-1}$  CA and (C) 9 g  $L^{-1}$  zirconia II suspensions without CA at a deposition voltage of 150 V.

#### **5.2.2.5 Surface chemistry studies**

The adsorption of CA on  $MnO_2$  and zirconia was studied by the FTIR method. Figure 5-23 shows FTIR spectra of the deposits prepared from  $MnO_2$  and zirconia I suspensions containing CA additive. The bands at 1622 and 1564 cm<sup>-1</sup> (Figure 5-23a) and 1628, 1568 and 1495 cm<sup>-1</sup> (Figure 5-23b) were attributed to stretching vibrations

of the aromatic ring v(C-C)v(C=C) [187] of adsorbed CA. The bands at 1397 and 1344 cm<sup>-1</sup> (Figure 5-23a), 1385 and 1335 cm<sup>-1</sup> (Figure 5-23b) were attributed to the stretching vibrations of the carboxylic group [188, 201, 205, 206]. The peaks at 1271 cm<sup>-1</sup> (Figure 5-23a) and 1274 cm<sup>-1</sup> (Figure 5-23b) represented C-O stretching vibrations [188, 201]. The band at 1120 cm<sup>-1</sup> was associated with bending C-H vibrations [188, 201]. Therefore, the results of FTIR studies confirmed that MnO<sub>2</sub> and zirconia particles contained adsorbed CA molecules.



Figure 5-23 FTIR spectra for deposits prepared from (a) 9 g  $L^{-1}$  MnO<sub>2</sub> and (b) 9 g  $L^{-1}$  zirconia I suspensions in ethanol, containing 0.4 g  $L^{-1}$  CA.



#### 5.2.2.6 Composition and crystallinity studies for MnO<sub>2</sub>

Figure 5-24 (A) TGA, (B) XRD and (C) deposition yield data for  $MnO_2$ . The XRD patterns are presented for (a) as-prepared material and annealed at (b) 300, (c) 400 and (d) 500 °C during 1h, •-JCPDS file 87-1497, •-JCPDS file 44-1386. The deposition yield versus annealing temperature data are presented for films prepared from suspensions, containing  $MnO_2$ , annealed at different temperatures during 1h, and 0.4 g L<sup>-1</sup> CA, at a deposition voltage of 20 V and a deposition time of 2 min.

The results presented above indicated that catechol group of CA allowed for CA absorption on  $MnO_2$  and zirconia. However, the CA adsorption can also be influenced by the properties of the adsorbent. It is therefore important to analyze the influence of adsorbent composition and structure on the CA adsorption and film deposition. TGA data showed that  $MnO_2$  contained adsorbed water. A sharp reduction of the  $MnO_2$ 

sample mass was observed below 200 °C, and then it decreased gradually with increasing temperature (Figure 5-24A). Observed mass loss of 13.3 % at 420 °C can be related to dehydration of the powders. Mass gain of 0.7 % observed in the range of 420–475 °C can be attributed to oxidation. Such mass gain indicated that MnO<sub>2</sub> was non-stoichiometric and contained Mn<sup>4+</sup> and Mn<sup>3+</sup> ions. Similar mass gain was observed in other investigations of MnO<sub>2</sub> powders prepared by chemical precipitation methods [207].

X-ray diffraction studies of as-prepared MnO<sub>2</sub> (Figure 5-24B) showed small diffraction peaks of a birnessite phase, corresponding to the JCPDS file 87-1497. It is known that the birnessite phase has near MnO<sub>2</sub> stoichiometry [208]. The birnessite formula is generally expressed as  $A_xMnO_{2+y}(H_2O)_z$ , where A represents an alkali metal cation [208, 209]. The oxidation state of Mn usually falls between 3.6 and 3.8, which represents a predominance of Mn<sup>4+</sup> with a minor amount of Mn<sup>3+</sup>. Thermal annealing can result in the formation of a dehydrated form of birnessite [208]. Figure 5-24B shows X-ray diffraction patterns of the sample annealed at different temperatures during 1 h. The XRD pattern of the sample annealed at 300 °C showed peaks of birnessite. At 400 °C a transformation to the cryptomelane phase was observed. The intensity of the peaks of cryptomelane phase increased with increasing temperature. The X-ray diffraction pattern of the sample annealed at 500 °C showed well defined peaks of the cryptomelane phase, corresponding to JCPDS file 44-1386. The

experimental data shown in Figure 5-24A and B indicated that thermal treatment resulted in dehydration and changes in crystalline structure of the powders. The  $MnO_2$  powders annealed at different temperatures were used for EPD. Figure 5-24C shows deposition yield data for 9 g L<sup>-1</sup> MnO<sub>2</sub> suspensions containing 0.4 g L<sup>-1</sup> CA. EPD was performed at a deposition voltage of 20 V and deposition time of 2 min. The deposition yield decreased with increasing annealing temperature (Figure 5-24C). The decrease in deposition yield correlated with the reduction of water content in the samples with increasing temperature.

# 5.2.2.7 Composition and crystallinity studies for ZrO<sub>2</sub>



Figure 5-25 (A) TGA, (B) XRD and (C) deposition yield data for zirconia I. The XRD patterns are presented for (a) as-prepared material and annealed at (b) 300, (c) 400 and (d) 500  $^{\circ}$ C during 1h, $\nabla$ -JCPDS file 50-1089. The deposition yield versus annealing temperature data are presented for films prepared from suspensions, containing zirconia I, annealed at different temperatures during 1h, and 0.4 g L<sup>-1</sup> CA at a deposition voltage of 150 V and deposition time of 2 min.

The TGA data for zirconia I (Figure 5-25A) showed that sample mass decreased with increasing temperature. The total mass loss at 600 °C was found to be 28 %. The reduction of the sample mass was attributed to dehydration. It is in this regard that other investigations showed that hydrolysis of ZrOCl<sub>2</sub> solutions resulted in the formation of hydrous zirconia [210]. XRD studies showed that as-prepared zirconia I was amorphous (Figure 5-25B). The powders remained amorphous after annealing at 300 and 400 °C for 1h. The crystallization of a metastable tetragonal phase was observed after annealing at 500 °C in agreement with the results of other investigations [211]. The corresponding X-ray diffraction pattern shows broad peaks corresponding to the JCPDS file 50-1089 of tetragonal zirconia (Figure 5-25B). However, it is difficult to distinguish between tetragonal and cubic phases due to peak broadening, which was attributed to small size of the crystals. The zirconia I powders annealed at different temperatures were used for EPD. Figure 5-25C shows deposition yield data for 9 g  $L^{-1}$  zirconia I suspensions containing 0.4 g  $L^{-1}$  CA. EPD was performed at a deposition voltage of 150V and deposition time of 2 min. The deposition yield decreased with increasing annealing temperature (Figure 5-25C). The decrease in deposition yield correlated with the reduction of water content in the

samples with increasing temperature.

# 5.2.2.8 Morphology studies

The deposition yield data for MnO<sub>2</sub> and zirconia I indicated that changes in crystallinity and phase content had no appreciable effect on the EPD of both materials. Two different materials, MnO<sub>2</sub> and ZrO<sub>2</sub> showed reduction in the deposition yield with increasing annealing temperature. It is suggested that surface OH groups of the materials play an important role in CA adsorption on the particle surface. Thermal treatment resulted in condensation of OH groups and water release. The removal of surface OH group resulted in reduced adsorption of CA, which, in turn, led to reduced particle charge and decreased deposition rate. It is in this regard that the chemical composition of the metal hydroxide/oxide, rather than the crystal structure, was found to determine the structure of the ligand–surface complex [212]. Recent studies demonstrated that organic acids bind to mineral surfaces simultaneously as inner- and outer-sphere complexes [197]. However, it was found [194] that catechol forms primarily outer-sphere complexes (Figure 5-20C) with MnO<sub>2</sub>.



Figure 5-26 SEM image of MnO<sub>2</sub> film prepared at a deposition voltage of 20 V.

The films of MnO<sub>2</sub>, zirconia I and zirconia II were studied by SEM. Figure 5-26 shows SEM image of MnO<sub>2</sub> film. The film contained nanoparticles of MnO<sub>2</sub> with particle size below 50 nm. Film porosity can be attributed to the packing of MnO<sub>2</sub> particles. Figure 5-27 compares the SEM images of zirconia I and zirconia II films. The films were porous and contained nanoparticles. The SEM image of zirconia I films showed agglomerates. The size of the agglomerates was in the range of 0.2-1 µm. Previous investigations [210] showed that hydrous zirconia, prepared by hydrolysis of ZrOCl<sub>2</sub> solutions, exhibits hard aggregation among primary particles. Such aggregation is attributed to strong interactions among the nanoparticles [210]. In contrast, agglomeration was avoided using CA as an additive during the synthesis of zirconia. It is suggested that CA was adsorbed on the surface of zirconia particles and prevented their aggregation. As a result, agglomerates were not observed in the SEM images of zirconia II films.



Figure 5-27 SEM images of (A) zirconia I and (B) zirconia II films prepared at a deposition voltage of 150 V, arrows show agglomerates.

The results of this investigation pave the way for the EPD of nanocomposite oxide films. CA can be used as a common charging and dispersing agent for  $MnO_2$  and zirconia I. It was found that  $MnO_2$  and zirconia I can be co-deposited from suspensions containing both materials. Figure 5-28 shows typical images of the composite films, which contained particles of both materials. The EDS studies of the films (Figure 5-28) prepared from 9 g L<sup>-1</sup> MnO<sub>2</sub> suspensions, containing 2 and 8 g L<sup>-1</sup> zirconia I, showed that Zr/Mn atomic ratio in the films was 0.22 and 0.68, respectively. The results indicated that film composition can be varied. It is suggested that CA can be used for surface modification, dispersion, electrophoretic deposition and co-deposition of other oxide materials. Therefore, composite films can be obtained using CA as a charging and dispersing agent. It is in this regard that improved capacitive behavior was obtained in composite films, containing MnO<sub>2</sub> and other oxides [213].



Figure 5-28 SEM images of composite films prepared from 9 g  $L^{-1}$  MnO<sub>2</sub> suspensions containing (A) 2 and (B) 8 g  $L^{-1}$  zirconia I at a deposition voltage of 150 V.

The results of this investigation indicated that bio-inspired chemical approach has been developed for the surface modification and electrophoretic deposition of MnO<sub>2</sub> film and composites. The analysis of experimental data for CA, TCA, PCA and DCA showed that adsorption of CA was attributed to catecholate type of bonding. The mechanism of CA adsorption was similar to that of catecholic amino acid, DOPA. The use of CA allowed for agglomerate-free synthesis. Adsorbed CA allowed for efficient dispersion, charging, electrophoretic deposition and co-deposition of different nanoparticles. The deposition yield data coupled with the results of TGA, XRD and FTIR results showed that surface chemistry, rather than the crystal structure, determined the adsorption behavior. Electron microscopy and energy dispersive spectroscopy investigations showed the formation of nanostructured oxide films and composites. The deposit composition can be varied by the variation of suspension composition. The bio-inspired chemical approach can be used for the surface modification and electrophoretic deposition of other nanostructured materials and composites.

# **5.2.3 Dispersion and deposition using other additives**

As a continuous investigation, other additives with chemical structure similar with DA and CA were used for the preparation of MnO<sub>2</sub>-MWCNTs composites. The results presented below showed that phenolic molecules can be used as common charging additives for two different materials: MnO<sub>2</sub> and MWCNTs. TA and GA were utilized for the fabrication of composite films by cathodic or anodic EPD. The investigations of the microstructure and electrochemical properties showed that the composites prepared by cathodic EPD are promising electrode materials for ES.

### 5.2.3.1 Structures of TA, GA, ChA and BA



Figure 5-29 Structures of (a) tyramine (TA), (b) gallic acid (GA), (c) chromotropic acid disodium salt (ChA) and (d) benzoic acid (BA).

Four different charging additives were investigated for the EPD of  $MnO_2$ , such as cationic TA and anionic GA, BA and ChA (Figure 5-29). In order to investigate the adsorption mechanism, the results obtained for the phenolic molecules containing OH groups, such as TA, GA and ChA, were compared with corresponding experimental data for BA molecules without OH groups (Figure 5-29).

It should be noted that particle charge is usually derived from zeta-potential measurements. However, the concept of zeta potential was developed for hard particles [214]. The use of this concept for soft particles, such as nanoparticles, containing adsorbed organic molecules presents difficulties [214, 215], related to theoretical derivation and accurate determination of zeta-potential from electrophoretic mobility measurements. Therefore, in order to investigate the influence of organic charging additives on the EPD of  $MnO_2$  nanoparticles, the deposition yield was measured as a function of additive concentration in the suspensions.

The suspensions of  $MnO_2$  in ethanol were unstable, and exhibited relatively fast sedimentation after ultrasonication. Cathodic deposits obtained from such suspensions were non-uniform and highly agglomerated. The formation of cathodic deposits indicated that  $MnO_2$  particles were positively charged in the ethanol suspensions. The mechanism of ceramic particle charging in alcohol medium has been discussed in the literature [164]. This mechanism involved the adsorption and ionization of alcohol at the particle surface, which was described in equation (5-1). The protonated alcohol dissociated and desorbed together with the alkoxide ion, leaving a proton on the particle surface. This resulted in the formation of positively charged particles, which deposited cathodically under the influence of an electric field [164].

# 5.2.3.2 Effect of additive concentration on film mass using different additives

The addition of cationic TA to the suspensions of  $MnO_2$  resulted in the improved suspension stability and higher deposition yield. Figure 5-30a shows that the mass of the cathodic deposit increased with increasing TA concentration and no anodic deposition was observed. It is suggested that adsorption of cationic TA, containing protonated amino groups, on the surface of  $MnO_2$  particles resulted in increased particle charge and increased cathodic deposition rate.



Figure 5-30 Film mass versus (a) TA, (b) GA, (c) ChA and (d) BA concentration in the 4 g  $L^{-1}$  MnO<sub>2</sub> suspension at the deposition time of 2 min ( $\blacktriangle$ -anodic deposits,  $\bullet$ -cathodic deposits).

In order to obtain anodic deposits, the influence of anionic additives, such as GA, ChA and BA, on the deposition of  $MnO_2$  has been studied. The anionic properties of GA and BA in the solutions are attributed to the COO<sup>-</sup> groups, whereas the anionic properties of ChA are related to the SO<sub>3</sub><sup>-</sup> groups (Figure 5-29). The addition of GA to the MnO<sub>2</sub> suspensions resulted in the reduction in the cathodic deposition rate, which can be attributed to the adsorption of anionic GA on the surfaces of positively charged MnO<sub>2</sub> particles and charge compensation. As a result, no cathodic deposition was observed at GA concentration of 0.05 g L<sup>-1</sup> (Figure 5-30b). However, anodic deposits were obtained at higher GA concentrations. The anodic deposition rate increased with increasing GA concentration. Significant increase in the deposition rate was observed in the concentration range of 0.05-0.25 g L<sup>-1</sup> GA. These results indicated that the

addition of anionic GA to the suspension of  $MnO_2$  particles resulted in the adsorption of GA on the particle surface and charge reversal.

Figure 5-30c shows the deposition yield as a function of CA concentration in  $MnO_2$  suspensions. The addition of ChA to the  $MnO_2$  suspensions resulted in the reduction in the cathodic deposition rate and no cathodic deposition was observed at CA concentrations of about 0.05 g L<sup>-1</sup>. However, anodic deposition was observed at higher ChA concentrations. The anodic deposition rate was relatively low in the range of 0.05-0.12 g L<sup>-1</sup> ChA, and then a significant increase in the deposition yield was observed. The anodic deposition rate from  $MnO_2$  suspensions containing 0.3 g L<sup>-1</sup> ChA was comparable with that observed for  $MnO_2$  suspensions containing 0.3 g L<sup>-1</sup> GA. However, the deposition rate decreased at higher ChA concentrations. Moreover, the increase in the ChA concentration above 0.3 g L<sup>-1</sup> resulted in reduced suspension stability. It is suggested that the increase in ChA concentration in the suspensions and ChA dissociation resulted in increasing concentration of Na<sup>+</sup> ions, which promoted particle flocculation [97] in agreement with the DLVO theory.

Figure 5-30d shows the deposition yield as a function of BA concentration in the  $MnO_2$  suspensions. The increase in the BA concentration in the range of 0-0.45 g L<sup>-1</sup> resulted in the reduced cathodic deposition rate. However, no anodic deposition was observed from the  $MnO_2$  suspensions containing BA.

It is suggested that adsorption of GA, ChA and BA can be governed by the electrostatic attraction between the anionic organic molecules and positively charged MnO<sub>2</sub> particles or surface complexation of the Mn ions at the MnO<sub>2</sub> particle surface. The results shown in Figure 5-30b and c indicated charge reversal of MnO<sub>2</sub> particles in the suspensions containing GA and ChA with different anionic groups. However, the MnO<sub>2</sub> particles remained positively charged in the suspensions containing BA (Figure 5-30d). It should be noted that electrostatic interactions can result in adsorption of the anionic molecules on the MnO<sub>2</sub> surface, charge compensation and reduced cathodic deposition rate. However, this mechanism cannot explain the charge reversal in the MnO<sub>2</sub> suspensions containing ChA and GA. The comparison of the axperimental data for GA and ChA, containing OH groups, with the corresponding data for BA without OH groups indicated that OH groups play an important role in the adsorption of the phenolic molecules on the MnO<sub>2</sub> surface. This is in good agreement with the QCM data presented in Figure 5-31.

### 5.2.3.3 Adsorption study

Figure 5-31 shows the kinetics of GA and BA adsorption from ethanol solutions on the 2  $\mu$ g MnO<sub>2</sub> deposit formed on the gold-coated quartz electrode. It should be noted, that GA and BA have similar chemical structures, and the difference is related to OH groups of GA. The injection of 0.05 g L<sup>-1</sup> of BA or GA into the ethanol solution

resulted in mass gain, which was attributed to the adsorption of the organic molecules. The mass gain related to the adsorption of BA was relatively small. In contrast, much higher mass gain related to the GA adsorption was observed. The essentially higher mass gain related to the GA adsorption indicated that OH groups are involved in the GA adsorption mechanism.



Figure 5-31 Mass gain, measured using QCM for the 2  $\mu$ g MD film deposited on a gold coated quartz crystal versus time after the injection of 0.05 g L<sup>-1</sup> of (a) BA and (b) GA into the ethanol solutions.

# 5.2.3.4 Effect of deposition time on film mass



Figure 5-32 Film mass versus deposition time for the 9 g  $L^{-1}$  MnO<sub>2</sub> suspensions containing (a) 0.015 g  $L^{-1}$  TA and (b) 0.45 g  $L^{-1}$  GA.

The cationic TA and anionic GA were investigated for the fabrication of MnO<sub>2</sub> films and composite MnO<sub>2</sub>-MWCNT films by EPD. It should be noted that deposition can also be achieved using anionic ChA as a charging additive. However, the suspensions containing GA showed improved stability, compared to the suspensions containing ChA. Figure 5-32 shows deposit mass of the MnO<sub>2</sub> obtained from the MnO<sub>2</sub> suspensions containing TA and GA. The deposit mass increased with increasing deposition time. Nearly linear dependences were obtained. These results indicated that the deposition yield of the cathodic and anodic deposition can be controlled. The deposits were removed from the substrates and studied by FTIR.





Figure 5-33 FTIR spectra for (a)  $MnO_2$  deposited from the 9 g L<sup>-1</sup>  $MnO_2$  suspension, containing 0.02 g L<sup>-1</sup> TA, (b) as-received TA, (c) as-prepared  $MnO_2$ , (d)  $MnO_2$  deposited from the 9g L<sup>-1</sup>  $MnO_2$  suspension, containing 0.45 g L<sup>-1</sup> GA, (e) as-received GA.

Figure 5-33a-c compares the FTIR spectrum of the deposit prepared from the MnO<sub>2</sub> suspension containing TA with FTIR spectra of as-prepared MnO<sub>2</sub> and as-received TA. The FTIR spectrum of as-prepared MnO<sub>2</sub> showed a broad peak centered at 3400 cm<sup>-1</sup>, which was related to the stretching vibration of OH group of absorbed water molecules [167, 168]. Strong peaks at 1538 and 1412 cm<sup>-1</sup> were associated with the interaction of Mn with surface OH groups [167, 168]. The FTIR spectrum of the deposit (Figure 5-33a) showed an additional strong absorption at 1620 cm<sup>-1</sup> which can be attributed to the C-C ring stretching vibrations of adsorbed TA. The FTIR spectrum of pure TA (Figure 5-33b) showed a similar peak in agreement with the literature data [216]. The peaks at 1050 and 1110 cm<sup>-1</sup> in the spectrum of the deposit were attributed to the aryl-oxygen stretching vibrations [170, 171]. However, the bending vibration of OH group [216] of TA at 1353 cm<sup>-1</sup> (Figure 5-33b) was not observed in the FTIR spectrum of MnO<sub>2</sub> modified with TA. It is suggested that TA binding to MnO<sub>2</sub> is achieved via the deprotonated OH groups, as shown in Figure 5-34a.



Figure 5-34 (a) TA and (b) GA adsorption on MnO<sub>2</sub>.

The FTIR spectrum of anodic deposits prepared from the  $MnO_2$  suspension containing GA showed (Figure 5-33d) a broad peak around 1614 cm<sup>-1</sup> which could be attributed 117

to the C-C ring stretching vibrations of adsorbed GA. The absorption at 1715 cm<sup>-1</sup> was attributed to the C-O stretching of the -COO<sup>-</sup> group of GA. The broad peak at 1402 cm<sup>-1</sup> can be attributed to the -COO<sup>-</sup> stretch mode [217]. The peaks at 1022 and 1095 cm<sup>-1</sup> in the spectrum of the deposit were related to the aryl-oxygen stretching vibrations [170]. Therefore, the FTIR data indicated the adsorption of GA on MnO<sub>2</sub>. Taking into account the literature data [218] on the formation of binary complexes of metal ions and GA in solutions, it was suggested that the adsorption mechanism of GA involves the formation of binary complexes at the MnO<sub>2</sub> surface (Figure 5-34b). However, binding of GA can also be achieved via one deprotonated -OH group.



Figure 5-35 SEM images for the nanocomposites prepared from the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing (a) 15 mg  $L^{-1}$  TA and 0.6 g  $L^{-1}$  MWCNTs and (b) 0.4 g  $L^{-1}$  GA and 0.6 g  $L^{-1}$  MWCNTs.

# 5.2.3.6 Morphology study

Composite  $MnO_2$ -MWCNTs films were prepared by EPD using TA and GA as common charging additives for  $MnO_2$  and MWCNTs. Figure 5-35 shows SEM images of the cathodic and anodic deposits prepared from the suspensions containing TA and GA, respectively. The deposits were porous with pore sizes below 100 nm and contained  $MnO_2$  nanoparticles and MWCNTs (Figure 5-35). Therefore,  $MnO_2$  and MWCNTs were positively charged in the suspensions containing TA and co-deposited cathodically. In contrast,  $MnO_2$  and MWCNTs were negatively charged in the suspensions containing GA and formed anodic deposits. The SEM results are in good agreement with the TGA and DTA data, which showed the formation of composite films.



Figure 5-36 TGA (a)–(c) and DTA (d)–(f) data for (a) and (d) as-prepared MnO<sub>2</sub>, and the deposits obtained from the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 0.015 g  $L^{-1}$  TA and (b) and (e) 0.3 g  $L^{-1}$  or (c) and (f) 0.6 g  $L^{-1}$  MWCNTs.



Figure 5-37 TGA (a) and (b) and DTA (c) and (d) for the deposits obtained from the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 0.4 g  $L^{-1}$  GA and (a) and (c) 0.6 g  $L^{-1}$  or (b) and (d) 1.2 g  $L^{-1}$  MWCNTs. Dashed line is the TGA curve for as-prepared MnO<sub>2</sub> (same as Figure 5-36a), presented for the comparison of the TGA data.

## 5.2.3.7 Composition study

Figure 5-36 compares TGA and DTA data for as-received MnO<sub>2</sub> and composite deposits prepared from the suspensions containing MWCNTs. The as-prepared MnO<sub>2</sub> showed mass loss, which could be mainly attributed to the dehydration. The total mass loss at 850 °C was found to be 14.0 mass%. A small mass gain at ca. 460 °C and a corresponding exotherm in the DTA curve could be attributed to the oxidation of non-stoichiometric MnO<sub>2</sub>. Similar mass gain was reported in the literature [207] for the MnO<sub>2</sub> powders prepared by other chemical precipitation methods. The deposit prepared from the 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension, containing 0.3 g L<sup>-1</sup> MWCNTs showed a total mass loss of 17.9 mass% at 850 °C. The additional mass loss, compared to the

mass loss for as-prepared MnO<sub>2</sub>, is related to the burning out of MWCNTs. Therefore, TGA data indicated the codeposition of MnO<sub>2</sub> and MWCNTs. Moreover, the composition of the MnO<sub>2</sub>-MWCNTs deposits can be varied. The increase in the MWCNTs concentration in the suspension resulted in increased MWCNTs content in the composite (Figure 5-37). For example, the deposit prepared from 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension, containing 0.6 g L<sup>-1</sup> MWCNTs showed a total mass loss of 22.2 mass% at 850 °C (Figure 5-36). Similar results were obtained for anodic deposits prepared from the suspensions containing GA (Figure 5-37). The total mass loss of 19.8 and 22.1 mass% at 850 °C was observed for the deposits prepared from MnO<sub>2</sub> suspension containing 0.6 and 1.2 g L<sup>-1</sup> MWCNTs, respectively. The additional mass loss, compared to that of as-prepared MnO<sub>2</sub>, was attributed to burning out of MWCNTs and indicated the formation of MnO<sub>2</sub>-MWCNTs composites with different MWCNTs contents.

## 5.2.3.8 Cyclic voltammetry study

As mentioned before, equation (2-10) indicates that high electronic and ionic conductivity are necessary in order to utilize the high theoretical SC (1370 F g<sup>-1</sup>) of  $MnO_2$  [162]. The improved ion access to the surface of  $MnO_2$  can be achieved by the development of porous electrodes. However, it is known that SC decreases significantly with increasing film thickness due to the low electronic conductivity of

MnO<sub>2</sub>. SCs of 210-240 F g<sup>-1</sup> were reported [6] for material loading of 150-180  $\mu$ g cm<sup>-2</sup>. Previous investigations [119] showed that SC at a scan rate of 2 mV s<sup>-1</sup> decreased from 400 to 177 F g<sup>-1</sup> when the film mass increased from 50 to 200  $\mu$ g cm<sup>-2</sup>. Conductive additives, such as carbon nanotubes and carbon black are usually used in order to achieve high electronic conductivity in the composite materials. The advantages of CNTs include their good conductivity and high aspect ratio (>1000), which provides percolation effect at very low volume fractions. Moreover, CNTs mechanically reinforce the matrix and prevent cracking. However, CNTs possess a rather low SC [219], typically in the range of 10-40 F g<sup>-1</sup>. Therefore, the amount of CNTs in the composite materials and composite microstructure must be optimized.

High SC can be obtained in porous composites containing well dispersed CNTs in the  $MnO_2$  matrix. A complicating factor in the fabrication of  $MnO_2$  is the lack of stable Mn (IV) precursors in aqueous solutions.  $MnO_2$  powders can be formed by reduction of the KMnO<sub>4</sub> or NaMnO<sub>4</sub> salts. The precipitation of  $MnO_2$  on carbon materials is an attractive approach to the fabrication of  $MnO_2$ -CNTs composites. However, difficulties are related to the degradation of carbon materials in the permanganate solutions according to the following reaction [220]:

$$4KMnO_4 + 3C + 2H_2O \rightarrow 4MnO_2 + 3CO_2 + 4KOH$$
(5-5)



Figure 5-38 CVs at scan rates of (a) 2 mV s<sup>-1</sup>, (b) 5 mV s<sup>-1</sup> and (c) 10 mV s<sup>-1</sup> for the 0.6 mg cm<sup>-2</sup> MnO<sub>2</sub>-MWCNTs nanocomposite prepared from the 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension containing 15 mg L<sup>-1</sup> TA and 0.6 g L<sup>-1</sup> MWCNTs.



Figure 5-39 CVs at scan rates of (a) 2 mV s<sup>-1</sup>, (b) 5 mV s<sup>-1</sup> and (c) 10 mV s<sup>-1</sup> for the 0.6 mg cm<sup>-2</sup> MnO<sub>2</sub>-MWCNTs nanocomposite prepared from the 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension containing 0.4 g L<sup>-1</sup> GA and 0.6 g L<sup>-1</sup> MWCNTs.

Another problem is related to the dispersion of the carbon materials in the permanganate solutions. Moreover, the accurate measurements of the mass and specific capacitance of the precipitated  $MnO_2$  present difficulties owing to the mass loss, attributed to the degradation of the carbon additives. Such difficulties can be

avoided by the use of chemically precipitated  $MnO_2$  nanoparticles and the formation of composite materials by EPD from colloidal suspensions, containing dispersed similarly charged  $MnO_2$  nanoparticles and MWCNTs.



Figure 5-40 SC versus scan rate for the  $MnO_2$ -MWCNTs nanocomposites prepared from the 9 g L<sup>-1</sup> MnO<sub>2</sub> suspensions containing 0.6 g L<sup>-1</sup> MWCNTs and (a) 15 mg L<sup>-1</sup> TA or (b) 0.4 g L<sup>-1</sup> GA.

Figures 5-38 and 5-39 show CVs for the MnO<sub>2</sub>-MWCNTs nanocomposite films with mass of 0.6 mg cm<sup>-2</sup>, prepared using TA and GA, respectively. The CVs indicate capacitive behavior in the voltage window of 0-0.9 V. The films were well adherent to the substrates during electrochemical cycling. The CVs of nanocomposites prepared using TA (Figure 5-38) have larger areas compared to the CVs of the nanocomposites obtained using GA (Figure 5-39). The difference is attributed to the higher SC of the nanocomposites prepared using TA. SCs calculated from CV data at different scan rates are shown in Figure 5-40. The films deposited anodically using GA showed a SC of 220 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>. The highest SC of the films prepared cathodically using TA was 553 F g<sup>-1</sup> at the scan rate of 2 mV s<sup>-1</sup>.
with increasing scan rates in the range of 2-100 mV s<sup>-1</sup> (Figure 5-40). The lower SC of anodic films can be attributed to the anodic oxidation of the substrates and the formation of interfacial layer with a low capacitance. Therefore, the composite films prepared by cathodic EPD method are promising materials for the application in ES.

The investigations of organic molecules, such as cationic TA and anionic GA, ChA and BA showed that TA, GA and ChA can be used for the surface modification and charging of MnO<sub>2</sub> nanoparticles. The addition of TA to the MnO<sub>2</sub> suspension resulted in an increased cathodic EPD yield, whereas the addition of GA and ChA enabled the  $MnO_2$  charge reversal and the formation of anodic deposits. The deposition yield measurements, QCM and FTIR data showed that OH groups were involved in the adsorption of the phenolic compounds on the MnO<sub>2</sub> nanoparticles. The adsorption mechanism was based on the deprotonation of the OH groups and surface complexation of Mn ions. It was shown that TA, GA and ChA can be used as charging additives for EPD of MnO<sub>2</sub>. A route to prepare the MnO<sub>2</sub>-MWCNTs composites by EPD was developed using the phenolic molecules as common charging additives for  $MnO_2$  and MWCNTs. Composite  $MnO_2$ -MWCNTs films were prepared by cathodic and anodic EPD using TA and GA, respectively. SEM studies showed the formation of composites containing well-dispersed MWCNTs in the MnO<sub>2</sub> matrix. The results of the thermogravimetric analysis demonstrated that the amount of the MWCNTs in the composite materials can be varied. The composite MnO<sub>2</sub>-MWCNTs electrodes

showed good capacitive behavior in the 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte in a voltage window of 0-0.9 V. The films prepared by cathodic EPD showed higher SC compared to the films prepared by anodic EPD with the highest SC of 553 F g<sup>-1</sup> at the scan rate of 2 mV s<sup>-1</sup>. The nanocomposites prepared by cathodic EPD are promising electrode materials for ES.

## 5.2.4 Dispersion and deposition using polyacrylic acid

Polyacrylic acid (PAA) is of great technological interest for applications in electrochemical [221, 222] devices. PAA has been utilized as a binder and solid electrolyte for lithium ion batteries [223] and ESs [224, 225]. PAA-MnO<sub>2</sub> composites showed a high electrochemical capacitance in aqueous electrolytes [226, 227]. It was shown that chemical stability of metal oxide nanoparticles in electronic and electrochemical devices can be improved by the use of PAA coatings [228]. PAA grafting onto the surface of NiO nanoparticles was performed for the protection of the metal oxide against leaching in aqueous solutions. Improved chemical stability was attributed to the formation of a PAA layer, which restricted the direct contact of the aqueous solution and the nanoparticles [228].

PAA coatings and thin films were prepared by electrosynthesis [229, 230] from acrylic acid monomer solutions. Several investigations were focused on the development of

new methods for the deposition of PAA films and composites, including plasma polymerization [231], chemical deposition [232] and self-assembly [233] methods.

EPD of organic-inorganic composites can be achieved from stable suspensions of inorganic particles in the polymer solutions. It was found that PAA provides efficient electrosteric stabilization of oxide particles in suspensions [234]. PAA showed the strong adsorption on  $MnO_2$  [235] and enabled efficient particle dispersion. Lee et al. [226] fabricated PAA-MnO<sub>2</sub> composites using spray-dried method. High SC of around 280 F g<sup>-1</sup> was obtained at a scan rate of 2 mV s<sup>-1</sup> for a 1.1 mg cm<sup>-2</sup> sample. A strong binding of the PAA chains to the CNT surface enabled efficient dispersion of CNTs in aqueous solutions [236]. PAA was used as a charging additive and dispersing agent for the EPD of ceramic materials [237].

The goal of this investigation was the fabrication of PAA and composite films by EPD and investigation of film microstructure, composition and deposition yield. We demonstrated the feasibility of the EPD of PAA films of controlled thickness and proposed a deposition mechanism. As an extension of these investigations, we developed EPD strategies for the deposition of composite films containing MWCNTs and oxide particles, such as  $MnO_2$  and NiO, in the PAA matrix.

#### 5.2.4.1 Structure and cross section SEM study of PAA



Figure 5-41 Structure of PAA.

Figure 5-41 shows a chemical structure of PAA. It is known that the negative charge of PAA in the solutions at pH > 4 is attributed to the deprotonated COOH groups [238]. The PAA molecules become protonated below  $pH\sim4$ .

EPD was performed from aqueous  $0.5-2 \text{ g L}^{-1}$  PAA solutions at pH = 8. Therefore, the PAA molecules were negatively charged in such solutions. It should be noted that stable solutions of charged polymers or ceramic particles are necessary for EPD. However, the same polymer macromolecules or ceramic particles must coagulate at the electrode surface in order to form a film. The electrostatic or electrosteric repulsion of the polymer macromolecules or ceramic particles at the electrode surface can prevent their deposition. It is suggested that electric field provided the electrophoretic motion of the PAA molecules, containing anionic COO<sup>-</sup> groups, towards the anode. The following electrode reaction resulted in a decreasing pH at the anode surface:

$$2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{O}_{2} + 4\mathrm{H}^{+} + 4\mathrm{e}^{-}$$
 (5-6)

(5-7)

The protonation of the anionic COO<sup>-</sup> groups of PAA in the low pH region at the electrode surface resulted in the charge neutralization.

 $COO^- + H^+ \rightarrow COOH$ 

Figure 5-42 SEM image of a cross-section of a PAA film, deposited on a platinized silicon substrate from the 1 g L<sup>-1</sup> PAA solution at a constant voltage of 5 V and a deposition time of 2 min.

It is suggested that the electrophoretic accumulation and the charge neutralization of PAA macromolecules at the electrode surface promoted their coagulation and film formation. Figure 5-42 shows a typical SEM image of a cross-section of a PAA film on the platinized silicon wafer substrate.

The deposition method allowed the formation of relatively uniform and dense films (Figure 5-42). It is known that the uniformity of thin films of non-conductive materials, deposited by EPD, is controlled by the electric field [104, 239]. The SEM studies showed that film thickness was varied in the range of 0-3  $\mu$ m by the variation

of the deposition time. This is in good agreement with the experimental data shown in Figure 5-43, which indicated that the amount of the deposited material increased with the increasing deposition time at a constant deposition voltage. However, the deposition rate decreased with increasing deposition time.

#### 5.2.4.2 Effect of time on PAA deposition

The deposition rate in the electrophoretic deposition process is described by the equation:

$$W = \frac{C\mu U}{\delta}$$
(5-8)

where C and  $\mu$  are the polymer concentration and mobility, respectively, U = U<sub>ap</sub>- U<sub>dep</sub>, U<sub>ap</sub> is the applied voltage, U<sub>dep</sub> is the voltage drop in a deposit, and  $\delta$  is the distance between electrodes [104]. The electrophoretic mobility of a polyelectrolyte, in which electric charges are distributed at a uniform density  $\rho_{fix}$ , can be derived from the equation [240].

$$\mu = \frac{\rho_{\text{fix}}}{\alpha\beta^2} \left[1 + \frac{2}{3} \left(\frac{\beta}{\sigma}\right)^2 \frac{1 + \beta/2\sigma}{1 + \beta/\sigma}\right]$$
(5-9)

where  $\beta = (\gamma/\alpha)^{\frac{1}{2}}$ , and  $\gamma$  is the frictional coefficient of the polyelectrolyte,  $\alpha$  is the viscosity of the liquid, and  $1/\sigma$  is the Debye length. U<sub>dep</sub> is proportional to the deposit resistance, which increases with the increase in deposit thickness. Therefore, the decrease in the deposition rate with increase in the deposition time (Figure 5-43) was

attributed to the decrease in the electric field  $E = U/\delta$  in the suspension due to the increasing voltage drop U<sub>dep</sub> [104] in the growing film.



Figure 5-43 Deposit mass versus deposition time for films prepared from the 1 g  $L^{-1}$  PAA solution at a deposition voltage of 5 V.

## 5.2.4.3 Morphology study of PAA-MWCNTs composites

The suspensions of MWCNTs were unstable and showed rapid sedimentation immediately after ultrasonic agitation. No EPD was observed from such suspensions. Sedimentation experiments showed that the addition of PAA provided stability of MWCNTs in aqueous suspensions. The 0.2 g L<sup>-1</sup> MWCNT suspension, containing 1 g L<sup>-1</sup> PAA, was stable during 24 h. It is in this regard that literature data showed a strong non-covalent binding of the PAA chains to MWCNTs, which enabled good dispersion of MWCNTs [241, 242]. The strong binding of the PAA chains to the MWCNTs surface was attributed to the hydrophobic interactions and the affinity of PAA for high-energy surfaces [241, 242].



Figure 5-44 SEM images of (a) surface and (b) cross-section of a composite PAA-MWCNTs film prepared from the 1 g  $L^{-1}$  PAA solution, containing 0.1 g  $L^{-1}$  MWCNT at a deposition voltage of 5 V and deposition time of 2 min, arrows in the top of the image (b) show MWCNTs.

Composite PAA-MWCNTs films were prepared from 1 g L<sup>-1</sup> PAA solutions containing 0-0.2 g L<sup>-1</sup> MWCNTs. The PAA adsorption on MWCNTs provided the charge, required for the EPD of MWCNTs. Figure 5-44 shows SEM images of a surface and cross-section of a PAA-MWCNTs film prepared by EPD. The SEM data (Figure 5-44a) indicated that MWCNTs were well dispersed in the polymer matrix. The good dispersion of the MWCNTs in the suspensions was beneficial for the MWCNTs dispersion in the composite films. It is well-known that the CNT dispersion strongly influences the properties of composites. The analysis of the cross-sections of the composite films showed that their thickness can be varied in the range of 0-5  $\mu$ m by the variation of the deposition time at a deposition voltage of 5 V.

The incorporation of MWCNTs into the PAA enabled the formation of thicker films,

compared to pure PAA films. The SEM image shown in Figure 5-44 indicated that composite PAA-MWCNTs films were relatively porous. In contrast, relatively dense PAA films were obtained from pure PAA solutions without MWCNTs (Figure 5-42). It was suggested that porous films, containing conductive MWCNTs, provided improved electron and ion transfer required for the H<sup>+</sup> generation in the electrochemical reactions (Equation 5-7) and charge neutralization of COO<sup>-</sup> groups (Equation 5-8). As a result, thicker films were obtained from PAA solutions, containing MWCNTs, compared to those without MWCNTs.

**5.2.4.4 Effects of time on PAA-MWCNTs composites deposition** 



Figure 5-45 Deposit mass versus deposition time for composite films prepared at a deposition voltage of 5 V from 1 g  $L^{-1}$  PAA solutions, containing 0.1 g  $L^{-1}$  MWCNTs.

Figure 5-45a shows deposit mass of the PAA-MWCNTs films versus deposition time at a constant deposition voltage. The deposition rate decreased with increasing deposition time due to the voltage drop in the deposited layer. A similar dependence was observed for pure polymer films (Figure 5-43).

#### 5.2.4.5 Crystallinity studies for PAA-MnO<sub>2</sub> and PAA-NiO composites

Electrophoretic deposition method has been investigated for the fabrication of composite films containing oxide particles in the PAA matrix. It should be noted that many applications, such as electrodes of ESs and batteries, require relatively large metal oxide content in the PAA based composites [223, 226, 227]. Moreover, porosity is an important factor controlling charge-discharge behavior of the composite electrodes in electrolyte solutions. In order to obtain such composites by EPD, the metal oxide concentration in suspensions was varied in the range of 0-4 g  $L^{-1}$ .

The aqueous suspensions of  $MnO_2$  and NiO were unstable and showed rapid sedimentation when ultrasonic agitation was interrupted. No electrophoretic deposition, cathodic or anodic, was observed from such suspensions. The addition of PAA to the suspensions of  $MnO_2$  and NiO allowed the formation of stable suspensions for EPD. Sedimentation experiments showed that the 4 g L<sup>-1</sup> suspensions of the ceramic particles containing 1 g L<sup>-1</sup> PAA were stable at least 24 h. This was in good agreement with the results of other investigations [234, 235, 243, 244], which showed that PAA macromolecules adsorbed on the surfaces of oxide particles provided the efficient stabilization of the particles. Moreover, the adsorbed PAA macromolecules provided the charge required for electrophoretic deposition. The electrophoretic mobility of polyelectrolyte-coated spherical colloidal particles is described by the following equation [240]:

$$\mu = \frac{\varepsilon \varepsilon_{o}}{\tau} \frac{\phi_{o} / \sigma_{m} + \phi_{DON} / \omega}{1 / \sigma_{m} + 1 / \omega} f(\frac{d}{a}) + \frac{\rho_{fix}}{\tau \omega^{2}}$$
(5-10)

where  $\varepsilon$  is the dielectric constant of the solvent,  $\varepsilon_0$  is the vacuum dielectric permittivity,  $\varphi_0$  is the potential at the boundary between the polyelectrolyte and the surrounding solution,  $\varphi_{DON}$  is the Donnan potential,  $\sigma_m$  is the Debye-Hückel parameter of the polyelectrolyte layer, d is the thickness of polyelectrolyte layer, a is the particle radius. The function f(d/a) tends to 1 as d/a decreases, whereas it becomes 2/3 as d/a increases. According to the literature [240], the  $\varphi_0$  and  $\varphi_{DON}$  values are highly dependent on  $\rho_{fix}$ . Therefore, the electrophoretic mobilities of PAA (Equation 5-9) and ceramic particles, containing adsorbed PAA (Equation 5-10), are influenced by the charge density of PAA macromolecules. It should be noted that the equation for electrophoretic mobility of oxide particles, containing adsorbed polymer, does not include zeta-potential. As pointed out previously, the electric charge of PAA is attributed to the deprotonated COOH groups. The formation of composite PAA-metal oxide films is a final result of two processes, one involving the electrophoresis of PAA macromolecules and the other based on the electrophoresis of oxide particles, containing adsorbed PAA. The charge neutralization of PAA at the electrode surface (Equation 5-7) and coagulation resulted in the formation of composite films. It should be noted that Equation 5-11 cannot be used for MWCNTs and HNTs due to their tubular geometry. However, it is suggested that the formation of PAA-MWCNTs composites is governed by a similar mechanism.

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Figure 5-46 shows the X-ray diffraction patterns of the composite films, obtained by co-deposition of PAA and oxide particles. The diffraction spectrum of the deposit prepared from the PAA solutions, containing dispersed MnO<sub>2</sub>, showed small peaks corresponding to the JCPDS file 87-497 of MnO<sub>2</sub>. This was in good agreement with the results of previous investigations [245], which showed that as-precipitated MnO<sub>2</sub> powders were mainly amorphous and contained a small amount of a birnessite phase. The X-ray diffraction patterns of PAA-NiO deposits showed well defined peaks of NiO.



Figure 5-46 X-ray diffraction patterns for deposits prepared from the 1 g  $L^{-1}$  PAA solutions containing 4 g  $L^{-1}$  of oxide materials: (a) MnO<sub>2</sub> and (b) NiO ( $\Delta$ -JCPDS file 87-1497, •-JCPDS file 47-1049).

### 5.2.4.6 Composition study for PAA-MnO<sub>2</sub> and PAA-NiO composites

The composite deposits, prepared from the 1 g  $L^{-1}$  PAA solutions containing 4 g  $L^{-1}$  of

oxide materials, were studied by TGA and DTA. The mass loss at temperatures below

600  $^{\circ}$  observed in the TGA data and corresponding broad DTA exotherms (Figure 5-47) were attributed to burning out of PAA in agreement with the data for pure PAA (Figure 5-47c).

However, the TGA data showed the incorporation of oxide powders into the deposits. The mass content of oxide materials in the composite deposits was estimated from the corresponding sample mass at 800 °C. The mass content of  $MnO_2$  and NiO was found to be 65.2 % and 67.3 %, respectively. The amount of the deposited material can be varied by the variation of the deposition time, as shown in Figure 5-48. The slope of the curves decreased with increase in the deposition time.



Figure 5-47 TGA and DTA data for deposits prepared from the 1 g  $L^{-1}$  PAA solutions containing 4 g  $L^{-1}$  of oxide materials: (a) MnO<sub>2</sub>, (b) NiO and (c) as-received PAA.



#### 5.2.4.7 Effects of time for PAA-MnO<sub>2</sub> and PAA-NiO composites

Figure 5-48 Deposit mass versus deposition time at a deposition voltage of 5 V for deposits prepared from the 1 g  $L^{-1}$  PAA solutions containing 4 g  $L^{-1}$  of oxide materials: (a) MnO<sub>2</sub> and (b) NiO.

As shown in Figure 5-48, the decrease in the deposition rate was attributed to the increase in the voltage drop in the growing films and the corresponding decrease in the electric field in the suspensions in agreement with Equation 5-8.

#### 5.2.4.8 Morphology studies for PAA-MnO<sub>2</sub> and PAA-NiO composites

The films, prepared from the PAA solutions, containing MnO<sub>2</sub> and NiO were studied by SEM. The SEM images showed the formation of continuous and crack free films (Figure 5-49), containing oxide particles in a polymer matrix. It is suggested that PAA acts as a binder, which prevents film cracking during drying and improves film adhesion. The results of SEM investigations were in good agreement with the corresponding TGA, DTA and XRD data, which indicated the formation of composite films. The films with a relatively large concentration of an inorganic phase showed porosity. As an example, Figure 5-49 shows SEM images of the films prepared from PAA solutions containing 4 g L<sup>-1</sup> of MnO<sub>2</sub> and NiO. The film porosity can be attributed to the oxygen evolution (Equation 5-6) at the electrode surface during deposition. However, relatively dense films were obtained from pure polymer solutions at the same deposition voltage. Film porosity can result from the packing of oxide particles or agglomerates. It is in this regard that PAA polymer can provide bridging of small particles. The SEM images showed that some pores were significantly larger than particle diameters. For example, Figure 5-49a showed relatively large pores with diameter of ~200 nm, whereas the size of primary silica particles was far below 100 nm. It should be noted that porous films are beneficial for many applications. For example, the development of MnO<sub>2</sub> and NiO electrodes for ESs and batteries requires the use of porous materials. The porosity allows an efficient electrolyte access to the electrochemically active oxide phase.

The results of this investigation showed that EPD is a versatile method for the fabrication of PAA based composite materials. One of the important challenges in the EPD of advanced composites is the development of a common dispersing agent suitable for charging and deposition of different materials. Previous investigations highlighted the importance of such dispersing agents for the co-deposition of various oxides, the fabrication of multilayers of different materials and functionally graded materials with controlled layer thickness and composition [97, 203, 246].



Figure 5-49 SEM images of films on stainless steel substrates, prepared from the 1 g  $L^{-1}$  PAA solutions containing 4 g  $L^{-1}$  of oxide materials: (a) MnO<sub>2</sub> and (b) NiO.

In this investigation, PAA has been utilized for the efficient dispersion, charging and deposition of MWCNTs and oxide materials. It is suggested that similar strategies can be used for the deposition of new composites containing other inorganic and organic functional materials in a PAA matrix. Therefore, the reported results pave the way for the deposition of new and advanced composites for various applications. It is in this regard that the application of MnO<sub>2</sub> and NiO as electrode materials for ESs requires efficient electron and ion access to the surfaces of the electrochemically active materials. The co-deposition of MnO<sub>2</sub>, MWCNTs and PAA solid electrolyte [226, 227] can be used for the fabrication of porous composites with improved ionic and electronic conductivity.

The results presented in this chapter showed that EPD method has been developed for the deposition of PAA films. The method allowed the formation of uniform PAA films of controlled thickness in the range of 0-3  $\mu$ m. The deposition mechanism was based on the electrophoresis of anionic PAA macromolecules, charge neutralization in the low pH region at the anode surface and film formation. The feasibility of EPD of composite films, containing MWCNTs, MnO<sub>2</sub> and NiO in a PAA matrix, has been demonstrated. The adsorption of PAA on the nanotubes and oxide particles provided improved suspension stability and electric charge required for EPD. The film composition and thickness can be varied by the variation of the suspension composition and deposition time. The results indicated that PAA can be used as a common dispersing agent suitable for charging and codeposition of various materials.

## 5.2.5 Dispersion and deposition using organic dyes

Previous studies [247, 248] investigated the phenolic molecules, such as DA, TA and GA, for the deposition of composites MnO<sub>2</sub>-MWCNTs, where the phenolic molecules can serve as a common charging additive for both MnO<sub>2</sub> nanoparticles and MWCNTs. This method neither affects the properties of CNTs, nor introduces undesired impurities. The addition of these phenolic molecules can be easily controlled. However, they only have one aromatic ring in their chemical structures, which can limit their adsorption affinity on CNTs [249]. Many attempts to obtain pure CNTs deposits by using these phenolic molecules have failed [247, 248].

The goal of this investigation was EPD of MWCNTs using pyrocatechol violet (PV), containing three aromatic rings, and the fabrication of MnO<sub>2</sub>-MWCNTs for the ES application. The results presented below showed that CNTs films were deposited by EPD using the dispersing agent PV for the first time. The adsorption mechanism of PV on MWCNTs and its application in ES was investigated.

## 5.2.5.1 Dispersion stability testing



Figure 5-50 (A) Chemical structure of PV, (B) Photo of film on stainless steel substrate deposited from 2 g  $L^{-1}$  PV in ethanol at a deposition voltage of 150 V and a deposition time of 10 min, (C) comparison of dispersion ability of 1.6 g  $L^{-1}$  MWCNTs suspension in ethanol without (left) and with (right) 1 g  $L^{-1}$  PV, and (D) photo of film on stainless steel substrate deposited from 1.2 g  $L^{-1}$  MWCNTs suspension in ethanol, containing 1.2 g  $L^{-1}$  PV, at a deposition voltage of 150 V and a deposition time of 2 min.

Figure 5-50 demonstrates the dispersion ability of PV for MWCNTs in ethanol solution. The right bottle in Figure 5-50C, containing PV and MWCNTs in ethanol solution, shows excellent stability even for several months. Smooth MWCNTs film

was able to be deposited in such conditions (Figure 5-50D). On the contrary, the left bottle in Figure 5-50C, without the addition of PV, demonstrates rapid precipitation after the ultrasonication is interrupted. As one of the aromatic compounds (Figure 5-50A), PV can interact strongly with sidewalls of CNTs through  $\pi$ - $\pi$  stacking [249-251]. Moreover, pure PV films could be deposited, as shown in Figure 5-50B.

5.2.5.2 Effects of concentration, time and voltage on MWCNTs deposition



Figure 5-51 (A) Film mass as a function of (A) PV concentration, (B) time and (C) voltage for 1.2 g  $L^{-1}$  MWCNTs suspension in ethanol: (A and B) at a deposition voltage of 100 V, (B and C) at a PV concentration of 1.2 g  $L^{-1}$ , and (A, B and C) at a deposition time of 2 min.

We developed a new approach to deposit MWCNTs and deposited pure MWCNTs

film using dispersant for the first time. Figure 5-51 shows typical deposition yield of MWCNTs versus PV concentration, deposition time and voltage. The deposition rate increased with an increase in PV concentration (Figure 5-51A). The mass of deposited CNTs increased with the increasing deposition time and voltage (Figure 5-51B and C), indicating the formation of CNTs films with different thickness. The deposition yield of CNTs can be varied by changing PV concentration, deposition time or voltage.

#### **5.2.5.3 Morphology studies of MWCNTs films**

SEM images (Figure 5-52) of deposits obtained from MWCNTs solution containing PV could be regarded as the direct evidence to the existence of and MWCNTs deposition. Figure 5-52 shows SEM images of MWCNTs deposits obtained at 100 and 150 V, respectively. The deposition process resulted in co-deposition of MWCNTs and PV. However, the deposition rate of PV was relatively low at deposition voltages below 150V. The SEM images at different magnifications (Figure 5-52A and B) of the film prepared at a deposition voltage of 100V showed MWCNTs. The film was continuous and porous. Such porous films are beneficial for application in ES. Further increase in the deposition voltage resulted in reduced porosity. The pores between MWCNTs were filled with deposited PV. Figure 5-52C and D show a film deposited at a deposition voltage of 150V. The SEM image shows a relatively dense film, containing MWCNTs in a PV matrix.



Figure 5-52 SEM images of films deposited from 1.2 g  $L^{-1}$  MWCNTs suspension in ethanol containing 1.2 g  $L^{-1}$  PV, at deposition voltages of 100 V and 150 V, respectively.

Basing on the experimental results aforementioned, we could make such an assumption that the adsorption of PV onto the surface of MWCNTs enables the stabilization of MWCNTs in ethanol solution, and the deposition of PV ensures the formation of MWCNTs films. According to the literature [252, 253], the SCs of MWCNTs are in the range of 10-40 F g<sup>-1</sup>, which is not useful for the SC application. Therefore, further research was focused on co-deposition of MWCNT and MnO<sub>2</sub>

### 5.2.5.4 Effects of concentration, time and voltage on MnO<sub>2</sub> deposition

As pointed out above,  $MnO_2$  particles were positively charged in the ethanol solution. The charging mechanism of ceramic nanoparticles in alcohol solution has been



discussed in the literature [164]. The mechanism is expressed in the equation (5-1).

Figure 5-53 (A) Film mass as a function of (A) PV concentration (a-cathodic and b-anodic), (B) time and (C) voltage for 9 g  $L^{-1}$  MnO<sub>2</sub> suspension in ethanol (A and B) at a deposition voltage of 100 V, at a (B and C) PV concentration of 1.2 g  $L^{-1}$ , and at a (A and C) deposition time of 2 min.

It is known that the fabrication of stable suspensions of  $MnO_2$  nanoparticles with a particle concentration of >1 mM presents difficulties [254]. The dilute suspensions with a concentration of <1 mM cannot be used for practical applications of EPD. It is in this regard that the deposition rate in the EPD process is proportional to the particle concentration in suspensions [97]. The suspension of concentrated  $MnO_2$  is unstable and can show rapid precipitation after the ultrasonication is interrupted. EPD of  $MnO_2$ 

from such suspension presents difficulties, and such deposits are usually highly-agglomerated and non-uniform. Contrarily, uniform deposits are obtained from well-dispersed and stable MnO<sub>2</sub> suspension containing PV as a dispersant. Figure 5-53 demonstrates the deposition yield of MnO<sub>2</sub> vesus PV concentration, deposition time and voltage. The addition of anionic PV to the MnO<sub>2</sub> suspension resulted in the reduction of cathodic deposition rate, which can be ascribed to the adsorption of anionic PV on the surfaces of positively charged MnO<sub>2</sub> nanoparticles and charge compensation. As a result, no cathodic deposition was observed at PV concentration of 0.05 g  $L^{-1}$  (Figure 5-53A). However, anodic deposits were obtained at higher PV concentrations. The anodic deposition rate increased with increasing PV concentration. Significant increase in the deposition rate was observed in the concentration range of 0.05-0.4 g  $L^{-1}$  PV. These results indicated that the addition of anionic PV to the suspension of MnO<sub>2</sub> particles resulted in the adsorption of PV on the nanoparticle surface and charge reversal. Moreover, the deposition mass of MnO2 increased with increasing deposition time and voltage (Figure 5-53B and C). Nearly linear dependences were obtained. These results indicated that the deposition yield of  $MnO_2$ can be controlled. The deposits were removed from the substrates and studied by FTIR.

#### 5.2.5.5 Surface chemistry study



Figure 5-54 FTIR spectrum for deposit prepared from 9 g  $L^{-1}$  MnO<sub>2</sub> suspension, containing 1.2 g  $L^{-1}$  PV.

Figure 5-54 shows the FTIR spectrum of the deposit obtained from the  $MnO_2$  suspension containing PV. The FTIR peaks at 1630, 1566 and 1473 cm<sup>-1</sup> were attributed to the stretching of the aromatic ring [187]. The FTIR spectrum showed peaks at 1342 cm<sup>-1</sup>, which was related to the C-O vibration [252, 255]. The FTIR peak at 1224 cm<sup>-1</sup> was attributed to the C=O vibration [255]. FTIR peak at 1186 cm<sup>-1</sup> was ascribed to the SO<sub>3</sub><sup>-</sup> vibration [253, 255]. The peaks at 1090 and 1020 cm<sup>-1</sup> were related to the aryl-oxygen stretching vibration [170]. Therefore, the FTIR data indicated the adsorption of PV on MnO<sub>2</sub> nanoparticles. As shown in Figure 5-50, PV has two different complexing sites: an anionic SO<sub>3</sub><sup>-</sup> group does not play a significant role in surface complexation process [255]. Therefore, it was suggested that the adsorption mechanism of PV involved the formation of binary complexes at the MnO<sub>2</sub>

nanoparticles surface (Figure 5-55). The adsorbed PV could enhance the charge of  $MnO_2$  nanoparticles and thus increase the stability of the suspension.



Figure 5-55 Proposed adsorption mechanism of PV on MnO<sub>2</sub> nanoparticles.

#### 5.2.5.6 Morphology studies of MWCNTs, MnO<sub>2</sub> films and composites

Figure 5-56 demonstrates the cross section SEM images obtained from MWCNTs and  $MnO_2$  suspensions containing PV. Figure 5-56A shows the MWCNTs deposits with a thickness of ~3 µm, indicating the formation of MWCNTs film. While Figure 5-56B demonstrates the  $MnO_2$  deposits with a thickness of ~6 µm, indicating the formation of  $MnO_2$  film. The results indicated the possibility of deposition of relatively thick films. The corresponding surface SEM images for MWCNTs and  $MnO_2$  films were shown in Figure 5-57A and 5-57B. The deposits were porous with pore sizes below 100 nm and contained MWCNTs (Figure 5-57A) and  $MnO_2$  nanoparticles (Figure 5-57B). Composite  $MnO_2$ -MWCNT was prepared by EPD using PV as a common dispersing agent for  $MnO_2$  and MWCNTs (Figure 5-57C). The composite was porous

and contained MWCNTs in a  $MnO_2$  matrix. The SEM results are in good agreement with the DTA and TGA data, which shows the formation of  $MnO_2$ -MWCNTs composites.



Figure 5-56 Cross-section SEM images of films deposited from (A) 1.2 g  $L^{-1}$  MWCNTs in ethanol containing 1.2 g  $L^{-1}$  PV and (B) 9 g  $L^{-1}$  MnO<sub>2</sub> suspension in ethanol containing 1.2 g  $L^{-1}$  PV, at a deposition voltage of 100 V.



Figure 5-57 SEM images at a higher magnification for film deposited from (A) 1.2 g  $L^{-1}$  MWCNTs suspension containing 1.2 g  $L^{-1}$  PV, (B and C) 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 1.2 g  $L^{-1}$  PV, (B) without and (C) with 1.2 g  $L^{-1}$  MWCNTs. Arrows shows MWCNTs.

## 5.2.5.7 Composition study



Figure 5-58 TGA (a, b and c) and DTA (d, e and f) data for deposits obtained from (a and f) 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 1.2 g  $L^{-1}$  PV, and (b, c, d and e) 9 g  $L^{-1}$  MnO<sub>2</sub> suspension containing 1.2 g  $L^{-1}$  PV, with (b and e) 1.2 g  $L^{-1}$  and (c and d) 2.4 g  $L^{-1}$  MWCNTs, respectively, at a deposition voltage of 100 V.

Figure 5-58 compares DTA and TGA data for as-received MnO<sub>2</sub> and composite deposits prepared from the MnO<sub>2</sub> suspension containing MWCNTs. The as-prepared  $MnO_2$  showed mass loss, which could be mainly attributed to the dehydration. The total mass loss at 850 °C was found to be 13.9 mass%. A small mass gain at ca. 460  $\,^{\circ}$  C and a corresponding exotherm in the DTA curve could be attributed to the oxidation of non-stoichiometric MnO<sub>2</sub>. Similar mass gain was reported in the literature [207] for the MnO<sub>2</sub> powders prepared by other chemical precipitation methods. The deposit prepared from the 9 g  $L^{-1}$  MnO<sub>2</sub> suspension, containing 1.2 g  $L^{-1}$  MWCNTs showed a total mass loss of 29.3 mass% at 850 °C. The additional mass loss, compared to the mass loss for as-prepared MnO<sub>2</sub>, was related to the burning out of MWCNTs. Therefore, TGA data indicated the codeposition of MnO<sub>2</sub> and MWCNTs. Moreover, the composition of the MnO<sub>2</sub>-MWCNTs deposits can be controlled. The increase in the MWCNTs concentration in the suspension resulted in increased MWCNTs content in the composite (Figure 5-58). For instance, the deposit prepared from 9 g  $L^{-1}$  MnO<sub>2</sub> suspension, containing 2.4 g  $L^{-1}$  MWCNTs, showed a total mass loss of 32.3 mass% at 850 °C (Figure 5-58), which indicated a higher MWCNTs content when  $1.2 \text{ g L}^{-1}$  MWCNTs was used.

#### 5.2.5.8 Cyclic voltammetry and impedance spectroscopy studies

The MnO<sub>2</sub>-MWCNTs composites were prepared for the ES application. Figure 5-59 shows the electrochemical properties of MnO<sub>2</sub> and MnO<sub>2</sub>-MWCNTs films with a similar mass of 0.6 mg cm<sup>-2</sup>. The box-shape CVs (Figure 5-59A) indicated the good capacitive behavior in the voltage window of 0-0.9 V. The CV of MnO<sub>2</sub>-MWCNTs composite has a larger area than that of MnO<sub>2</sub> film, which could be ascribed to the high SC of the MnO<sub>2</sub>-MWCNTs composite. SCs calculated from CV data at different scan rates are demonstrated in Figure 5-59B. The MnO<sub>2</sub> film showed a SC of 224 F g<sup>-1</sup> at a scan rate of 2 mV s<sup>-1</sup>, which the MnO<sub>2</sub>-MWCNTs composite demonstrated a SC of 335 F g<sup>-1</sup> at the same scan rate. The SC decreased with increasing scan rates in the range of 2-100 mV s<sup>-1</sup>. The impedance data of MnO<sub>2</sub> film, which indicated a smaller charge transfer resistance [1]. The lower SC of MnO<sub>2</sub> could be due to the low conductivity of MnO<sub>2</sub> films. Therefore, the MnO<sub>2</sub>-MWCNTs composites are promising materials for the ES application.



Figure 5-59 (A) CVs at 20 mV s<sup>-1</sup>, (B) SC vs scan rate and (C) Nyquist plot of complex impedance for films prepared from 9 g L<sup>-1</sup> MnO<sub>2</sub> suspension containing 1.2 g L<sup>-1</sup> PV, (a) without and (b) with 2.4 g L<sup>-1</sup> MWCNTs.

In summary, MWCNTs films have been deposited for the first time by EPD using PV as a dispersing agent. PV has shown to be an effective charging additive, which provides the stabilization of two different materials: MWCNTs and  $MnO_2$  nanoparticles.  $MnO_2$  and  $MnO_2$ -MWCNTs films are deposited by using PV as a common dispersing agent. TGA, DTA and SEM data give significant proof of the co-deposition of  $MnO_2$  and MWCNTs and formation of the  $MnO_2$ -MWCNT composites. CV data of the films tested in the 0.5 M Na<sub>2</sub>SO<sub>4</sub> solutions showed capacitive behavior in the voltage window of 0-0.9 V. The highest SC of 335 F g<sup>-1</sup> is obtained at a scan rate of 2 mV s<sup>-1</sup>. The SC decreases with an increasing scan rate in

the range of 2-100 mV s<sup>-1</sup>. The MnO<sub>2</sub>-MWCNTs composites prepared using PV are promising electrode materials for ES.

# **5.3 In-situ impregnation methods**

Porous current collectors, such as Ni plaques and foams, are widely used in industry for the fabrication of electrodes for rechargeable batteries [256, 257]. Ni plaques are current collectors of choice for battery applications demanding high power and reliability, along with long cycle life, such as batteries for aerospace and railway applications, power tools, and portable electronics. Significant advances in the development of Ni plaques were achieved by the use of filamentary Ni particles with high surface area, which provided improved contact with active material [258, 259]. The pore size of Ni plaques is usually much smaller compared to that of other industrial current collectors, such as Ni foams. The smaller pore size decreased the distance for electrons to travel from the current collector into the active material during cell discharge and, consequently, improved the discharge rate characteristics [258, 259]. Ni hydroxide is used as a positive electrode material for a number of alkaline secondary cells such as Ni/Cd, Ni/Fe, Ni/Zn, and Ni/MH cells [260]. Due to the small pore size of Ni plaques, the impregnation of the plaques with Ni hydroxide was achieved by in-situ chemical or electrochemical synthesis in pores using Ni nitrate solutions [260-262]. Chemical impregnation is based on multiple dipping of the plaques in the Ni nitrate solutions and treatment in basic solutions. Electrochemical synthesis is based on the cathodic electrogenerated base method [97].

A new wave of interest in the use of Ni plaques as current collectors in electrochemical energy storage devices is related to the ES development [227] for high power applications in electric and hybrid vehicles. Ni plaques are especially attractive for the fabrication of advanced ES electrodes, containing MnO<sub>2</sub> as an active material. The interest in MnO<sub>2</sub> is related to low cost of this material, which exhibited high SC in environmentally friendly aqueous electrolytes [227, 263]. As mentioned before, high electronic and ionic conductivity are necessary in order to utilize the high theoretical SC (1370 F  $g^{-1}$  [162]) of MnO<sub>2</sub>. However, the electronic conductivity of MnO<sub>2</sub> is low. As a result, the SC decreased significantly with increasing film thickness [7, 254]. Therefore, it is expected that similar to the battery technology, porous Ni plaques with high surface area can provide improved contact with active material and higher conductivity of ES electrodes.

The important task is the development of chemical and electrochemical methods for the impregnation of Ni plaques with  $MnO_2$ . A complicating factor in the fabrication of  $MnO_2$  is the lack of stable Mn (IV) precursors in aqueous solutions.  $MnO_2$  powders can be formed by reduction of KMnO<sub>4</sub> solutions using various reducing agents such as  $Mn^{2+}$  salts and organic acids [158, 264]. However, the use of  $Mn^{2+}$  salts and organic acids for the in-situ synthesis in pores of Ni plaques presents difficulties, attributed to the removal of anions and organics from the pores after the chemical precipitation of  $MnO_2$ . In the previous investigations [11, 12] it was shown that thin  $MnO_2$  films with good capacitive behavior can be obtained by cathodic reduction of  $Mn^{7+}$  species using solutions of  $KMnO_4$  or  $NaMnO_4$  salts. The latest achievement in this process was attained by the use of reverse pulse electrosynthesis, which enabled the formation of porous films with improved capacitive behavior [117].

The goal of this investigation was the development of chemical and electrochemical strategies for the impregnation of Ni plaques and investigation of the capacitive behavior of the prepared electrodes for application in ES. The results presented below indicated that isopropanol can be used as a reducing agent for the impregnation by a chemical method. In this approach, the problem related to the washing of the prepared material and removal of the reducing agent and reaction products can be avoided. Cathodic electrosynthesis from solutions of KMnO<sub>4</sub> salts has been utilized for the electrochemical impregnation, using galvanostatic or reverse pulse deposition techniques. The results obtained by different methods were analyzed and compared.

#### 5.3.1 Crystallinity study for MnO<sub>2</sub> sintered at different temperatures



Figure 5-60 X-ray diffraction patterns for the powder prepared by reduction of KMnO<sub>4</sub> solution with isopropanol: (a) as-precipitated and after annealing at different temperatures during 1 h : (b) 200, (c) 300, (d) 400 and (e) 500 °C.

It is suggested that the following redox reaction resulted in the reduction of KMnO<sub>4</sub> and formation of MnO<sub>2</sub>:

$$2MnO_4^{-} + 3(CH_3)_2CH - OH + 2H^{+} \rightarrow 2MnO_2 + 3(CH_3)_2CO + 4H_2O$$
(5-11)

This is in good agreement with the results of other investigations, which showed that the oxidation of isopropanol resulted in the formation of acetone [265, 266]. The XRD pattern of as-precipitated  $MnO_2$  (Figure 5-60) indicated that the material was mainly amorphous. Small diffraction peaks can be attributed to the birnessite phase (JCPDS file 87-1497). The peaks of the birnessite phase became more distinct after annealing at 200 and 300 °C. It is suggested that annealing resulted in the crystallization of an amorphous phase. Further increase in the annealing temperature resulted in enhanced intensity of the peaks of the birnessite phase. According to the literature, the birnessite has near-MnO<sub>2</sub> stoichiometry with a formula generally expressed [208] as  $A_xMnO_{2+y}(H_2O)_z$ , where A represents an alkali metal cation. The average oxidation state of Mn usually falls [208] between 3.6 and 3.8, which represents a predominance of Mn<sup>4+</sup> with minor amount of Mn<sup>3+</sup>. ICP studies showed that MnO<sub>2</sub> powder contained K with the Mn/K atomic ratio of 3.1. The MS of manganese was found to be 3.63.

## 5.3.2 FTIR study

The FTIR spectrum for as-prepared  $MnO_2$  (Figure 5-61) showed a broad peak centered at 3430 cm<sup>-1</sup> which can be attributed to the vibration of OH groups of adsorbed water molecules [165, 168, 267]. The bands at 1628, 1540 and 1047 cm<sup>-1</sup> represented the vibrations associated with interactions of Mn with OH, O and K [167, 268]. The adsorptions at 1384 and 1258 cm<sup>-1</sup> were attributed to the vibrations of adsorbed isopropanol [269, 270]. The bands at 450 and 512 cm<sup>-1</sup> are characteristic adsorptions of birnessite, related to the Mn-O stretching vibration of the MnO<sub>6</sub> interlayer [17, 267].



Figure 5-61 FTIR spectrum for the powder, prepared by reduction of KMnO<sub>4</sub> solution with isopropanol.

## 5.3.3 Composition study

TGA data (Figure 5-62) showed a sharp reduction in sample mass below 250 °C, and then the mass decreased slowly with increasing temperature. The observed mass loss of 10.2 wt.% at 250 °C and a broad endotherm around 100 °C in the corresponding DTA data could be related to the liberation of adsorbed water. The broad exotherm in the DTA data in the range of 150-250 °C can be attributed to the crystallization of an amorphous phase in agreement with the results of the XRD study (Figure 5-60). The total mass loss at 800 °C was found to be 15.91 wt.%.


Figure 5-62 (a) TGA and (b) DTA data for the powder, prepared by reduction of KMnO<sub>4</sub> solution with isopropanol.

### 5.3.4 Morphology study of MnO<sub>2</sub> particles

TEM study showed that as-prepared  $MnO_2$  powders consisted of nanoparticles with diameter in the range of 20-50 nm (Figure 5-63). The inset in Figure 5-63 is a selected area electron diffraction pattern, which indicated that as-prepared powders contained polycrystals. However, the TEM data coupled with the results of XRD studies showed that powders contained a significant amount of an amorphous phase.



Figure 5-63 TEM image of the powder prepared by reduction of KMnO<sub>4</sub> solution with isopropanol. The insert shows a selected area electron diffraction pattern.



Figure 5-64 (A) and (B): SEM images of the as-precipitated powder at different magnifications.

Low magnification SEM image (Figure 5-64A) of the powder showed large agglomerates with typical size of 1-20  $\mu$ m. The SEM image at higher magnification

(Figure 5-64B) showed that agglomerates consisted of nanoparticles in agreement with the TEM data. It is suggested that drying of the as-precipitated  $MnO_2$  nanoparticles resulted in their agglomeration. Such agglomerated powders cannot be used for the impregnation of Ni plaques shown in Figures 5-65A and B. Therefore, in order to impregnate Ni plaques with active material, the synthesis of  $MnO_2$  was performed in-situ in pores of the plaques. Commercial Ni plaques used in this study consisted of a perforated Ni foil and sintered filamentary Ni particles, which formed a porous network. Figures 5-65A and B show SEM images of the surface of a Ni plaque at different magnifications. The plaques exhibited porous microstructure with pore sizes in the range of 0-20  $\mu$ m (Figure 5-65A). The SEM image obtained at higher magnification (Figure 5-65B) showed that the size of Ni particles was in the range of 0.5-2  $\mu$ m. The porosity and conductivity of commercial Ni plaques are beneficial for their application as current collectors of ES.



Figure 5-65 SEM images of Ni plaques at different magnifications: (A) and (B) before impregnation, and (C) and (D) after impregnation using dipping-reduction method, mass loading 4.7 mg cm<sup>-2</sup>.

#### 5.3.5 Effects of number of dipping and charge on deposit mass



Figure 5-66 Mass of  $MnO_2$  (A) impregnated into a Ni plaque using a dipping-reduction method versus number of dippings, (B) (a) impregnated into a Ni plaque and (b) deposited on a Ni foil versus charge passed using cathodic electrodeposition, and (C) impregnated into a Ni plaque versus charge passed during cathodic pulses of electrodeposition in the reverse pulse regime.

Ni plaques were impregnated with  $MnO_2$  by dipping in KMnO<sub>4</sub> solutions and reduction of the impregnated material with isopropanol. Figure 5-66A shows mass gain of a Ni plaque as a function of the number of the dipping-reduction procedures (N). The observed mass gain indicated that the reduction of KMnO<sub>4</sub> can be performed in-situ in the pores of Ni plaques. The mass gain increased in the range of 0-5 mg cm<sup>-2</sup> with increasing N, indicating the possibility of the fabrication of electrodes with different material loadings.

The Ni plaques impregnated with MnO<sub>2</sub> using the dipping-reduction procedure were studied by SEM. Figures 5-65C and D show typical SEM images of the Ni plaques after impregnation. Low magnification image (Figure 5-65C) of the plaque with material loading of 4.7 mg cm<sup>-2</sup> showed that the impregnation resulted in a reduced porosity, compared with unloaded plaques (Figure 5-65A). However, only relatively small pores with pore size below 1  $\mu$ m were closed, whereas large number of pores with diameters of 1-20  $\mu$ m remained open. In this process, open pores of the plaques provided a space for impregnation during the next dipping-reduction step. Further increase in material loading resulted in a decreased porosity.

The SEM image at a higher magnification (Figure 5-65D) showed that dipping-reduction procedures resulted in the formation of  $MnO_2$  coatings on Ni particles. The precipitation of  $MnO_2$  on Ni particles can explain the large number of open pores remained after impregnation. The SEM image (Figure 5-65D) showed that the size of  $MnO_2$  nanoparticles was on the nanometric scale. As pointed out above, the SEM images of the microstructure showed large pores with diameter of 1-20 µm between coated Ni particles (Figure 5-65C). Such electrode microstructure is beneficial for application in ES. Recent studies highlighted the advantages of porous nanostructured coatings, which can provide high surface area for electrochemical reactions [17]. However, it was shown that large pores are necessary for improved electrolyte access to the active material [17]. The formation of nanostructured  $MnO_2$ coating on Ni particles enabled good contact of the active material and current collector. As a result, electrodes showed good capacitive behavior, described below. Ni plaques were also impregnated galvanostatically by cathodic reduction of  $MnO_4^ (Mn^{7+})$  species. The reduction mechanism was described in equation (2-22).

Figure 5-66B shows deposits mass of impregnated material as a function of charge passed. The deposition yield increased with increasing charge passed. Therefore, the amount of the impregnated material can be controlled. The mass of impregnated material after 30 min of electrosynthesis at a current density of 5 mA cm<sup>-2</sup> was comparable with that obtained after 25 dipping-reduction procedures. The deposition yield was also studied using Ni foil substrates. However, the slope of the deposit mass versus charge passed curve was lower, compared to that obtained for Ni plaque substrates (Figure 5-56B, curve a). After 10 min of deposition, deposit spalling was

observed, which resulted in a decrease in deposit mass (Figure 5-66B, curve b). The deposition yield measurements presented in Figure 5-66B showed that much higher material loading can be achieved using Ni plaque substrates. This can be attributed to accumulation of the impregnated material in pores of Ni plaques. However, it should be noted that due to the use of anionic  $MnO_4^-$  species for cathodic electrosynthesis, the kinetics of deposition is governed by  $MnO_4^-$  diffusion and electromigration [117]. Previous investigation showed the influence of adverse potential gradient on the cathodic electrosynthesis of  $MnO_2$  from the solutions containing anionic  $MnO_4^-$  species. It is suggested that the screening effect of Ni plaques can reduce the adverse electromigration rate of  $MnO_4^-$  in the plaque pores during electrosynthesis. This can explain the higher electrosynthesis rate in pores of Ni plaques (Figure 5-66B, curve a versus curve b).

Electrosynthesis was also performed in a reverse pulse regime. Figure 5-66C shows the deposition yield as a function of cathodic charge passed. The comparison of the data presented in Figures 5-66B and C showed that the impregnation rate in the reverse pulse regime was higher than that in the galvanostatic regime. It is suggested that galvanostatic deposition can result in electrolyte depletion in the electrode area. Therefore, reverse pulse deposition can provide reduced electrolyte depletion and a higher deposition rate during the cathodic pulses.

# **5.3.6** Morphology study of Ni plaques after impregnation using different methods



Figure 5-67 SEM images of Ni plaques at different magnifications after impregnation with manganese dioxide using (A) and (B) cathodic electrolytic deposition, and (C) and (D) reverse pulse electrodeposition, mass loading 4.7 mg cm<sup>-2</sup>.

Figure 5-67 shows SEM images of Ni plaques impregnated using electrochemical methods. The SEM analysis of the surfaces of such plaques revealed reduced macroporosity compared to the plaque impregnated using dipping reduction procedure (Figures 5-65C and D) for the same active material loading. The blocked macroporosity resulted in partial accumulation of MnO<sub>2</sub> on the plaque surface, which was especially evident for the plaques impregnated galvanostatically (Figure 5-67A and B). The MnO<sub>2</sub> accumulated on the surface of galvanostatically impregnated plaques showed cracked mud morphology, which contained areas of relatively dense material (Figure 5-67B). The plaque, impregnated using reverse pulse method showed

larger number of unblocked macropores (Figures 5-67C and D), compared to the plaques impregnated galvanostatically (Figures 5-67A and B).

#### 5.3.7 Cyclic voltammetry study



Figure 5-68 CVs at scan rates of (a) 5, (b) 10, and (c) 20 mV s<sup>-1</sup> for the electrodes prepared using (A) dipping-reduction method, (B) cathodic electrodeposition, and (C) reverse pulse deposition with mass loadings of 1.4 mg cm<sup>-2</sup>.

The capacitive behavior of the electrodes prepared using different impregnation methods was studied in  $0.5M Na_2SO_4$  solutions. Figure 5-68 shows typical CVs obtained at different scan rates. The box shape of the CVs indicated capacitive properties of the coatings in the voltage window of 0-0.9 V. The increase in material

loading resulted in increased area of the CVs (Figure 5-69), which was related to increased capacitance of the electrodes. The samples prepared by dipping-reduction methods showed larger CV areas, which indicated better capacitive behavior. The comparison of the capacitive behavior of the electrodes prepared using electrochemical impregnation methods showed higher SC of the electrodes prepared by reverse pulse deposition methods (Figure 5-70). The highest SC was observed for electrodes prepared using dipping-reduction method at a scan rate of 2 mV s<sup>-1</sup>. The SC at a scan rate of 2 mV s<sup>-1</sup> varied in the range of 215-236 F g<sup>-1</sup> with variation in material loading in the range of 0.6-5 mg cm<sup>-2</sup>. The SC decreased with increasing scan rate due to the electrolyte diffusion limitation in pores [17]. The results of SC measurements correlate with SEM observations of microstructures of impregnated plaques. The plaques prepared by the dipping-reduction method showed larger number of open macropores, which provided improved electrolyte access to the impregnated active material. This resulted in higher SC, especially at high scan rates (Figure 5-70).

Turning again to the literature data on the capacitive behavior of MnO<sub>2</sub>, it should be noted that SC of impregnated electrodes was much lower compared to the theoretical SC of 1370 F g<sup>-1</sup> [162] and SC of 700 F g<sup>-1</sup> reported for very thin films (~1  $\mu$ g cm<sup>-2</sup>) [7]. However, it is known that SC decreases significantly with increasing film thickness [5] due to the low electronic conductivity of MnO<sub>2</sub>. SC of 210-240 F g<sup>-1</sup> was reported for material loading of 150-180  $\mu$ g cm<sup>-2</sup> [6]. Previous investigations showed [119] that SC at a scan rate of 2 mV s<sup>-1</sup> decreased from 400 F g<sup>-1</sup> to 177 F g<sup>-1</sup> when the film mass increased from 50  $\mu$ g cm<sup>-2</sup> to 200  $\mu$ g cm<sup>-2</sup>. It is seen that due to the use of Ni plaque current collectors, the material loading can be increased significantly and relatively high SC (236 F g<sup>-1</sup>) can be obtained at the same scan rate.



Figure 5-69 CVs at a scan rate of 10 mV s<sup>-1</sup> for the electrodes prepared by (A) dipping-reduction method, (B) cathodic electrodeposition, and (C) reverse pulse electrodeposition with mass loadings: (a) 0.6 and (b) 4.7 mg cm<sup>-2</sup>.



Figure 5-70 SCs versus scan rate for the electrodes prepared using (a) dipping-reduction method, (b) cathodic electrodeposition, and (c) reverse pulse electrodeposition method for mass loading of 1.4 mg cm<sup>-2</sup>.

#### 5.3.8 Impedance spectroscopy study



Figure 5-71 Nyquist plot of the complex impedance  $Z^* = Z' - iZ''$  for the electrodes prepared by (a) dipping–reduction method, (b) cathodic electrodeposition method, and (c) reverse pulse electrodeposition method for the mass loading of 1.4 mg cm<sup>-2</sup>.

The results of electrochemical impedance studies (Figure 5-71) are in good agreement with the SC measurements and SEM data. The detailed analysis of the behavior of complex impedance  $Z^* = Z' - iZ''$  using equivalent circuits for impregnated electrodes present difficulties and can be a subject of separate theoretical and experimental study. However, the electrode prepared using dipping-reduction method showed much lower Z' in the whole frequency range studied, which indicated lower electrode resistance. On the other hand, higher capacitance of the electrodes prepared by this method resulted in lower Z''.

The results of this investigation showed that similar to the alkaline secondary cells, Ni plaques can be chemically and electrochemically impregnated with an active material

for application in ES. The dipping-reduction method, which was used in our investigation, combines material synthesis and plaque impregnation in one procedure. Therefore, some procedures, required for the electrode fabrication by other methods, can be avoided. They included washing, drying, and milling of powders, fabrication of slurries, impregnation, drying, calendering, and other processing steps [34]. It is in this regard that such steps often result in agglomerated nanopowders and reduced SC. The use of isopropanol as a reducing agent is beneficial, because washing steps, related to the removal of the reducing agent and reaction products can be avoided. It is expected that the approach developed in this investigation can be used for the impregnation of other porous conductive materials for application in ES. The electrode fabrication procedure enabled improved performance for relatively high material loadings. The electrochemical methods offer the advantage of higher impregnation rate. However, higher SC was obtained using the reduction-dipping method.

The results of XRD, SEM, TEM, FTIR, and chemical analysis presented in this chapter indicated that  $MnO_2$  nanoparticles with particle size of 20-50 nm can be prepared by reduction of KMnO<sub>4</sub> solutions with isopropanol. After drying, the nanoparticles formed large agglomerates, which cannot be used for the impregnation of porous Ni plaques. It was shown that the chemical synthesis of  $MnO_2$  can be performed in similar conditions in-situ in pores of Ni plaques. The dipping-reduction

method has been developed for the impregnation of Ni plaques. In this approach, the problem related to the particle agglomeration and removal of the reducing agent or reaction products can be avoided. The impregnation of Ni plaques with MnO<sub>2</sub> was also achieved using cathodic electrosynthesis method and reverse pulse electrodeposition methods. The amount of the impregnated material can be varied by the variation of the number of dipping-reduction procedures in the chemical impregnation method or by the variation of charge passed in the electrochemical methods. The electrodes prepared by dipping-reduction method showed higher macroporosity, higher specific capacitance, and lower impedance compared with the electrodes prepared by the electrochemical methods. The electrodes prepared using reverse pulse electrodeposition showed improved capacitive behavior compared with electrodes prepared galvanostatically. The chemical precipitation method offered the advantage of higher specific capacitance, whereas electrochemical methods allowed higher material synthesis rate. The highest specific of 236 F  $g^{-1}$  was obtained at a scan rate of 2 mV s<sup>-1</sup>. The specific capacitance decreased with increasing scan rate. Testing results showed that the electrodes prepared by chemical and electrochemical in-situ precipitation methods can be used for application in ES.

## **Chapter 6 Conclusions**

Advanced  $MnO_2$  based electrodes with excellent electrochemical behaviors have been fabricated for the ES applications. New methods of synthesis of  $MnO_2$  nanoparticles with controlled particle size, low agglomeration, high purity and controlled phase contents have been developed. It was demonstrated that the phase contents and particle size were important factors that could affect the electrochemical performance of  $MnO_2$ .

New strategy for the preparation of MnO<sub>2</sub>-CNTs composites have been developed through the cathodic ELD of MnO<sub>2</sub> nanoparticles on CNTs, which were grown by CVD on the stainless steel meshes. The binder-free process could significantly reduce the contact resistance, which was important for the fabrication of efficient ESs with high charge–discharge rates. Another attempt to lower the contact resistance and increase SC has been succeeded in the preparation of Ag-doped MnO<sub>2</sub> films by cathodic ELD from KMnO<sub>4</sub> solution containing AgNO<sub>3</sub>. It was discovered that ELD was important for the surface modification of current collectors and the reduction of interfacial resistance.

Novel method for the fabrication of MnO<sub>2</sub>-MWCNTs composites has been developed through EPD. Suspensions, containing MnO<sub>2</sub> nanoparticles and MWCNTs, were

stabilized using different dispersants, which allowed dispersion of both materials  $MnO_2$  and MWCNT. It was discovered that anodic and cathodic nanocomposite deposits could be obtained, depending on the charges of the dispersants. New fundamental dispersion and adsorption mechanisms have been developed. Investigation of the influence of functional groups of dispersants on their adsorption has been investigated.

In-situ chemical precipitation of  $MnO_2$  on current collectors with high surface area has been developed. It was demonstrated that low cost metallic substrate could be utilized for the fabrication of ES electrode, which paves the way for the mass production in industry.

The electrodes prepared by new electrochemical methods can be used for the fabrication of advanced ESs.

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