FABRICATION OF LITHIUM YTTRATE GALVANIC CELLS

FABRICATION OF LiYO₂ GALVANIC CELLS TO DETERMINE THE THERMODYNAMIC PROPERTIES OF LITHIUM ALLOYS

By

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ABSTRACT

LiYO₂ is a lithium ion conductor stable to pure lithium metal. The goal of the present work was to design and construct an electrochemical cell and demonstrate the use of LiYO₂ as an electrolyte since this has never been previously done. The electrolyte was fabricated by slip casting in powder molds. A Y₂O₃-MgO composition was identified and used to fabricate a lid for the cell. Impervious cells were obtained by liquid phase joining and sintering techniques. Heating rate was found to be a key parameter in the success of this procedure. The cell was evaluated in terms of stability as a sensor and chemical pump by measuring EMF for two different Li-Zn alloys between 250 and 600°C. The configuration was as follows:

(RE) (-) Ta
$$\text{Li},\text{Sn} \mid \text{Li}\text{YO}_2 \mid \text{Li},\text{Zn} \text{Ta}$$
 (+) (WE)

The cell showed no significant attack after 40 days working with pure lithium. Stability and reproducibility of EMF values was obtained for the concentrations of Li studied. Solidus and liquidus temperatures were determined for the 5 and 10 mol% Li compositions in good agreement with published phase diagrams. Variations of EMF with respect to temperature or concentration followed the expected thermodynamic relationships. Results indicate that the LiYO₂ electrolyte cell could be useful in assessment of the thermodynamics of lithium alloys.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Consumption of lithium minerals has increased significantly over the years. In 1999 the production of such materials contained 15,000 tons of lithium, which reflects the growing number of practical applications that use lithium and its compounds. Lithium has an acceptable cost and its compounds are easy to handle. To mention two examples, in the metallurgical industry lithium is used to reduce the density of aluminum alloys up to 10% while enhancing its mechanical properties. Secondly, in energy conversion, molten carbonate fuel cells contain molten Li salts in the electrolyte.

A significant portion of lithium production goes into the fabrication of solid electrolytes. Three decades of investigation have led to development of applications in secondary chemical batteries, chemical pumps, catalysts, electrochemical probes and chemical sensors among other devices based on lithium ion conductors.

The high reactivity of lithium is a strong limitation to the widespread use of this metal. It restricts the finding of new applications at intermediate and high temperature. Corrosion and degradation of materials in contact with lithium reduces life and

1

performance.

Only a few solid electrolytes are known to be thermodynamically stable against molten lithium and some of these are stable over only a short range of voltage or temperature. For practical applications, it is necessary that these solid electrolytes come to equilibrium in a relatively short period of time at a given temperature [1].

LiYO₂ is a lithium ion conductor that is thermodynamically stable against molten lithium [2,3]. It has been found as a surface coating on Y_2O_3 exposed on molten lithium [4]. This ceramic also has been mentioned as a catalyst for the oxidative coupling of methane [5], as a sintering aid for AlN [6], as an inorganic phosphor [7,8] and as a lithium ion conductor at high temperature [9,10]. In spite of its high ionic conductivity, close to that of β -alumina, no application as a solid electrolyte has been developed.

An interesting application of $LiYO_2$ is for the measurement of thermodynamic properties of lithium alloys. The stability of $LiYO_2$ against pure lithium makes it a useful tool for this purpose.

Kiukkola and Wagner [11] outlined the potential of solid electrolytes in determining the thermodynamic stability of alloys and compounds at elevated temperatures in 1957. In subsequent work by Rapp and Maak [12] in 1962, activities of copper and nickel in Cu-Ni alloys at 700°C and 1000°C were measured using a galvanic cell, involving CSZ (0.85 $ZrO_2 + 0.15$ CaO) as solid electrolyte. Many phase diagrams have been refined and more accuracy has been achieved by the EMF technique.

The utilization of solid lithium-ion conductors to determine thermodynamic properties of lithium alloys at high temperatures is illustrated by the following examples. In 1981, the Li-Ag binary system was investigated between 800 and 900 K using LiF as the solid electrolyte [13]; in 1985, a lithium orthosilicate-phosphate solid solution (Li₃PO₄-Li₄SiO₄) was used to study Al-Li alloys at temperatures above 673 K [1]. In 1985, lithium β -alumina was used to determine lithium concentration in molten aluminum [14]. In 1993, the Li-Zn phase diagram was revised by Gasior and Moser [15] and in 1997, work on Li-Pb alloys was carried out using Na β -alumina [16]. All these studies have been hindered to some extent by the stability of the solid electrolyte, and reaction with components of the apparatus or the surrounding atmosphere, resulting in experimental errors in the measured values.

1.2 Research objectives and thesis outline

The objective of this thesis was to investigate the capability of lithium yttrate to serve as a solid electrolyte in a galvanic cell. This was to be demonstrated by measurements of the electromotive force as a function of concentration and temperature for the Li-Zn binary alloy. The results are compared with those of Gasior and Moser [15].

The galvanic cell configuration has molten lithium as the reference electrode and a lithium binary alloy as the working electrode. This design can be used as a sensor or transducer of lithium concentration. The electrolyte can be formed into gas-tight closedend tubes by the slip casting technique.

This thesis comprises five chapters including the introduction. A literature review on lithium solid electrolytes, liquid phase sintering, transient-liquid-phase joining and thermodynamic measurement using the EMF method is presented in chapter 2. A description of the preparation of material, the experimental methods and the assembly of the apparatus is presented in chapter 3. Experimental results are compiled in chapter 4. The discussion and conclusion follow in chapters 5 and 6.

CHAPTER 2

LITERATURE REVIEW

This chapter develops in the first two sections a review of the work done on lithium solid electrolytes and the properties of lithium yttrate. Also, the basis of the EMF method to determine the thermodynamics of binary alloys is discussed. Finally, a description is given of transient-liquid-phase sintering and joining processes that will help to explain the fabrication procedure of the electrochemical cells used in this work.

2.1 Solid electrolytes

Solid electrolytes are materials that have the capability of conducting specific ions but are electronic insulators. This conductivity depends on the presence of mobile ionic defects. Materials that conduct both ions and electrons are known as mixed electronicionic conductors (MEIC).

In solid electrolytes, a current of the specific ion is induced upon application of an electrical field or a concentration gradient. This movement is possible when sites are available due to Schottky defects or Frenkel defects. The most common technique to increase defects has been through dopant ions on lattice sites.

Solid electrolytes are highly dependent on the working conditions. Their ionic conductivity is influenced by temperature, following an Arrhenius relationship. Some exhibit high conductivity at low temperature. For example, AgI, RbAg₄I₅ and Ag6I₄WO₄ have conductivities in the range of 10^{-1} S/cm at 150° C [17]. Others have high ionic conductivity at moderate temperatures, such as sodium β -alumina, one of the earliest fast conductors, with a conductivity in the order of 10^{-1} S/cm at 300° C. Those with fluorite structure are good electrolytes over 600° C due to the primary influence of anionic Frenkel defects. Materials with close-packed crystal structure generally do not show appreciable ionic conductivity until 10 degrees below their melting point.

Some minimum requirements are necessary for acceptable performance of a solid electrolyte. Density should be more than 94% of theoretical according to Worrel [17] and conductivity must be higher than 10^{-6} S/cm according to Schmalzried and Pelton [18]. For high temperature batteries, 0.15 S/cm at 400°C with no electronic conductivity is considered an ideal value [19].

Solid electrolytes have been used as ion selective membranes and have a variety of applications. They have been used as electrochemical probes, sensors, pumps, etc. Among these applications the use of lithium ion conductors is of special interest with growing commercial importance.

2.1.1 Lithium solid electrolytes

In order to extract thermodynamic properties from measurements with lithium solid electrolytes, it is necessary to have equilibrium with pure lithium metal as the

reference. In spite of the numerous compounds that show lithium ion conductivity, the number that are thermodynamically stable against pure lithium is rather small. To have a reasonable stability a difference of 350 kJ/mol in Gibbs energy between the electrolyte and lithium oxide is necessary [20]. Meeting this condition leads to a scarcity of experimental data on thermodynamic properties of lithium alloys especially at temperatures higher than 400°C.

Extensive work has been done to find high temperature lithium solid electrolytes. A selected list grouped by families is shown on Table 2.1. Those that are stable against pure lithium are shown in Table 2.2.

Solid solutions in the lithium orthosilicate system show a good conductivity. Combinations with Li_4GeO_4 or Li_4TiO_4 have a conductivity of 5 x 10⁻⁴ S cm⁻¹ at 300°C; interstitial solid solutions or partial substitutions with aliovalent, divalent and trivalent species can achieve a conductivity of 1.5 x 10⁻² S cm⁻¹ at 400°C [21].

LISICON (*Lithium Super Ionic Conductors*) are either Li₄GeO₄ or Li₄TiO₄ doped with aliovalent elements. They have a conductivity of 0.125 S cm⁻¹ at 300°C. Addition of vanadium leads to compounds with 4 x 10⁻⁵ S/cm at room temperature [22]. LISICON (Li_{16-2x}Zn_x(GeO₄)₄) is not stable against molten lithium or molten LiNO₃ (m.p. 261°C) but doping with ZrO₂ improves resistance to nitrate attack [23].

For lithium ion conductors with NASICON structure there are two types of solid solutions, $Li_{1-x}M_{2-x}A_x(PO_4)_3$ and $Li_{1+x}M_{2-x}M'_x(PO_4)_3$. Solid solutions with M = Ti have a conductivity of 0.1 S cm⁻¹ at 300°C [24] but are unstable towards Li metal as most titanate compounds are. On the contrary, Ge and Hf analogues have relatively more

stability against lithium but are more costly to produce [25]. Incorporation of (Sc,Cr) allows lower sintering temperatures and reduction of grain boundary resistance. For example, $Li_3Sc_{1.8}Cr_{0.2}(PO_4)_3$ increases conductivity to 8.6 x 10⁻² S cm⁻¹ at 470°C [26]. The grain boundary resistance has been also a factor that reduces significantly the total conductivity.

TABLE 2.1

Families of Li ion conductors (19)

System		Example	S/cm	Т
Lithium Orthosilicate	Li ₄ SiO ₄	Li _{4-2x} Mg _x SiO ₄	1.50 10 ⁻²	400°C
Lithium Metal Oxide	Li ₅ MO ₄	Li _{5.9} Al _{0.1} Zn _{0.9} O ₄	$1.50 \ 10^{-3}$	300°C
LISICON	Li _{2+2x} Zn _{1-x} GeO ₄	Li ₁₄ Zn(GeO ₄) ₄	1.25 10 ⁻¹	300°C
NASICON	$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$	$Li_{3}Sc_{1.8}Cr_{0.2}(PO_{4})_{3}$	8.60 10 ⁻²	470°C
Lithium β -alumina	LiAl ₁₁ O ₁₇	Li Al ₁₁ O ₁₇	3.00 10 ⁻³	25 °C
Lithium lanthanum titanate	Li _{0.5-3x} La _{0.5+x} TiO ₃	Li _{0.5-3x} La _{0.5+x} TiO ₃	$1.00\ 10^{-3}$	25 °C
Dilithium Sulfate	Li ₂ SO ₄	Li _{0.22} Na _{1.33} Zn _{0.22} SO ₄	$1.00\ 10^{-1}$	325°C
Lithium Nitride	Li ₃ N	Li ₈ N ₄ Si	5.00 10-4	25°C
Lithium composites		[LISICON]-ZrO ₂	1.08 10 ⁻¹	300°C
Lithium Rare Earth Oxides	Li-RE-O ₂	LiSmO ₂ , LiLaO ₂ ,	1.00 10 ⁻²	500 °C
		LiYO ₂ , LiNdO ₂		
Lithium Metal Halides	Li ₂ M-halide	LiInCl ₆	2.00 10 ⁻¹	300°C

TABLE 2.2

List of selected lithium ion conductors stable against pure lithium

Compound	Limitations	Reference
LiI	low melting temperature	29
LiF		30
LiCl		30
LiBr		30
Li ₈ ZrO ₆		10, 24
Li ₂ ZrO ₃		31
Li ₅ AlO ₄	Hygroscopic	2, 10
LiYO ₂		9, 10
Li SmO ₂		24
LiScO ₂		2, 10
LiLaO ₂		2
LiNdO ₂		2
Li ₃ N	decomposes at 0.44 V	2
Li ₃ P	decomposes at 2.2 V vs. Li	19
Li ₉ SiAlO ₈	up to 6.5V at100 °C	19
Li _{3.4} Si _{0.4} V _{0.6} O ₄	at least up to 220°C	32

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The compounds $RE_{2/3-x}Li_{3x}TiO_3$ and $Li_{0.5-x}RE_{0.5+x}TiO_3$ have a perovskite-type structure. Cation deficiency at the A-sites is favorable for high ionic mobility of monovalent cations. For instance, lithium lanthanum titanate ($Li_{0.51}La_{0.34}TiO_{2.94}$ or $Li_{0.3}La_{0.57}TiO_3$) shows high lithium conductivity, 10^{-3} S/cm at 25°C [27,28]. It cannot be used as an electrolyte with Li metal because it intercalates lithium ions and the electronic conductivity increases. The high sintering temperature (1300°C) causes evaporation of lithia. High grain boundary resistance is also a problem.

Li₃N is a fast ionic conductor at room temperature, with conductivity in the order of 10^{-3} S cm⁻¹ for single crystals and 10^{-4} S cm⁻¹ for polycrystalline samples. Vacancies of 1-2% associated with H impurities are largely responsible for the high conductivity of this electrolyte. The low decomposition potential, 0.445 V, limits its practical application. Substitution with Al, Mg or Si increases the conductivity to 5×10^{-4} S cm⁻¹ at 125°C [33].

Some ceramic materials stable against pure lithium are shown in Table 2.3. Evaluation of commercial ceramic materials has shown that beryllia, yttria, yttriumaluminum garnet, aluminum nitride and magnesia have acceptable resistance to lithium attack at 400°C but this resistance decreases with temperature probably due to impurities. For example, MgO is heavily attacked at 800°C [31]. Elements such as Ti, V, La or U, can cause reduction of Y_2O_3 to a non stoichiometric form when heated in vacuum or in contact with molten lithium. Although these materials are not lithium ion conductors, they are useful components for other parts of the cell.

TABLE 2.3

Some materials stable against pure lithium

Material	Tested at	Remark	Ref
AIN	400°C		31
Si3N4, BN			34
Yttrium Oxide	500°C		4,31
Magnesium Oxide	400 °C		31
Calcium Oxide		Hydration	
Beryllium Oxide (99.5%)	400 °C	For short time	31
Yttrium aluminum garnet	400 °C	Without alumina residual	31
Electrolytic Iron	750 °C	Used as crucible	13
UNS 316 Crucible	500 °C	Austenitic stainless steel	4
Nickel crucible	250 °C	Used to melt lithium	2

2.2 Properties of LiYO₂

2.2.1 Physical properties of lithium yttrate

Lithium yttrate is thermodynamically stable with respect to pure lithium. It has been reported as a NaCl variant consisting of mixed cation layers between layers of closest-packed O^{-2} [5]. In 1959, R. Hoppe [35] found that LiYO₂ has a tetragonal structure. Later work by Gondrand [36] and Hoop [37] concluded that the tetragonal

structure is stabilized by small levels of impurity. The structure of the pure crystal is always monoclinic at least up to 1100°C, as are most compounds of the type LiREO₂, such as LiSmO₂, LiLaO₂ and LiNdO₂ [38,39]. All belong to the same space group $(P2_1/c)$. The high temperature crystallographic transformation of doped LiYO₂ (t \rightarrow m) is reversible with temperature. Fig 2.1 shows a schematic of this transformation; the crystal parameters reported for both structures are shown in Table 2.4.

TABLE 2.4

LiYO₂ crystal parameters [37]

	Monoclinic	Tetragonal
a	6.120 Å	4.38 Å
b	6.185 Å	
c	6.210 Å	10.60 Å
β	118.8 °	
$\mathbf{V}_{\mathbf{M}}$ (cm ³)	31.0	30.62
$\rho (g / cm^3)$	3.55	

Faucher et al. [8] found that there are wide corridors made of two parallel and adjacent Li-O rows along the [100] direction. Similar rows occur in the perpendicular [010] direction. It is not understood why these corridors are so wide (the mean vertical Li-O distance is 3.06 Å). But they can explain the hydration process since hydrogen diffuses along the wide corridors. Similarly, Li ion conductivity could be facilitated by diffusion of Li through these corridors.



Figure 2.1 Tetragonal-Monoclinic transformation of LiYO₂

2.2.2 Thermal Properties of Lithium Yttrate

 $LiYO_2$ is the only phase known in the binary Li_2O and Y_2O_3 . The $LiYO_2-Y_2O_3$ phase diagram of Bondar and Koroleva [40] shows the melting point of the lithium yttrate at approximately 1880°C and a eutectic at 1830 ± 20°C (Fig. 2.2).



Figure 2.2 Binary $LiYO_2 - Y_2O_3$ [40]

It has been reported that $LiYO_2$ starts to decompose into Y_2O_3 and Li_2O when heated over 200°C in air [8] or into Y_2O_3 and Li_2CO_3 in CO₂ [5]. After 2 hours, the amount of Y_2O_3 formed from $LiYO_2$ was estimated at 5% [7]. The rate of the reaction of the carbonate with yttria is higher at the synthesis temperature than the evaporation of lithia. On the contrary, during cooling of $LiYO_2$ carbonate no longer decomposes but decomposition of $LiYO_2$ proceeds. Lambert and co-workers [5] demonstrated that CO_2 accelerates the decomposition. Faucher et al. [8] explain decomposition as a result of the destruction of the hydrogen bonds created by moisture. At room temperature, $LiYO_2$ is very stable; in fact sintered samples have shown no degradation in more than six years.

The average linear thermal expansion was found to be $11.8 \, {}^{\circ}\text{C}^{-1}$ between 30 and 1200 ${}^{\circ}\text{C}$ in this work (Fig. 2.3). For convenience, a comparison with other oxides is shown in Table 2.5.

TABLE 2.5

Linear Thermal Expansion of selected ceramic materials [41]

	(°C) ⁻¹	°C
Ceramabond™ 571	12.6 10 ⁻⁶	-
Aluminum oxide	9.0 10 ⁻⁶	550 – 1000
Magnesium oxide	15.8 10 ⁻⁶	550 - 1000
Yttrium oxide	9.4 10 ⁻⁶	650 - 1500
Lithium yttrate	11.8 10 ⁻⁶	500 - 1000



Figure 2.3

Thermal expansion versus Temperature on heating (upper line) and cooling

2.2.3 Electrical Properties of Lithium Yttrate

Pure $LiYO_2$ shows conductivity at high temperature comparable to lithium β alumina. At 500°C, the conductivity of $LiYO_2$ is 1.2×10^{-2} S/cm [42]. This is higher than the conductivity exhibited by Li_5AIO_4 , $LiAIO_2$ and Li_8ZrO_6 . Conductivity of several lithium electrolytes can be seen in Table 2.1 and Fig 2.4. Attempts to improve conductivity of lithium yttrate by doping with zirconia have shown that as little as 0.5% zirconia produces a transformation to the tetragonal form that decreases the conductivity by almost two orders of magnitude [42].



Figure 2.4 Conductivity vs 1/T of Li-ion conducting solid electrolytes [10]

Grain boundaries, dislocations and tunnels are defects that contribute to conductivity. The monoclinic structure, as was mentioned, has wide corridors that could

facilitate mobility of lithium ions [8] and explain the high ionic conductivity of $LiYO_2$. Conductivity of electrolytes such as $LiTi_2(PO_4)_3$ has been explained by the tunnel size in the phosphate that is suitable for Li^+ ion migration [43].

2.2.4 Thermodynamic Properties of Lithium Yttrate

The thermodynamic properties of lithium yttrate are not well known. Based on the Neumann-Kopp rule and the third law, an estimate of enthalpy, entropy and heat capacity have been made [44]:

 $\Delta H_{f} (LiYO_{2}) = -1423 \text{ kJ/mol.}$ $\Delta S_{f} (LiYO_{2}) = 68.3 \text{ J/mol K}$ $C_{p} (LiYO_{2}) = 78.3 \text{ J/mol K}$

2.3 Nernst equation for solid electrolytes

Among the electrochemical techniques developed to study the thermodynamics of binary systems are the EMF method, vapor pressure measurement, the transportation method, Knudsen cell-quadrupole, pseudo isopiestic, and Knudsen weight loss [45,46].

EMF measurements provide enough information to calculate the thermodynamic properties of the species in a binary alloy. Thus, the potential versus temperature method based on the Nernst equation has been used widely. Some systems studied by this technique are shown in Table 2.6.

An average accuracy of electrochemical cell measurements is assumed to be ± 1

mV, which is equivalent to ± 386 Joules per mole of O₂ in the Gibbs free energy ($\Delta G = -4FE = RT \ln (Po_2)$). Wagner pointed out that high temperature values using EMF are more reliable than those calculated by combining calorimetric measurements at 25 °C with heat capacity data [47].

TABLE 2.6

Examples of studies of thermodynamic properties with solid electrolytes

System	Electrolyte	Reference
Zn-Cd	$ZrO_{2}(+Y_{2}O_{3})$	I. Katayama, Mat. Trans. JIM 38, 2 (1997) 119-122
Li-Zn	LiCl-LiF	W.Gasior and Z. Moser. J Chim Phys, 90 (1993) 387-397.
Sn-Sb	RbCl,LiCl	V. Vassiliev et. al. J. of Alloys and comp. 247 (1997) 223
Li-Pb	LiCl-LiF	W. Becker et.al Z. Metallkde, Bd 72, H3 (1981) 186
Li-Ag	LiCl-LiF	W. Becker et.al Z. Metallkde, Bd 72, H3 (1981) 186
Li-Al	Li ₃ PO ₄ - Li ₄ SiO ₄	P.Yao and D.Fray, Metall. Trans. B, v 16B, (1985) 41.
Li-Zn	LiCl-KCl	M. Matsunaga, Denki Kaguku, 48, 11 (1980) 634-637.
CaO-NiO	Ni(II)-β-alumina	G. Rog, J. of Chemical Thermodynamic, 30,1 (1998) 43
Ga-Sn	$ZrO_2(+Y_2O_3)$	I. Katoyama, Mat. Trans. JIM 37,5 (1996) 988
Al in Pt-Al	CaF ₂	M. Nanko, Mat. Trans JIM 39 (1998) 12,1238
MgCl ₂	MgCl ₂ -NaCl- LiCl	B. Davis, J. of the Electroch. Soc. 139,4 (1992) 989
Ga in Ga-Sb-Ge	ZrO ₂	I. Katayama et al. Therm. Acta. 314,1-2 (1998) 175
Stability of Li ₃ NbO ₄	α - β -alumina	R. Subasri, Solid State Ionic 93 (3-4)(1997) 341-346
Stability of LiTa ₃ O ₈ -Li	lpha- eta -alumina	R. Subasri, Mat. Letters 30 (March 1997) 289-292
$\Delta G_{f} \text{ of } CaSb_{2}O_{4}$	Ca-F	S. Raghavan, j. of Alloys and Comp. 280, 1-2 (1998) L1-L2
ΔG_f of Sb ₂ O ₃	ZrO ₂ (+CaO)	N. Kemori, Can. Metallurgy in Quarterly (1996)35,3 269
ΔG_{f} of LaZrO ₃	CaF ₂	K. T. Jacob, J. Am. Ceram. Soc. 81, 7 (1998) 1926-1930

Coulometric titration can be used to change the composition of the alloy in the cell. A constant current I is provided by a galvanostat and passed through the cell for a given time. The change in the amount of the transported species is [48]:

$$m = \frac{It}{nF} \tag{2.1}$$

Phases in a binary system can be mapped using this technique. For instance, in Fig. 2.5 a plot of EMF vs. mol% Li in Li-Zn alloys shows plateaus at room temperature corresponding to three different phases.



Figure 2.5. Coulometric titration curve for the Li-Zn [49]

In addition, kinetics can be studied by performing charge-discharge experiments [49] and the polarization for two phases can be determined by plotting EMF versus current. A small slope (Fig. 2.6) means Li diffusion is fast (less polarization between charge and discharge).



Figure 2.6. Polarization curve for two-phase sample with overall composition Li₂Cd [49]

After the titration, there is a period of stabilization to reach equilibrium. The stability of the electromotive force depends on the electrochemical potential at the electrode-electrolyte interfaces and on the kinetics of the reaction. Continuing instability or shifting can be caused by electronic conductivity in the solid electrolyte, reaction within the electrodes or between the electrode and the electrolyte or with the electrical contact material and interference from elements in the working atmosphere. Evaporation

or changes in concentration also can cause instability.

According to the Nernst equation, the potential for a cell that uses a lithium solid electrolyte with a lithium alloy as cathode and pure lithium metal as anode is:

$$E = -\frac{RT}{F} \ln \begin{bmatrix} a_{Li}(we) \\ a_{Li}(re) \end{bmatrix}$$
(2.2)

From this relationship we can measure the activity of lithium in the alloy $a_{Li}(we)$, knowing the activity of the reference electrode $a_{Li}(re)$, with respect to pure Li.

Activity, temperature and composition are parameters needed to derive the Gibbs energies of formation, enthalpy, entropy, excess stability and phase boundaries.

$$\Delta G_{Li} = RT \cdot \ln(a_{Li}) = -FE \tag{2.3}$$

$$\ln(\gamma_{Li}) = -\frac{FE}{RT} - \ln(X_{Li})$$
(2.4)

$$\Delta H_{Li} = -F\left(\frac{\partial (E/T)}{\partial (1/T)}\right)_{X,P}$$
(2.5)

$$\Delta S_{Li} = F \left(\frac{\partial E}{\partial T}\right)_{X,P} \tag{2.6}$$

The properties of the second element in the alloy can be calculated using Gibbs-Duhem integration

$$\ln(\gamma_{\rm B}) = -\int_{-\infty}^{\infty} \frac{X_{\rm Li}}{X_{\rm B}} d(\ln \gamma_{\rm Li})$$
(2.7)

The integral property Y_m is given by

$$Y_m = X_{Li}Y_{Li} + X_BY_B \tag{2.8}$$

For dilute solutions in the molten alloy, a linear relationship between activity and mole fraction is expected:

$$a_{Li} = \gamma_{Li}^{\circ} \cdot X_{Li} \tag{2.9}$$

where γ_{Li}° is the Henrian activity coefficient and X_{Li} is the mole fraction

This is equivalent to a linear relationship between potential and composition at constant temperature.

$$E = E^{\circ} - \frac{RT}{F} \ln(X_{Li})$$
(2.10)
2.4 Sintering Process

Sintering is the process of increasing the density of a body by reducing the amount and size of porosity and other defects that affect the total surface area. The sintering is carried out at temperatures in excess of half the absolute melting temperature. The first step is the compaction of particles followed by the application of heat. As a consequence, grain boundary and surface area decrease through grain growth and the creation of bonds between the particles. The driving force in this process is the reduction of the surface area and consequently the surface energy. Mass transport by diffusion plays an important role at this stage. The final result is a dense body with a low concentration of defects.

There are different sintering methods such as sintering with or without pressure, sintering by a solid-solid process or a liquid-solid process. During reactive sintering, different phases present cause an exothermic reaction and a change in phase composition. Figure 2.7 shows a schematic of all these possibilities.





In general, sintering progresses through stages which vary from the loose powder filling to a final almost porosity free, compact body. Adhesion, neck growth, densification and pore closing are the most important steps.

The temperature schedule can affect the final quality of a sintered body. Commonly, the heating schedule has two major steps, a lower temperature step with a long dwell time and then a second step at maximum temperature and short time to minimize grain growth. At low temperature, bonding develops without densification whereas at high temperature, densification is the dominant process.

2.4.1 Liquid-phase sintering

In this project, liquid-phase sintering was used for densification of lithium yttrate. This technique makes use of a low-viscosity phase at the sintering temperature. It flows due to the capillary forces of the liquid among the solid particles. The solid can dissolve into the liquid or only be wetted and compacted by the liquid. The liquid can be transient or persistent during sintering. Both cases result in densification [50]. The degree of which depends on liquid volume, temperature, particle size, initial density and sintering time.

In liquid-phase sintering, densification depends greatly on solubility. Low liquid solubility in the solid associated with a high solubility of the solid in the liquid results in high densities. On the contrary, high liquid solubility in the solid with a low solubility of the solid in the liquid leads to swelling and a transient liquid. Also, closed porosity in the matrix depends on solubility; if the liquid dissolves rapidly into the solid, pores are

formed in the matrix. The diffusion rate into the grains determines the level of porosity.

The stages of liquid phase sintering are shown in figure 2.8. The process begins with a mixture of powder and low melting additive. At low temperature, bonds start to develop between grains. When additive particles melt and start to spread due to capillary forces, a rearrangement of particles takes place in a way that promotes densification. As



Figure 2.8 Schematic diagram of the classic liquid-phase sintering stages [50]

the liquid content increases, the pores are filled. Solution and precipitation become predominant as liquid volume is reduced. This process is accompanied by grain growth. The final step, depending on solubility, could end in solid-solid densification.

In most liquid phase sintering processes unlike solid-solid sintering, a prolonged final-stage leads to degradation and low densification of the sintering body due to reaction or decomposition of the liquid phase [50].

2.4.2 Transient liquid-phase sintering

Liquid during sintering can be persistent or transient. A microstructure showing large pores indicates that a transient liquid phase formed during heating before homogenization. Figure 2.9 shows an example where large pores were formed via transient liquid phase sintering.

Among the requirements for transient liquid-phase sintering are: solubility between components and a single phase at the peak temperature. The sequence is as follows (Fig. 2.10):

- 1- swelling by interdiffusion prior to melt formation
- 2- melt formation

3- spreading of the melt and generation of pores at prior additive particle sites

- 4- melt penetration along solid-solid contacts
- 5- rearrangement of the solid grains
- 6- solution-reprecipitation-induced densification

- 7- diffusional homogenization
- 8- loss of melt
- 9- formation of a rigid solid structure
- 10- densification by solid state sintering.





Samples of a) Fe-3Ti and b) Fe-7Ti showing pores formed via transient liquid-phase sintering [50].

This process is heavily dependent on heating rate and maximum temperature. More swelling occurs at slower heating rates due to diffusional homogenization, which reduces the peak quantity of liquid.



Figure 2.10 Sequence of the transient liquid-phase sintering process

The liquid volume V_L is related to the temperature change with time by:

$$1 - \left(\frac{V_L}{\varepsilon C}\right)^{\frac{1}{3}} = \kappa \left(\frac{T_L}{dT/dt}\right)^{\frac{1}{2}}$$
(2.11)

where ε and κ are proportionality constant, T_L is the liquid formation temperature and C is the concentration of the low melting species. Rapid heating suppresses solid-state bonding, leading to better densification. According to equation 2.11, more liquid is

formed with faster heating rates and larger quantities of liquid forming additive. This relationship is expected since solubility is a diffusion process and depends on heating rate and particle size.

During this process pores are formed due to spreading and penetration of the melt away from the additive particle sites. Pore refilling often does not occur because of a short liquid duration, resulting in large pores in the final microstructure. Large particle size favors swelling and small particle size promotes densification. Figure 2.10 shows a schematic of this process.

2.5 Joining Process

2.5.1 Transient liquid phase bonding

One of the goals of this thesis was to find a method of joining the $LiYO_2$ tube with good electrolyte properties to a lid with good mechanical properties. As will be discussed later, the best lid material was a mixture of Y_2O_3 and MgO.

The joining process is based on transient-liquid-phase (TLP) bonding. Because yttrium oxide grains are present in both the tube and the lid, the same mechanism applies to both the sintering process and to the joining process. In this case, no additive was needed as the lithium yttrate produces the liquid needed for joining. The dissolution is possible because of the similarity of the two media.

The stages in TLP bonding according to Zou et al. [51] can be summarized as

follows:

- I. a heating stage to melting temperature and interdiffusion between the two phases along a phase boundary.
- II. the solid dissolves into the liquid and the liquid solidifies as a result of solute diffusion into the solid at the bonding temperature.
- III. a stage of homogenization where solid state diffusion takes place.A schematic illustration of TLP bonding can be seen figure 2.11.



Figure 2.11 Schematic illustration of the mechanism of the TLP bonding process

As in sintering, the heating rate has a critical effect on the kinetics of TLP bonding since solidification can occur before the selected bonding temperature is reached. It has been proved that solidification occurs when the heating rate is very slow, since there is more time for diffusion into the matrix to occur. Consequently, the amount of liquid at the joining temperature decreases affecting negatively the bonding [24] because solid-solid joining becomes predominant.

CHAPTER 3

MATERIALS AND PREPARATION

The procedures for the lithium yttrate powder preparation, the production of a closed-end lithium yttrate tube and cell construction are presented in this chapter.

3.1 Formation of LiYO₂

The lithium yttrate powder was synthesized by solid state reaction starting with analytical grade lithium carbonate and yttrium oxide (99.99%). The compositions tested ranged from -4 to 10 mol% excess Li_2O relative to the stoichiometric composition.

The appropriate amounts of Li_2CO_3 and Y_2O_3 were weighed, mixed and ground in a ceramic mortar. The powder was pressed into pellets of 24 mm diameter and 2 to 4 mm thick at 35 MPa. The pellets were fired in alumina crucibles at 705°C for 12 h and at 1250°C for 6 h. Samples were tested by XRD using Cu-K α radiation with Ni-filter.

3.2 Slip preparation

To produce the slip used to cast the lithium yttrate tubes, the calcined powder was ground in a mortar. Absolute ethanol was added in a ratio of powder:liquid of 10:11 by weight. The suspension was vibro-milled in a 250 ml Nalgene bottle for 24-48 hours using alumina balls as the grinding media.

The grain size analysis was carried out in a Horiba Particle Size Distribution Analyzer Model Capa 700. The analysis is based on light absorbance of a suspension during sedimentation.

3.3 Tube fabrication

Different techniques are available to produce tubes, such as extrusion, electrophoretic deposition, isostatic pressing, but slip casting is a simple and economical way to produce them.

Byckalo et al. [52] used slip casting of a suspension in water with plaster molds to fabricate tubes of β -alumina. Pelton made tubes by slip casting using a methanol suspension into alumina powder molds [53]. We follow the Pelton procedure with absolute ethanol as the medium to prepare the suspension. With powder molds, problems inherent to the removal process from a plaster mold can be avoided. In addition, powder molds do not need to be dried between castings.

To make the molds, α alumina powder was hand pressed into a beaker around a mandrel (10 mm dia). The suspension of lithium yttrate in ethanol was poured into the mold cavity. A time of 1 to 2 minutes was required for a wall thickness of about 1 mm. A shorter casting time indicates excessive grain size of the powder.

The tubes were left in the powder mold overnight, then demolded, and allowed to dry at room temperature for several hours. Residual alumina powder was brushed off the surface and then the tubes are polished with fine sandpaper. A schematic of the process is shown in Fig. 3.1.



Figure 3.1 Slip casting in powder mold

3.4 Sintering of LiYO₂

Impervious tubes have been produced with different compositions, packing procedures and sintering schedules as explained later. The tubes used as galvanic cells in this work were simultaneously sintered and joined to the lid.

3.5 Lid Fabrication

The lids were made with a mixture of yttria and magnesia (12-15% MgO by weight worked well). The appropriate amount of each oxide was mixed with alcohol and then vibromilled for more than 15 hours. The powder was dried at room temperature and pressed into pellets of 25 x 20 mm at 17.6 MPa (2500 psi) followed by isostatic pressing at 276 MPa (40,000 psi).

The isostatic-pressed lids were presintered at 1250°C for three hours. At this temperature, the pellets had sufficient rigidity to allow drilling a hole (3.2 mm or 1/8") through the center. After cleaning and grinding the surfaces of the presintered lids with 600 grit SiC paper, the final sintering was performed in two steps, the first at 1670°C for twelve hours followed by an anneal at 1175°C for one hour. The fully sintered lids were then machined with a 45° cone-shaped countersink with mirror finish.

3.6 Joining Process

The join was made by heating the tube and the lid at a temperature of 1390°C at a rate shown in Table 3.1 or faster. The surfaces of the tube and the lid to be joined should be smooth for maximum contact. Tubes used with this procedure had a composition of

6% excess Li_2O and could be fully sintered tubes or tubes pre-sintered at 1325°C (in alumina crucibles and packed in coarse $LiYO_2$ powder). Green tubes are not recommended because of high shrinkage.

TABLE 3.1

Sintering-Joining Heating Rate

Temperature (°C)	°C /min
25 - 700	70
700 - 1100	40
1100 - 1300	20
1300 - 1400	10

3.7 Cell Assembly

Figures 3.2 and 3.3 show a schematic of the cell used in this thesis.

The cells (joined lithium yttrate tube and lid) were tested in a Veeco leak detector MS-9. Those that did not reach a vacuum below 1.3×10^{-8} atm were rejected. Electrode materials such as lithium 99.99% or Zn 99.9999%, were loaded through the hole in the lid in a glovebox. A tantalum cone was used to plug the center hole in the lid and provide an electrical feed-through. A tantalum wire attached to the cone was used as a lead.

The cell is set into a Zr-2% Nb holder. A torque of 300 kg·cm was applied to the holder cap, creating a hermetic seal between the Ta cone and the countersunk lid, as shown in Fig. 3.2.



Figure 3.2 The cell assembly



Figure 3.3 Cell layout for EMF measurements

3.8 Experimental Apparatus

As described earlier, lithium (99.99%) was used as the reference. The working electrode was initially 99.9999% Zn; lithium was added to the half-cell by coulometric titration. The apparatus operated in an argon atmosphere glovebox. The working and reference electrodes were immersed in a counter electrode (a metal bath of Sn-1% Li in a tantalum crucible). The counter electrode maintained conductivity between the half-cells and allowed Li cations to be titrated into the working cell.

A HP 3478A multimeter was used to measure the cell and the thermocouple voltages. A Princeton Applied Research model 173 potentiostat/galvanostat was used for titration. A chart recorder plotted temperature and EMF data. The precision of the potentiometer was \pm 0.1 mV. After titration at 600°C, cells were left for a period of 3-4 hours to allow voltage stabilization. Subsequently the potential was very stable. The EMF was measured for both increasing and decreasing temperatures between 600°C and 250°C.

CHAPTER 4

EXPERIMENTAL RESULTS

There is nothing published on methods of fabrication of $LiYO_2$ products except powders synthesis. To test experimentally this lithium ceramic as a solid electrolyte for Li alloys, it was first necessary to establish a method of producing hermetically sealed cells. Therefore, great effort and time were spent to develop a sintering and joining procedure. Parameters such as composition, temperature, heating rate and milling schedule were evaluated. $Li_2O-Y_2O_3$ compositions with -2 mol%, 0%, +4 mol% and +6 mol% excess Li_2O with respect to the stoichiometric ratio were tested. Galvanic cells using LiYO₂ as solid electrolyte were assembled and the EMF measured for Li-Zn alloys.

4.1 Powder Preparation

To establish the best procedure to synthesize $LiYO_2$ powder from Li_2CO_3 and Y_2O_3 , samples were heated at 706°C for 12 hours, then sintered at 1230°C and 1250°C for 6 hours. The XRD patterns of the pellets reacted at 706°C show a single Y_2O_3 phase (Fig.4.1). It is possible that some remaining lithium oxide, lithium carbonate, lithium

hydroxide or a small amount of lithium yttrate was present but they could not be detected by this method. Li_2O and LiOH are XRD amorphous and Li_2CO_3 has a very low intensity [2,5].



Fig. 4.1 XRD of Li₂CO₃ and Y₂O₃ mix (4% excess) Pellets heated at 706°C for 12 h

On the contrary, samples sintered at 1230°C (6 h) and samples at 1250°C (6 h) showed a single lithium yttrate phase (Fig.4.2a and 4.2b). As before, the other compounds including yttrium oxide could not be detected.



Figure 4.2 XRD of Li₂CO₃ - Y₂O₃ mixture (4% excess)
a) after 1250°C for 6 hours
b) after 1230°C for 6 hours

The decomposition and evaporation of lithium was evaluated through weight loss of different compositions and temperatures. Samples were assumed to contain negligible amounts of moisture and carbon dioxide as well as residual polyethylene eroded from the mill jar. Results are shown in Table 4.1.

The weight loss after the solid reaction had a slight tendency to be above the expected values. After sintering, the weight loss ranged between 6 to 8 wt% and increased with excess lithium composition. At 1420°C, -2 mol% lost 6.7 wt%, 0% lost between 7.2 wt% and 7.8wt%, and +4 mol% lost 8.5 wt%. It can be seen that the dwell time had a more significant effect than temperature. For instance, a hypostoichiometric sample sintered at 1415°C for 6 min lost more weight than samples at higher temperature with no dwell time. The stoichiometric sample sintered at 1465°C for 12 h lost 15.5% while a sample at the same temperature but no dwell time lost 6.27%, a percentage at the same level of samples sintered at 1410-1430°C.

Effect of soaking time on decomposition of $LiYO_2$ powder at low temperature was evaluated by heating at 250°C, 300°C and 400°C for three hours. XRD patterns showed very small amounts of $LiYO_2$ in all samples. The diffraction peaks of Y_2O_3 increase in intensity with temperature as is shown in chapter 5 (Fig. 5.1).

TABLE 4.1

Weight loss (wt%) after reaction and after sintering

(No dwell time at sintering temperature except where shown in brackets)

Reaction: $Li_2CO_3 + Y_2O_3 --- 2LiYO_2 + CO_2$

	Reaction (1250°C) Weight Loss (%)			Sintering	
mol%			# Samples		
	theoretical	observed	_	°C (h)	Weight L. (%)
-2% hypostoichiometric	14.2	14.7	3	1420	6.70
(49% Li ₂ CO ₃ : 51% Y ₂ O ₃)				1425	6.87
				1430	6.33
				1415 (0.1)	6.87
0% stoichiometric	14.7	15.5	4	1410	7.21
(50% Li ₂ CO ₃ : 50% Y ₂ O ₃)				1425	7.79
				1430	5.82
				1465	6.27
				1440 (6)	9.22
				1465 (12)	15.55
4% hyperstoichiometric	15.6	14.5	1	1325	6.8
(52% Li ₂ CO ₃ : 48% Y ₂ O ₃)				1420	8.5
6% hyperstoichiometric	16.1	16.3	2	1360	7.01
(53% Li ₂ CO ₃ : 47% Y ₂ O ₃)				1385	7.85

4.2 Slip

Ball milling proved to be a slow process in reducing powder size. After milling the suspension of a powder:ethanol ratio of 10:11 for 48 hours, the grain size was $1.47\mu m$ (98%) as is shown below in Table 4.2. The grain size before milling was $2.67\mu m$.

The addition of Darvan 7 as dispersant agent also was tested. No effect on casting quality or in the sintering of the tubes was observed.

TABLE 4.2

Milling time (h)	Grain Size Average (µm)	Standard Deviation	Surface (cm ² /g)
0	2.67	1.32	0.858
20	1.91	1.38	1.038
24	1.61	0.95	1.328
48	1.47	0.87	1.342
70	1.06	0.62	-

Grain Size of LiYO₂ versus milling time

4.3 Sintering

The degree of sintering of $LiYO_2$ tubes in this investigation was evaluated by way of shrinkage, ink absorption, phases present in the sample and measurement of helium leak resistance. In addition, the texture of the sample was an important indication of the tube quality since high density solid electrolytes are typically translucent and have a white or cream color. Hydration after firing was a persistent problem. Therefore, effects of parameters such as heating rate, cooling rate and composition were investigated.

Shrinkage was calculated assuming the initial diameter to be equal for all tubes. If the tubes had an oval section after sintering, the shrinkage with respect to the minimum and maximum diameters are reported. Heating rates greater than 70° C/min have been included under the heading 70° C/min for simplicity. Heating rates and temperature intervals are shown in Table 4.3.

TABLE 4.3

Detail of the rapid heating rate used in sintering LiYO₂ tubes

Heating Rate	Temperature Range
70 °C/min	100°C - 700°C
50 °C/min	700°C - 1200°C
20 °C/min	1200°C - 1400°C

4.3.1 Hyperstoichiometric Composition

Preparation of hyperstoichiometric compositions (excess Li_2O) is a common approach when lithium compounds are to be prepared at high temperature. Some lithium excess helps to compensate for the evaporation during both reaction and sintering. The sintering schedule has two steps, one of ten hours at 1250°C and a second step of 6 minutes at 1325°C. The second high temperature step is believed to produce a liquid phase and fills any remaining porosity (Table 4.4).

TABLE 4.4

Initial Sintering Conditions

	Mix: 4 m	ol% excess (:	52% Li ₂ CO ₃	: 48% Y ₂ O ₃)	Milling: 6 h	
			Heating Ra	ate		
Heating	Temp 1	dwelling	Ramp	Temp 2	dwelling 2	
6 h	1250°C	10 h	10 min	1325°C	6 min	cooling
	_	Ex	ternal dian	neter:	······································	
initial final (ideal) Shrinkage					<u> </u>	
9.7 mm 7			n		24.0 %	

4.3.1.1 4 mol% Li excess (52% Li₂CO₃:48% Y₂O₃)

The variables in fabricating lithium yttrate tubes with 4 mol% excess Li were as follows:

- i. heating and cooling rates
- ii. sintering temperature
- iii. firing with and without packing material

The sintering conditions in Table 4.4, with very few exceptions, led to either hydration or low shrinkage with high levels of helium leakage. Increasing the ramp time

to 1325°C from 10 minutes to 1 h, or up to 2.5 h, gave poor shrinkage of 14.6% versus 26% expected. Increasing the calcination temperature to 750°C for 10 h, instead of 706°C for 12 h, using the original schedule, resulted in hydration after cooling. The effect of hydration was that tubes which appeared sound after sintering began to crack within seconds of exposure to air.

When the sintering schedule was changed to one ramp directly to 1420° C with a 7 minute dwell, the tubes were deformed and poorly sintered as showed by ink absorption. At these sintering conditions, the XRD analysis showed a two-phase mixture of mainly LiYO₂ and a high fraction of Y₂O₃ estimated to be between 40 and 50 %.

When the temperature was increased to 1430° C with no dwell time, the tubes achieved almost full shrinkage. As before, XRD analysis showed between 35 and 50% Y_2O_3 content. In these samples, more deformation occurred and poor leak test results were achieved.

Introducing a short dwell time (0.1 or 0.2 h) gave no improvement to the leaktightness (only $1.2x10^{-3}$ atm was achieved in the leak test) and increased the tendency to hydration. The same happened with any combination of temperatures. Heating and cooling rate variation could not increase the vacuum resistance to more than $1.3x10^{-6}$ atm. An acceptable leak rate corresponds to a sustained vacuum of better than $1.3x10^{-8}$ atm.

Comparison of Y_2O_3 powder from two different suppliers showed no significant differences between the quality of the tubes. After sintering, both sets of tubes showed 21.5% shrinkage, considered quite far from 26.2%, the shrinkage for fully sintered pieces.

The effect of using crushed sintered tubes (scrap) as packing material was evaluated. 4 mol% excess lithium yttrate tubes were packed with fresh scrap into a closed crucible. After sintering, tubes were porous with high ink absorption and low shrinkage. Reducing the amount of packing material or the degree of compaction had no effect. Tubes were consistently porous in all cases. The same result was obtained when broken green tubes or re-used scrap was tested as packing material.

4.3.1.2 6 mol% Li excess (53% Li₂CO₃:47% Y₂O₃)

Tubes containing 6 mol% Li_2O excess were sintered using heating rates of 5°C/min, 10°C/min, 15°C/min and 70°C/min. Results are shown in Table 4.5.

Tubes 168, 173 and 174 sintered at 70°C/min were He leak-tight. Tubes 167, 169 and 170 treated at lower heating rates (5, 10 and 15°C/min) absorbed ink and showed very poor sintering.

A second rapid heating of porous tubes 167 and 170 to 1400°C in 15 min gave good sintering. These tubes were hard to crush, showed no hydration, did not absorb ink and had a vacuum resistance better than 1.3×10^{-8} atm. Tubes 192, 195 and 198 sintered well after a second heating at 70°C/min, and kept their He-leak tightness. Very thin tubes had a tendency to deform or kink and develop a crack.

TABLE 4.5

Tube	Shrinkage %	°C	°C/min	Vacuum	Sintering
167	8.1	1425	5	-	Poor
	-	1400	70	-	Good
168	-	1410	70	1.3x10 ⁻⁹ atm	Good
169		1400	15	-	Poor
	26.4	1400	10	-	Poor
170	-	1400	10	-	Poor
	-	1400	70	-	Good
173	26.2-34.3	1380	70	1.3x10 ⁻⁹ atm	Good
	-	1405	70	-	Melt
174	24.1-28.0	1380	70	1.3x10 ⁻⁹ atm	Good
192		1399	70	-	Good
		1392	70	1.3x10 ⁻⁹ atm	Good
195	21.2-24.6	1360	70	-	Good
	-	1389	70	1.3x10 ⁻⁹ atm	Good
198	22.0-24.6	1361	70	-	Good
	-	1385	70	6.6x10 ⁻⁸ atm	Good

4.3.2 Stoichiometric mix

In order to improve the sintering and diminish the hydration tendency, the lithium content was lowered to the stoichiometric amount. Although a high degree of shrinkage

was obtained by sintering at 1400°C, 1410°C and 1425°C, all tubes showed cracks after sintering, or hydration when reheated for attaching the lid.

To promote sintering and reduce the Li excess that causes hydration, higher temperatures were used. Heating at 1450°C, 1455°C and 1465°C, with a second step at 1410°C and slower cooling (3°C/min), always produced cracks in the tubes.

Reducing the heating rate to 3.8° C/min at lower temperature to allow the remaining carbonate to decompose did not improve the leak tightness beyond 1.3×10^{-7} atm.

An annealing period of 45 min at 1175°C, followed by slow cooling (10 hours) was included in the schedule to increase the time to decompose and evaporate lithium excess. Results showed tubes had less than full density and poor leak resistance.

After lowering the heating rate still further, the tubes were generally found to have fine cracks and were sintered to the alumina container. The weight loss was twice as high as for a heating rate of 5°C/min. More probability of cracks was found after a second heating due to hydration.

Those schedules with longer dwell times (13 h for 1250°C and 0.2 h for 1410°C) produced two tubes with excellent shrinkage and no ink absorption but a second heating at the same temperatures produced cracks.

To test the effect of the mixing process, the powders were mixed in a mortar with alcohol as a mixing aid. Tubes from this mix fired at 1425°C or 1430°C had no better results.

4.3.3 Hypostoichiometric mix

To reduce the hydration after sintering, the Li content was lowered below stoichiometric. Table 4.6 shows results of tubes 102, 103, 104 and 135, of hypostoichiometric composition $(49\%\text{Li}_2\text{CO}_3 : 51\% \text{ Y}_2\text{O}_3)$. When heated in air at 5°C/min up to 1425, 1435 and 1465°C, the samples showed poor sintering and fast ink absorption. A second firing at 1500°C gave higher shrinkage but ink absorption was still present. Tube 141 from the same batch heated rapidly to 1380-1400°C in 15 minutes sintered very well with full shrinkage and was He leak-tight.

At high heating rates, for the same temperature, deformation increased indicating that the amount of liquid phase was higher during sintering than the liquid phase at lower heating rates. A small variation in temperature could lead to partial sintering or to complete melting of the tube.

As an illustration, it was seen that part of a tube whose surfaces was exposed to the heating elements was well sintered whereas surfaces shielded by the crucible wall were poorly sintered. A small temperature variation in the tube yields inconsistent degrees of sintering from end to end. Packing tubes in $LiYO_2$ scrap was effective in reducing the temperature gradient. In addition, it was observed that the weight loss was proportional to the fraction of the tube that reached the fully sintered state.

TABLE 4.6

Tubes	Shrinkage (%)	°C	Rate	Vacuum	Sintering
102		1425	5°C/min		Poor
102	20.9-25.4	1500	5°C/min		Poor
103	8.6	1435	5°C/min		Poor
104	13.1	1435	5°C/min		Poor
135	19.4	1465	5°C/min	6.6x10 ⁻⁴ atm	Poor
141	26.4-28.0	1380	70°C/min	1.3x10 ⁻⁹ atm	Good

-2 mol% Li tubes sintered at 1425, 1435 and 1465°C at different rates

The hypostoichiometric -2 mol% tubes were analyzed by XRD and showed consistently higher levels of yttrium oxide. Shrinkage was maximized and achieved a vacuum in the order of 1.3×10^{-8} atm. No cracks due hydration occurred.

Adding more steps to the heating schedule resulted in tubes sticking to the crucible and reduced significantly the amount of $LiYO_2$ as revealed by XRD.

4.3.4 Substitution of lithium carbonate by lithium oxide

Powder was prepared with lithium oxide instead of Li_2CO_3 . Tubes sintered at 1425°C or 1430°C, with milling times of 24 h and 48 h for -2 mol% Li failed the leak test. There was no difference in weight loss after sintering of these tubes compared to tubes made using Li_2CO_3 .

4.3.5 Effect of milling time

Initially, the vibromilling time was 6 h as shown in Table 4.4. Reducing the time to 3 h for a 4% excess mix and following the standard heating rate, led to good sintering in terms of shrinkage and texture but strong hydration tendency was observed after sintering. In most cases, cracks started to grow some minutes after cooling. The same mix heated to 1390-1400°C at a heating rate of 5°C/min gave white porous tubes that did not shrink completely. Tubes from a 6 h-milled slip or 72 h-milled slip also showed poor sintering at 1430°C with a heating rate of 5°C/min.

Tubes were made of stoichiometric mix for different milling times. Mixes milled for 17 h instead of 6 h gave better shrinkage and no cracks but the leakage resistance was poor. Using more steps in the heating schedule for a 17 h-milled slip resulted in all cases in rapid ink absorption.

In all cases, no positive effect on sintering was observed. An exception is described in the next section for mixes containing high Li_2CO_3 .

4.3.6 Lithium carbonate as sintering aid

Lithium salts have been found to help sintering because of their fluxing effect. Therefore, Li_2CO_3 was added to stoichiometric $LiYO_2$ powder in proportions of 25% and 30%. Unlike the other mixes tested in this work, XRD showed no Y_2O_3 phase after sintering for the $LiYO_2$ - Li_2CO_3 mixes with 75:25 and 70:30 ratios. Table 4.7 shows results for sintering the 75:25 mix at 1400, 1425 and 1450°C at 5°C/min and no dwell time. In this mix, the effect of milling time is clearly noticeable. None of tubes with 6 h milled slips was well sintered, despite the temperature increase from 1400 to 1450°C. Hydration was severe and worsened with temperature.

TABLE 4.7

Sintering of tubes	(75% LiYO,:25% Li,CO ₃)
	(1 - 1 - 1) = -2 = -2 = -3

Tube	Weight Loss	Shrinkage (%)	°C	Rate °C/min	Vacuum (atm)	Sintering	Milling Time (h)
	<u>(wt%)</u>						
129	22.7	25.1-31.7	1400	5	-	Poor	6
130	22.6	28.3-29.6	1425	5	-	Poor	6
131			1450	5	-	Poor	6
133	21.7	21.2-37.2	1425	5	-	Good	24
134	24.1	25.1-34.3	1425	5	-	Good	49
136	22.6	24.6-27.2	1425	5	1.3x10 ⁻⁹	Good	49
137	23.0	27.5-30.6	1425	5	-	Good	49
138	22.3	26.2-27.5	1425	5	-	Good	49

For 24 and 48 hours milling time, it was found that tubes sintered well at 1425°C at 5°C/min. No absorption of ink was found in these samples. Tube 136 was tested and showed He leak-tightness. Weight loss was three times higher than for tubes obtained from stoichiometric mixes.

Addition of 30% Li_2CO_3 to a stoichiometric mix again gave good sintering. Weight loss and shrinkage was higher in comparison with the 25% mix. A temperature of 1430°C gave more shrinkage than 1425°C (Table 4.8).

TABLE 4.8

Sintering of tubes (70% LiYO₂:30% Li₂CO₃)

Tube	Weight	Shrinkage	°C	°C/min	Vacuum	Sintering	Milling
ļ	Loss (wt%)						lime
121	27.6	30.1-33.8	1425	5	$6.6 ext{ x10}^{-7} ext{ atm}$	Good	48
124	29.9	22.5-40.6	1425	5	1.3x10 ⁻⁹ atm	Good	48
125	25.5	26.2-41.4	1400	5	-	Good	48
126	24.5	27.8-29.1	1425	5	-	Good	48
127	30.5	29.1-37.7	1425	5	1.3 10 ⁻⁶ atm	Good	48
128	26.4	24.9-42.9	1400	5	-	Good	48

Although, addition of lithium carbonate acted positively as a sintering aid, these two Li_2CO_3 mixes had the disadvantage of hydration after a second heating. This situation produced a limitation to the use of this method if a heating process is to follow.

Since Li_2CO_3 addition had a significant effect on sintering, pellets of stoichiometric mix where ground and mixed with 30 wt% of lithium carbonate. The new pellets were heated at 1250°C (6 h), as was established for solid reaction. The pellets showed much more shrinkage (19.7 mm diameter versus 22.9 mm for lower Li_2CO_3

content mixes) and hydrated more strongly than, for example, those with 6 mol% Li_2CO_3 . The weight loss was in the order of 21.5%, slightly less than the weight loss in the sintering of 30% Li_2CO_3 tubes.

Results of sintering are shown in Table 4.9. Unlike the addition of lithium carbonate to the slip, in this case, tubes cracked after sintering at 1415, 1425 and 1450°C. A second heating for sample 160 led to strong hydration in few seconds. Heating with longer dwell time at lower temperature gave very poor sintering. The decomposition of lithium carbonate prior to sintering nullifies the sintering aid effect.

TABLE 4.9

Sintering of tubes containing 70% LiYO₂:30% Li₂CO₃ reacted at 1250°C (10 h)

Tube	Weight loss (wt%)	Shrinkage (%)	°C	°C/min	Sintering
160	-	-	1250 (10h)	-	Poor
160	-	-	1425	5	Powder
161	30.1	30.9	1450	3	Poor
147	-	26.7	1425	5	Poor
149	-	-	1415	5	Poor
159	23.7	26.2	1415 - 12501175	-	Cracks

These 25 and 30% Li_2CO_3 mixes when heated at 1400°C at high rates produced single phase LiYO₂, according to XRD analysis.

Following the opposite approach, the addition of 2 wt% Y_2O_3 to stoichiometric slip to react with the excess of lithium oxide during sintering and reduce hydration tendency also was tested (Table 4.10). The weight loss was about 50% of that seen for stoichiometric samples but the sintering temperature increased to 1550°C. An increase in milling time showed higher shrinkage but sintering was poor in all samples except one. The exception was that a combination of high sintering temperature and high heating rate gave a good result, independent of milling time, as shown in Table 4.10. This information was exploited in future fabrication of tubes.

Table 4.10

Sintering t	ubes	made	of	stoic	hio	metric	e mix	plus	2%	\mathbf{Y}_2	0) ₃
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tube	Weight Loss (wt%)	Shrinkage (%)	°C	°C/min	Sintering	Milling Time (h)
111	0.7	7.6	1425 (8h)	5	Poor	24
	17.7	17.8-41.1	1550 (0)	70	Good	
112	2.9	12.6	1425 (8h)	5	Poor	48
113	3.0	12.8	1425 (8h)	5	Poor	48

4.3.7 Two stage heating LiYO₂ pellets

In order to assure the completion of the reaction and reduce the amount of Li_2CO_3 remaining in the mix, the pellets were heated twice with an intermediate cooling to room temperature. In the second heating, both open and closed crucibles were used, as well as different temperatures and dwell times to test the effect on sintering.

At a temperature of 1425°C, tubes shrank well but developed microcracks that produced poor vacuum resistance. No difference was seen between tubes sintered in crucibles packed with scrap and tubes sintered without packing. The weight loss increased with temperature from 16% to 19%.

A dwell of 0.1 hour with slower cooling rates (3 or 4°C/min) resulted in high deformation or melting above 1423°C.

XRD patterns showed 100% LiYO₂ after heating to 1325°C (7 min dwell) but decomposition of LiYO₂ was evident at higher temperatures. No effect on the LiYO₂ content was found with increasing dwell time from three to six hours at 1250°C in a closed and packed crucible. A schedule of sintering 10 h at 1250°C followed by 7 min at 1350°C decreased the fraction of lithium yttrate to 50%. All samples leaked under vacuum and weight loss was lower.

In conclusion, for double heating tests, sintering above 1400°C gave good shrinkage but produced deformation and microcracks resulting in a low number of impervious tubes. Lowering the temperature at 1350°C or less but adding a step with much longer dwell time at 1250°C reduced deformation but shrinkage and leakage were very poor. Packing the tubes with lithium yttrate scrap had no effect on the quality of the sintering.
4.3.8 Ball Milling effect

The use of ball milling in a ceramic jar was tested as a substitution to vibromilling to decrease the amount of alumina from milling media and organic material from the polyethylene bottle. Samples were milled for 24 hours.

Results showed lower shrinkage (23.0% versus 24.6%) and a lower weight loss (4.7% versus 6.3%) compared to those of stoichiometric mixes. After sintering, tubes had a vacuum resistance in the order of 1.3×10^{-7} atm, below the minimum of 1.3×10^{-8} atm considered adequate to construct a cell. XRD shows that lithium yttrate levels suffered no loss.

Using lower temperatures (1390°C) than those used for vibromilled slip samples gave the same results. Increasing the temperature to 1410°C or 1415°C, the tubes become deformed and stuck to the crucible and weight loss and shrinkage increased. Adding more steps to the heating schedule increased the weight loss. The shrinkage remained in the same range (25%) but hydration occurred after cooling to room temperature.

4.3.9 Low temperature heating

A test was carried out to investigate the characteristics of a 4 mol% excess green tube heated at temperatures below 800°C. Results showed a weight increase after heating at 200°C and 500°C due to hydration of the lithium oxide released from the partial decomposition of lithium carbonate or lithium yttrate. At 200°C, the burning of organic materials eroded from the jar could also be observed. After cooling, tubes developed long cracks. These tubes were calcined at 750°C for 10 hours and sintered at the regular temperatures of 1325°C (7 min) and 1250°C (10 h). Strong hydration was observed.

4.3.10 Tubes made of Li₂CO₃ and Y₂O₃

An alternative method was to fabricate tubes from precursor powder rather than from pre-reacted LiYO₂. Tubes cracked after cooling or were highly porous when no time was allowed to decompose the Li₂CO₃ at 706°C. Higher temperatures led also to hydrated tubes. High heating rates of $70^{\circ}C/min$ were not tested for this mix.

4.4 Sealing

Different materials and procedures were tested to obtain a strong hermetic seal between the tube and the lid (Table 4.11). The degree of leakage through the seal was evaluated by a He leak detector. The sealing material must be inert with respect to Li or the kinetics of the reaction with Li must be sufficiently slow to allow the EMF measurements to be completed. A description of the various sealing methods tried is presented in this section.

4.4.1 Lithium Yttrate and Aremco Binder (LY:AB)

A mixture of lithium yttrate and a silicate base binder (Aremco 571-L) heated to 900°C produced a foam structure although the recommended drying and curing processes

were followed. The level of vacuum obtained with this seal was less than 1.3×10^{-8} atm.

TABLE 4.11

Sealing Materials tested on LiYO₂ tubes and lids

Symbol	Material	Characteristics	m.p.(°C)
LF	Lithium Fluoride	Considered lithium compatible	845
LC	Lithium Carbonate	Lithium ion conductor	753
			1310 b.p [32]
LH	Lithium Hydroxide	Enhance conductivity	475
AP	Aremco 571-Powder	MgO base compound	1760
AB	Aremco 571-Binder	Silicate base compound	
AC	Aremco Cement	Binder 60% Power 40%	1760
CG	Corning Glass 3332		
FR	Frits		
LS	Lithium Silicate		
L2S	Lithium Metasilicate		1204
LA	Lithium Aluminates		1625
LY	Lithium yttrate slips	Lithium compatible	

÷

4.4.2 Lithium Yttrate-Lithium Hydroxide-Lithium Carbonate

A mixture of LiOH and Li_2CO_3 (1:1) melted in air at 600°C but became porous and powdery after cooling. Addition of $LiYO_2$ did not change or improve the result.

4.4.3 Pure Lithium Carbonate

Pressed pellets of lithium carbonate were heated in air at different temperatures. They softened at 850°C and became liquid above 880°C. When powder was used instead of pellets, it decomposed near 720°C. When a layer of lithium carbonate was placed between the surfaces to be attached, and heated at different temperatures between 720°C and 850°C (0.5 h), the seal had mechanical strength but the tubes cracked a few minutes after cooling to room temperature. No impervious cell was produced. Fine cracks due to CTE were observed in the seal under the optical microscope. A heating schedule that was recommended for sintering Li_2O [58] was tried but no improvement was found.

4.4.4 Lithium Fluoride (LF)

Lithium fluoride sintered at 850° C when heated in air but provided poor sealing. Leak test vacuum was in order of 1.3×10^{-6} atm. At increased temperatures, shrinkage and evaporation of LiF prevented formation of a seal.

4.4.5 Lithium Fluoride and Lithium Carbonate mixture

A combination of these two lithium salts was tested at different temperatures. It was found that a ratio of 70:30 started to melt at 910°C (0.1 h). Cells joined with the 70:30 mixture were easy to break and had no resistance to leakage. Higher LiF ratios did not melt and lower ratios decomposed. Using a first layer of lithium carbonate and a second layer of LiF, dried at 100°C and heated at 900°C, resulted in a weak joint. The problem appeared to be evaporation of the lithium salt.

4.4.6 Lithium Fluoride coated with Aremco Cement (LF:AC)

A layer of LiF was used as a barrier against attack of the Aremco cement by Li. Samples were heated at 800°C (1 h). The Aremco cement seemed to melt because of a reaction between the binder and LiF. As consequence, LiF peeled off from the tube and Aremco cement became foamy.

A test of a cell containing molten lithium, sealed with one layer of lithium fluoride and a second layer of Aremco cement failed in less than 7 h at 350°C, when the seal was destroyed.

4.4.7 Aremco binder (AB) and Corning Glasss (CG)

Cells joined with Aremco binder and Corning glass 3332 were heated at 1000°C (0.25 h) spiked to 1423°C and then cooled. No seal was formed. At lower temperature (950°C) and longer dwell time (24 h) cells had poor vacuum retention (5.3×10^{-7} atm).

The proportion used was 60% Aremco Binder and 40% Corning Glass. These mixtures showed porosity after heating, independent of the temperature or the heating rate. Therefore, they were not effective as sealing materials. At higher temperature, the glass reacted with $LiYO_2$ and the cement contained small bubbles.

By reducing the amount of binder to 50%, the amount of bubbles in the mixture diminished significantly. No impervious cells could be made at temperatures between 1000° C and 1200° C at different soaking times. A consistently low vacuum retention of 2.6×10^{-5} atm was obtained.

4.4.8 Aremco powder (AP) and Aremco binder (AB)

Aremco powder is a magnesia based compound. This makes it a candidate for a compatible sealing material. The ratio tested was AP 70% and AB 30%. The results were generally poor.

4.4.9 Lithium Silicate (LS)

A two layer coating was used: AB40%AP and Li_2SiO_3 . Li_2SiO_3 reacted with the tube at 1320°C and produced a neck at the join. The leak test gave very poor vacuum retention of 2.6x10⁻⁴ atm. If a third layer was used (AB50%CG), the vacuum improved up to $1.3x10^{-7}$ atm. Lower temperatures produced a gap between the Li_2SiO_3 and the lid. Other combinations either produced porous structure or reacted with the tube.

4.4.10 Lithium yttrate (LY) and Lithium Carbonate (LC) mix

 $LiYO_2$ was mixed with 10, 20 30, 40 and 50 wt% Li_2CO_3 and tested. All combinations were sintered at 900°C (10°C/min). None gave impervious sealing. A second heating at 700°C (24 h) or 1200°C showed no improvement.

4.4.11 Lithium yttrate and Lithium Silicate mix

Lithium silicate with 5%, 10%, 50%, 90%, and 95% $LiYO_2$ were tested at 1315°C. Results showed lower melting points for 10% and 50% mixtures.

Cells sealed with the 10% LiYO₂ mix and heated at 1150 and 1300°C (4°C/min) appeared good but cracks soon developed on the tubes.

A mix of 50% $LiYO_2$ at 1150°C or higher had enough mechanical strength to be handled without breaking but showed reaction with the surface of the tube. Below 1150°C no sintering of the joining material was observed.

4.4.12 Lithium Aluminate (LA)

Various combinations of lithium aluminate and lithium silicate were prepared to obtain a composition stable to pure Li and having a melting point lower than 1200°C according to the phase diagram showed in Fig. 4.3. The proportions used and the refractoriness at different temperatures are shown in Table 4.12.

TABLE 4.12

Composition of mixtures (wt%) of lithium silicate, lithium aluminate, and lithium phosphate prepared as sealant

	Α	В	С	D	Ε
Li ₂ SiO ₃	88.13	0.00	89.04	0.00	80.00
Li ₅ AlO ₄	11.86	100	-	-	-
Li ₂ CO ₃	-	-	4.61	34.24	8.40
Al_2O_3	-	-	6.35	-	11.60
P ₂ O ₅	-	-	-	65.76	-
Reaction	1100°C		1000°C (17 h)		
Temperature				:	
Target	Li ₂ SiO ₃	Li ₅ AlO ₄	Li ₂ SiO ₃	Li ₃ PO ₄	Li ₂ SiO ₃
phases	Li₅AlO₄		LiAlO ₂		Li₅AlO₄
		Experimen	tal Results	•	
At 1000°C			no melt	melt	no melt
			no melt	melt	no melt
At 1100°C					
At 1175°C			melt	melt	melt
At 1200°C	melt, glassy	no melt	melt	melt	decomposed



R. A. Eppler, J. Am. Ceram. Soc., 46 [2] 100 (1963).

Fig. 4.3 Ternary Phase Diagram Li₂O-Al₂O₃-SiO₂

Mix A (88.13% Li₂SiO₃) was used as sealant. It reacted with LiYO₂ and destroyed the tube at 1175°C (200°C/h). At lower temperatures, no joint was obtained. At faster heating rates the seal was not impervious. For instance, at 1300°C (300°C/h), the joint was weak; at 1250°C and annealing for 1 h at 1150°C, reaction with the surface of the tube was evident but the leak resistance was only 2×10^{-4} atm.

Mix B (Li_5AlO_4) was not tested on a cell because the melting point was over 1200°C. Mixtures C and E did not melt under 1175°C. Cells joined with these mixtures showed poor sealing. The lithium orthophospate mixture (D) was tested at 1000-1500°C. The joint was not impervious.

4.4.13 Li₂SiO₃:LiAlO₂

These mixtures started to sinter above 1350°C, and at 1400°C were completely melted. The proportions of the mixes tested are shown in Table 4.13.

TABLE 4.13

Mixtures of Li₂SiO₃ and LiAlO₂ tested at 1350 °C

	A	В	С	D			
Li ₂ SiO ₃ (%)	89	80	85	95			
LiAlO ₂ (%)	11	20	15	5			
Experimental results							
89:11 and 95:5	89:11 and 95:5 porous structure						
85:15 Decomposed							
80:20 low viscosity at high temperature produces a thin coating							

When tubes were sealed with mix A (89:11) at 1200°C (ramp: 30 min.), the sealant shrunk and the joint had sufficient mechanical strength to allow handling the tube but it was porous. When heated at 1250°C at a rapid heating rate, the sealant reacted with the surface of the tube and joined the lid. The excess sealing material disappeared, mechanical strength seemed higher but there was a gap between the tube and the lid due to the shrinkage. Leak resistance was only 3.9×10^{-4} atm. Adding more material or heating at a faster rate showed no improvement.

4.4.14 Eutectic

The lithia-alumina binary system has an eutectic point at 77 mol% $LiO_{0.5}$ and 23 mol % $AlO_{1.5}$ [54]. The eutectic mixture consisting of 84 mol% of Li_5AlO_4 and 16 mol% $LiAlO_2$ was tested. After heating at 1200°C, a weak join was obtained and at 1300°C, the sealant decomposed.

4.4.15 High heating rates

As in the sintering process, a heating rate above $70^{\circ}C/h$ was found to have a significant effect in the joining process. Sintered and pre-sintered tubes of varying lithium content developed strong joints with lids that held a vacuum greater than 1.3×10^{-8} atm. The most common composition for the tubes was 6 mol% excess Li and the best results were obtained by heating to 1390°C (ramp 35 min). This temperature depends on the heat treatment previously applied to the tube. The heat treatment affects the type of

lithium compounds in the tube. It was observed that Li_2CO_3 is a sintering aid and therefore the amount non-decomposed in the tube has a significant effect on the joining temperature.

Pre-sintering the green tubes at temperatures between 1320°C and 1340°C is useful to reduce the shrinkage during the sealing. It was carried out at the lowest temperature possible to prevent lithium evaporation and to retain sufficient lithium carbonate to help in the final joining.

4.5 Lid Fabrication

Lids are an important component in the cell assembly. They require high crush strength, matching thermal expansion with the tube and chemical compatibility with the electrode materials. Often glass is used to join the lid to the tube but glass cannot be used in this case because it will react with the lithium. Former experience showed that alumina is a good candidate for the lid but cannot be used in this case because of its reactivity with lithium. Several techniques such as coating and alternative ceramic oxides such as MgO, yttrium-aluminum garnet (YAG) and Y_2O_3 were examined to find an optimum lid material. Lids were fabricated by pressing disks of 25 mm diameter. A tapered bore was machined in the centre of the lid that allowed loading the electrode and then mechanically sealing the cell with a Ta cone.

4.5.1 Alumina lids

Coating alumina lids was the first approach in order to create a barrier against lithium attack. Alumina disks were prefired at 800°C (2 h), and then dipped into a lithium yttrate slip for 5 seconds. The lids were sintered at 1500°C. A strong reaction between the $LiYO_2$ and the alumina caused severe cracking.

In a second test, a thin layer of $LiYO_2$ powder was pressed together with alumina powder to make a homogeneous pellet. No adherence was found after sintering at 1500°C, and the layers split apart. No significant improvement could be obtained by a graded concentration of $LiYO_2$ and alumina powder before pressing.

The reaction of a non-coated Al_2O_3 -lid against molten lithium was evaluated. A lithium cell was constructed and run for 84 hours, until the EMF became unstable. A black reaction layer, with swelling and cracks, appeared on the side exposed to lithium. Microscopic examination showed that the lid was permeated by Li (Fig. 4.4). A gradient of porosity shows the direction of infiltration. The inner side has very small round porosity while the outer side exhibits larger pores and infiltration of the grain boundaries. The lid during the experiment worked apparently without any effect in the EMF reading.

4.5.2 MgO lids

Pure magnesia lids have been reported to be compatible with molten lithium up to 400°C [31]. At higher temperature a protective coating is needed.

Green lids of MgO powder were prefired at 800°C (2 h) and dipped in LiYO₂ slip for 5 seconds. Sintering at 1500°C (4 h), 1400°C (2 h), 1325°C (0.17 h), and 1000°C (2 h) was tried. Results showed that the coating of LiYO₂ sinters separately from the MgOlid, although in this case, no cracks or reaction were observed. When a layer of the LiYO₂ powder was pressed together with a layer of magnesia powder, cracks were observed in the MgO after sintering but not in the LiYO₂ layer.



Fig. 4.4 Boundary between black infiltration and the inner area of the Al₂O₃ lid after working 84 hours with molten lithium. Lithium was in contact with the right side that was attached to the tube.

Mixtures of MgO and $LiYO_2$ in ratios of 90:10, 81:19 and 5:95 were tested. All broke apart under pressure when tightening the cell holder.

Magnesia lids also were prepared. Technical grade (99.99%) and industrial grade (97%) MgO powder were sintered at 1550°C (6 h) and 1670°C (12 h). Vickers hardness was 50% lower for industrial grade lids sintered at 1500°C. Comparative values of hardness for lids made of different materials are shown in Table 4.14. The technical grade lid at high temperature presented moderate hardness that suggests sufficient mechanical strength. No obvious explanation was found for the low value of MgO (97%) when a load of 500 g was used.

TABLE 4.14

Ceramic	Sintering Temp.	Hv		
Oxides	°C	500 σ	1000 σ	
		500 g	1000 g	
Y ₂ O ₃ -12.5%MgO	1670 (12 h)	911	1021	
MgO (99.99%)	1670 (12 h)	1029	1208	
MgO (99.99%)	1550 (6 h)	434	664	
MgO (97.00%)	1670 (12 h)	144	727	
Y ₂ O ₃	1670 (12 h)	644	1017	
Al_2O_3	-	2295	3128	

Vickers hardness tests on samples of different oxides

The use of magnesia in cell fabrication had to be rejected. Results reported in the joining section, indicate that $LiYO_2$ is unable to join to magnesia by liquid phase bonding.

4.5.3 Yttrium aluminum garnet (YAG) Y₃Al₅O₁₂

YAG has been reported as compatible with molten lithium [31]. It was fabricated using stoichiometric mixtures of alumina and yttria. Lids were heated at 800°C (2 h) and dipped into $LiYO_2$ -slip. This composition sintered well at 1500°C alone but cracked when coated with $LiYO_2$. This behavior could be explained by presence of unreacted alumina in the pellet structure.

4.5.4 Lithium Aluminate (LiAlO₂)

Pellets of commercial lithium aluminate powder doped with yttria (LiAlO₂ + 0.2% Y₂O₃) were heated a 800°C (2 h) and dipped into LiYO₂ slip. After sintering at 1500°C (4 h), the coating could be separated from the lid with little effort.

 $LiAlO_2$ pellets with a $LiYO_2$ coating do not crack but a thin gap appears between the two layers. They could be separated easily. This lid was porous with low mechanical strength.

4.5.5 Yttrium oxide lids

Yttria-lithium reaction has been studied experimentally and showed compatibility at 400 and 500°C [4,31]. It has been proposed as coating protection on structural materials against lithium in nuclear plants [4]. Yttria powder pressed into pellets sintered well at 1670°C (12 h). They were brittle and broke under pressure during tightening of the cell holder. Table 4.14 shows that the Vickers hardness of Y_2O_3 is 40% lower than MgO and Y_2O_3 -12.5% MgO at a load of 500 g. However, at 1000 g the hardness of all three are comparable.

4.5.6 Lithium Yttrate lids

Lids of lithium yttrate developed cracks after sintering at 1500°C (3 h). The same result was observed when lithium yttrate was formed by sintering Li_2CO_3 and Y_2O_3 .

Mechanical strength was very low in comparison with alumina and yttria. The lid broke in the cell holder.

4.5.7 Yttria Magnesia lids

Magnesia-yttria powder isostatically pressed into a pellet was tested. The powder was vibromilled overnight. The sintering process is shown in Table 4.15.

For magnesia-yttria, there was no composition dependence of shrinkage (Table 4.16). All compositions (0 - 15% MgO) had good mechanical properties.

TABLE 4.15

Sintering conditions for yttria-magnesia lids

	Temperature	Shrinkage after cooling (%)
Pre-sintering	1250°C (2 h)	10.5
Sintering	1690°C (12 h)	20.0
Annealing	1175°C (1 h)	-

Table 4.16

Shrinkage of Y₂O₃-MgO lids after sintering at 1670 °C (12h)

MgO Content (%)	Shrinkage
0	22.1%
6	21.9%
15	22.2%

The compatibility of Y_2O_3 -MgO lids was evaluated after keeping them in contact with molten lithium at temperatures between 400°C and 610°C for sixty days. None was attacked or infiltrated by lithium. These lids were reused several times and showed no sign of mechanical weakness or other structural changes.

4.6 Zn - Li alloys

The main goal of this thesis was to develop a practical sealing method for $LiYO_2$ tubes in order to perform EMF measurements. The next goal was to test the $LiYO_2$ electrolyte as a tool in assessing the thermodynamics of binary alloys containing Li. The $LiYO_2$ was tested in two modes: as a sensor between 2 levels of Li concentration and as a pump by using coulometric titration.

The Li - Zn system was chosen because of the relatively low liquidus temperature and because a few studies of activity values and other thermodynamic properties for this system had already been reported [15,30,55].

As $LiYO_2$ is a Li^+ conducting electrolyte, pure Li metal was used as the reference electrode. Since alkali metals, particularly Li, are aggressive at high temperature, a lithium-tin alloy was calibrated against pure lithium and then utilized as the lithium reference cell for measurement of Li-Zn compositions.

The electromotive force measurements were carried out on a galvanic cell designed as follows:

(RE) (-) Ta
$$\text{Li},\text{Sn} | \text{Li},\text{YO}_2 | \text{Li},\text{Zn} \text{Ta}(+)$$
 (WE) (4.1)

Tantalum wire was used as the electrical contact lead. No reaction was observed between this metal and Li, Zn or Sn at working temperatures. A schematic of the apparatus is shown in section 3.7. To avoid oxidation of Li and the working alloys, the cells were prepared in an argon atmosphere glovebox with less than 2 ppm oxygen.

The reference cell (RE) was a Sn alloy with 1.62 mol% Li. For the calibration, the following cell was constructed:

(-) Ta; Li | LiYO₂ | Sn-Li; Ta (+)
$$(4.2)$$

Pure Li metal was the reference electrode with activity equal to one, and the (Sn, Li) alloy was the working electrode. Li was titrated through the $LiYO_2$ solid electrolyte to the required level. It is useful to maintain a liquid for the reference electrode for rapid equilibration. By using a tin alloy dilute in Li, the liquid phase is present from 230°C upwards. Furthermore, the variation of EMF with temperature is small and therefore errors associated with inaccurate temperature measurement are insignificant.

The measured EMF of the reference electrode with respect to pure Li was fitted to a parabolic equation using the least squares regression method. The following expression for the EMF of Sn-1.62 mol% Li versus pure Li was obtained:

$$E (mV) = 784.1 - 0.212 T + 6.782 10^{-4} T^{2} (^{\circ}C)$$
(4.3)

The calibrated reference cell was used to measure the EMF versus the working electrode. Pure molten Zn was the starting working electrode. Lithium was added by coulometric titration and readings were taken periodically. It was found that a titration current of 0.1 mA could be passed at 600°C with an applied overpotential of 300 mV. This corresponds to a transfer of 0.1 mole Li in 12 h.

It was necessary to allow 1-5 h for equilibration after titration. If solid phase was present, more equilibration time was needed.

The first cell was operated up to 600°C in a composition range from 0 to 32 mol% Li. It worked continuously for 42 days. Its failure by rupturing is attributed to a lack of volume to accept more lithium.

Fig. 4.5 shows the variation of EMF with temperature for 5 and 10 mol% Li. Both concentrations show a small positive slope in the liquid phase. The liquidus temperature at these compositions agrees to within \pm 4°C with the published phase diagrams of Hansen [60] as shown in Table 4.17 and Fig. 4.5a.

TABLE 4.17

Solidus and liquidus points for Li-Zn system

	Solidu	us (°C)	Liquidus (°C)	
X _{Li}	This Work	Hansen [60]	This work	Hansen [60]
0.05	403	403	413	409
0.10	417	419	452	445



Figure 4.5

a) Detail of Li-Zn phase diagram showing 5 and 10 mol% Lib) EMF versus T for 5 and 10 mol% Li-Zn alloys

Table 4.18 lists the thermodynamic properties at 500°C and 550°C for 5 and 10 mol% Li. The isothermal variation of EMF and other thermodynamic properties versus composition at 600°C are presented in Table 4.19.

TABLE 4.18

X _{Li}	Т	$\ln \gamma_{Li}$	$\ln \gamma_{Zn}$	$\Delta \mathbf{G}$	ΔS_{Li}	ΔH_{Li}
	(°C)			kJ/mol	J/mol/K	kJ/mol
0.05	550	-3.623	-0.00770	-2648	16.96	-31.33
0.05	500	-4.016	-0.01015	-2628	-8.60	-51.73
0.10	550	-3.220	-0.04130	-4682	50.68	3.92
0.10	500	-3.354	-0.06532	-4623	-9.60	-28.94

Thermodynamic properties of Li-Zn at T=500 and 550 °C

Thermodynamic properties were obtained from the measured EMF values. The cell reaction involves the solution of pure Li in the alloy. Since the EMF is proportional to the partial molar Gibbs energy of mixing and proportional to the logarithm of Li activity in the alloy, the partial molar Gibbs energy of mixing was calculated from Eq. 2.3.

TABLE 4.19

Thermodynamic properties of Li-Zn alloys at 600°C

X _{Li}	EMF	$ln \gamma_{Li}$	ΔG_{Li}	$\ln \gamma_{Zn}$	ΔG_{Zn}	ΔG	ES
	mV		kJ/mol		kJ/mol	kJ/mol	kJ/mol
1.1x10 ⁻³	892.5	-5.04	-86.11	3.200x10 ⁻⁵	-7.7	-101.5	-260.96
1.5x10 ⁻³	855.3	-4.87	-82.52	1.200x10 ⁻⁴	-10.0	-133.8	-259.29
2.0x10 ⁻³	829.5	-4.81	-80.03	1.100x10 ⁻⁴	-13.7	-173.8	-257.22
4.0x10 ⁻³	752.6	-4.48	-72.61	-7.99x10 ⁻⁴	-34.9	-325.2	-249.13
6.0x10 ⁻³	716.8	-4.41	-69.16	-0.0013	-53.1	-467.7	-241.31
1.0x10 ⁻²	669.5	-4.29	-64.59	-0.0025	-91.1	-736.1	-226.50
2.0x10 ⁻²	599.3	-4.05	-57.82	-0.0065	-193.7	-1346.2	-193.98
2.5x10 ⁻²	575.6	-3.96	-55.53	-0.0087	-246.6	-1628.8	-179.96
5.0x10 ⁻²	498.4	-3.63	-48.08	-0.0207	-522.4	-2900.5	-129.00
7.5x10 ⁻²	439.0	-3.25	-42.35	-0.0449	-891.6	-4001.1	-106.46
9.3x10 ⁻²	399.1	-2.93	-38.50	-0.0733	-1240.8	-4706.1	-94.13
0.010	391.4	-2.90	-37.76	-0.0766	-1320.6	-4964.5	-92.36
0.125	351.2	-2.59	-33.88	-0.1160	-1811.2	-5819.9	-90.37
0.155	314.1	-2.31	-30.30	-0.1613	-2392.9	-6718.7	-90.79
0.200	258.0	-1.82	-24.89	-0.2674	-3560.1	-7825.7	-84.23
0.250	214.5	-1.46	-20.69	-0.3725	-4791.4	-8766.4	-65.52
0.260	206.1	-1.39	-19.88	-0.3962	-5060.8	-8914.0	-62.69
0.280	188.1	-1.23	-18.14	-0.4551	-5687.4	-9175.2	-61.84
0.300	173.3	-1.10	-16.72	-0.5083	-6277.8	-9409.3	- 72.41
0.320	158.6	-0.97	-15.30	-0.5667	-6912.6	-9595.9	-102.08

The variation of EMF versus temperature for each composition was fitted to an equation of the form:

$$E = A + BT + CT \ln T$$
(4.4)

Results in the liquid phase are shown in Table 4.20.

Table 4.20

EMF dependence on temperature for the Li-Zn system

 $E(mV) = A + BT + CT \ln T (K)$

X _{Li}	A	В	С	Exp. Points
0.05	3805.9	-32.45	4.23	7
0.10	5564.1	-51.99	6.81	5

The activity coefficient γ_{Li} was obtained by Eq. 2.4

$$\ln \gamma_{Li} = -\frac{FE}{RT} - \ln X_{Li} \tag{2.4}$$

The temperature dependence of EMF given by Eq. 4.4 was used to calculate the partial molar entropy of mixing ΔS_{Li} according to Eq. 2.6:

$$\Delta S_{Li} = F \left(\frac{\partial E}{\partial T} \right)_{X,P} \tag{2.6}$$

With the energy and entropy values, the enthalpy can be obtained from Gibbs-Hemholtz equation.

The activity coefficient was calculated for each concentration using the isothermal data shown in Table 4.19. The activity coefficients of the second component (Zn) were calculated by the Gibbs-Duhem integration (Eq. 2.7), based on the polynomial representation of the activity coefficient.

Figure 4.6, shows the variation of the excess stability function *ES* with composition. A relative maximum in the curve reflects the concentration with highest ordering. Although there is no obvious peak in this range, that would indicate a "liquid compound", the smoothness of the function is a good indication of the very small degree of scatter in the experimental data.

$$ES = \frac{\partial^2 G^E}{\partial X^2} = RT/(1-XLi) \frac{\partial \ln \gamma_{Li}}{\partial X_{Li}}$$
(4.5)



Figure 4.6 Excess Stability Function

A second cell was operated in the dilute Li concentration range.Fig. 4.7 shows the theoretical Nernst slope obtained for a mole concentration of Li between 10^{-4} and 10^{-2} . The Nernst slope is 73.3 mV versus 75.6 mV theoretical.



Figure 4.7 EMF versus ln X_{Li} Nernst slope (-RT/F) in the dilute region

Finally, Table 4.21 gives a comparison with the work of Gasior and Moser [15]. At 550°C, the potential differs by 80 mV (~8 kJ) for 0.05 and 0.10 mole fraction. EMF was fitted to an equation A + BT, to be consistent with the Gasior and Moser methodology.

TABLE 4.	21
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Comparison with EMF from Gasior and Moser [15] at 550°C

	EMF (mV)					$\Delta S_{Li}(ex)$
	This work		Gasior and Moser		This work	Gasior and Moser
X _{Li}	T (K)	mV	T(K)	mV	J/mol/K	J/mol/K
0.05	384.1 + 0.128 T	489	590 - 0.024 T	570	-12.6	-27.2
0.10	334.0 + 0.062 T	385	483 - 0.022 T	465	-13.2	-21.2

CHAPTER 5

DISCUSSION

5.1 LiYO₂ formation

Some authors have suggested that the reaction between Li_2CO_3 and some ceramic oxides may start below 500°C in the solid state [56]. This could not be confirmed by XRD. Pellets heated below 706°C (12 h) showed only the Y_2O_3 phase (Fig. 4.1).

The three possible starting steps of the solid state combination of lithium carbonate and yttrium oxide to form $LiYO_2$ are:

- a) decomposition of Li₂CO₃ to Li₂O
- b) diffusion of Li^+ ions into Y_2O_3 lattice,
- c) formation of a low-temperature liquid phase or eutectic in the ternary

Li₂CO₃ - Li₂O - LiOH.

The reaction proceeds with the subsequent diffusion of Li^+ and the spread of the liquid phase over the Y_2O_3 particles. The liquid phase serves as a path for the remaining Li_2O to diffuse into yttria grains.

Additional steps in the reaction during heat treatment of $LiYO_2$ in air may result in the following:

d) formation of LiYO₂

e) evaporation of lithium oxide at high temperature

f) decompositon to Y₂O₃ and Li₂O during cooling and/or subsequent heatings

The steps in the formation of $LiYO_2$ were interpreted from the XRD patterns. From figure 4.2, it can be said that the solid state reaction was complete at 1250°C. The evaporation of lithium was calculated from the weight loss after the solid state reaction less the weight loss due to calcination. From Table 4.1, the lithium loss is estimated at 30% of the initial amount. Additional absorption of CO_2 and water from air was considered negligible.

Decomposition of the $LiYO_2$ is suggested by hydration and cracking of the tubes after sintering at low heating rates. If only the excess lithium evaporated, it is expected that after sintering, no free lithium oxide would exist leaving no reason for hydration. In addition, hydration occurred in both stoichiometric and hypostoichiometric samples, and is therefore not dependent on lithium excess. The hydration and cracking process also was independent of the reaction temperature and was more frequent for long dwell times.

The presence of lithium oxide in reacted pellets and green tubes is suggested by the occurrence of weight gain at low temperature. It was on the order of 2% after reheating at 200°C or 706°C. These two examples are indications of hydration or carbonate formation of the Li_2O . The presence of Li_2O could be explained only by decomposition of $LiYO_2$. The thermodynamics of formation and decomposition of $LiYO_2$ are not well understood.

Decomposition has been reported elsewhere when $LiYO_2$ interacts with a CO_2 atmosphere at 725°C [5] to form Y_2O_3 and Li_2CO_3 . If it is heated in air, it was found that $LiYO_2$ decomposition starts at 200°C forming Y_2O_3 and Li_2O [2,7,8]. This result was confirmed in this work as shown in figure 5.1. The XRD pattern of fresh $LiYO_2$ powder shows no Y_2O_3 . On the contrary, three samples heated in air at 200, 300 and 400°C respectively for three hours increased the intensity of Y_2O_3 diffraction peak with temperature.

It is proposed that a cycling process of decomposition and reformation of LiOH and Li_2CO_3 takes place during the heating and cooling process. Then, Li_2O undergoes hydrolysis or carbonate formation [2]. These low melting compounds facilitate the reaction with free yttria at higher temperatures. It is expected that there is no decomposition when samples are heated in inert atmospheres. Cell shows no sings of degradation after working at 600°C in argon.

According to the intensity of diffraction peaks of $LiYO_2$ sintered tubes exposed to different conditions, the range of concentration of $LiYO_2$ was between 50 and 90%. An exception was found for tubes cast from slip with Li_2CO_3 as a sintering aid. In this case, tubes contained only the $LiYO_2$ phase. Rapid heating to sintering temperature generally showed 75% $LiYO_2$ phase in the tubes. Due to decomposition during thermal cycling is



Fig. 5.1 XRD of LiYO₂ powder after 3 hours at a) 200°C b) 300°C c) 400°C

almost impossible to avoid second phases in the sintered pieces.

The presence of other phases in the $LiYO_2$ tubes should have no negative effects on its performance as a solid electrolyte. It has been demonstrated that lithium hydroxide enhances lithium ion conductivity and it is known that lithium carbonate is a lithium ion conductor [57]. Although the yttrium oxide phase is not a lithium conductor, the performance of the cell was satisfactory in this work.

The Y_2O_3 only reacts with impurities such as V, Ti, or U [34]. An example is shown in Fig.5.2. Yttrium oxide can be reduced to a non-stoichiometric compound in the presence of molten lithium, known to have lower electronic resistivity than the stoichiometric phase [4].

5.2 Sintering of LiYO₂

Hydration of $LiYO_2$ was the most common problem found after sintering. It depended greatly on the heating rate, cooling rate and Li_2O excess in the mix. The most significant improvements to overcome the hydration problem were obtained by two methods.

The first approach was the addition of 20-30 wt% Li_2CO_3 to the slip and sintering at 1420°C with a heating rate of 5°C/min. In this case, tubes were impervious and shrinkage was higher than the expected. Tubes were stable in air but hydration started after a second heating. This condition limits the joining process.



Fig. 5.2 Schematic drawing for mechanism of lithium corrosion to Y2O3 at 500°C [4]

Furthermore, addition of fresh Li_2CO_3 to $LiYO_2$ showed a favorable effect in avoiding decomposition during a second heating. It reacted with the reformed Y_2O_3 and replaced the evaporated lithium. This largely eliminated free yttria phase in the final product. Increasing the amount of Li_2CO_3 before the solid reaction took place neither helped the sintering nor avoided the yttria phase in the final microstructure of the solid electrolyte. It could be interpreted that the carbonate plays a key role that cannot be substituted by lithium hydroxide. The second approach was the implementation of a rapid heating rate of more than 70°C/min. The probability of achieving excellent sintering increased dramatically and the shrinkage was in the expected range. Tubes were stable after several heatings. This was the most reliable method to obtain useful cells. The first method seemed to indicate that lithium carbonate plays an important role in the sintering process. The second method showed that heating rate is a good technique to maintain the molten carbonate up to the sintering temperature.

Molten lithium carbonate has been reported as thermally unstable in air at temperatures higher than 750°C [59]. This temperature in fact depends greatly on the heating rate and on the surface area of the samples. Experiments showed that a pellet of Li_2CO_3 heated at more than 20°C/min started to soften at 880°C. The fact that molten Li_2CO_3 could exist above 1300°C helped the sintering and the joining process when high heating rates were used.

The effect of the high heating rate can be explained by liquid phase sintering. The increase in temperature is fast enough to keep the lithium carbonate or lithium hydroxide in the liquid state before decomposing or reacting with the yttrium oxide.

The process can be divided into several steps: partial decomposition of $LiYO_2$ into Li_2O and Y_2O_3 , at low temperature; hydration and carbonation of Li_2O ; melting of hydroxide and carbonate phases; wetting of $LiYO_2$ and Y_2O_3 grains; pore collapse and densification; reaction of Li_2CO_3 with Y_2O_3 with a consequent reduction of liquid phase; pore formation; evaporation of Li and CO_2 that also reduced the liquid phase; and
reformation of Y_2O_3 and Li_2O during cooling at low temperature. Some of these stages occur simultaneously.

Cooling has an important effect since decomposition of $LiYO_2$ takes place at low temperatures. Depending on the amount of precipitated lithium oxide, the combination with moisture and CO_2 at room temperature promotes cracking, and increases the porosity. TheY₂O₃ phase found in the final stage in almost all samples was the result of this decomposition. It was almost independent of the sintering conditions.

Low heating rates give more time for decomposition of $LiYO_2$ at low temperatures. Therefore, the sample increases in lithium oxide content at the end of the process. On the other hand, a low heating rate also increases the time for decomposition of LiOH and Li_2CO_3 , thereby leaving less liquid to enhance density by the effect of capillarity.

High heating rates can lead to bending, warping or melting when temperature is too high. It indicates that excess liquid phase is present at less than 1450°C, a temperature 300°C below the $LiYO_2$ melting point.

In the fast heating rate approach, an extra step was included before the final sintering. The tubes were packed into crushed scrap and heated to 1320°C, in order to have more uniform partial pressure (of Li and CO_2) and consequently more uniform evaporation and decomposition. The result was that most tubes achieved final sintering at 1395 ± 5°C. Otherwise, the final sintering temperature could vary by more than 30°C.

In some cases, a low limit temperature of 1360°C was enough to obtain fully sintered tubes that would melt completely at higher temperatures. On the contrary, some tubes with the same composition needed more than 1390°C to sinter.

The microstructure in figure 5.3 shows equiaxed grains and large pores, which is typical for transient-liquid phase sintering. The pore filling often does not occur because of a short liquid duration [50]. In this case, Li_2CO_3 reacts with Y_2O_3 and forms $LiYO_2$, resulting in consumption of the liquid phase and creation of pores.

Increasing the dwell time had a negative effect on sintering. It promoted evaporation and decomposition of lithium carbonate. Consequently, it reduced the chance of Li_2CO_3 to react with the reformed yttria. Tubes shrunk but they absorbed ink because of an evident porous structure. Depending on the composition, cracking sometimes occurred.

As was described in chapter 4, apart from the excess Li_2CO_3 method and the rapid heating rate method, there were other attempts to find an acceptable sintering procedure but none gave consistently impervious tubes or cells. Hydration was present after cooling or after the second heating needed for the joining process.

In general, the final characteristics of the tubes were: external diameter in the range of 7.3-7.6 mm, thickness 1 mm, shrinkage about 24% and weight loss after sintering about 7.5%. All tubes used for cells were tested to be sure they were impervious against a vacuum of up to 1.3×10^{-9} atm and most were He leak-tight.



Fig. 5.3. Tube after 42 days working with Li-Zn alloy between 400°C and 600°C

5.3 Sealing Process

Solid diffusion bonding, slip coating, cementing, lithium salt flux joining were among the sealing methods tested. The only one to consistently achieve a modest level of hermetic sealing was liquid phase joining at high heating rate. In addition to hydration, other limitations were found: CTE incompatibility, lithium reactivity, low melting point of joining materials, wetting, etc.

A good contact between the two surfaces to be sealed facilitated the diffusion of the liquid phase. It appears that the liquid reacted with the Y_2O_3 in the tube and Y_2O_3 or Al_2O_3 in the lid. This reaction created a bond strong enough to produce an excellent joint between the tube and lid surfaces (Fig. 5.4). The process worked well with lids made of pure yttrium oxide, yttria-magnesia or aluminum oxide but apparently, no reaction took place between the liquid phase and MgO lids because no joint was achieved. This may be explained by the fact that no binary compounds exist between magnesia and lithium oxide, unlike the case for alumina and yttria.

The liquid phase in the range of 1300-1400°C is likely lithium carbonate since lithium hydroxide decomposes at lower temperature and lithium oxide melts at higher temperature. The microstructure (Fig. 5.4) shows a gradient of porosity between the tube and the yttria-magnesia lid indicating that an infiltration or dissolution took place that resulted in a joint.

Most seals were hermetic to 1.3×10^{-8} atm. A small percentage of cells could not achieve high vacuum probably due to micro cracks at stress concentration points caused

by thermal expansion mismatch. In Fig 5.4, the micro crack in the lid was localized inside the cell chamber and did not affect the ultimate vacuum of the cell. When these microcracks are close to the outer surface, they may prevent He leak-tightness.



Fig 5.4 He-tight joint between LiYO₂ tube (upper) and Y₂O₃ lid (lower) formed by rapid heating (160X)

Attempts to use intermediate joining materials were unsuccessful. A paste of lithium carbonate, for instance, resulted in cracked tubes or non-impervious joints. This implies that Li_2CO_3 must be intimately mixed with $LiYO_2$ or Y_2O_3 ; otherwise the lithium

oxide formed after decomposition will cause hydration. The melting temperature of 700-800°C is insufficient to start the reaction with free yttria. In addition, cracks in the Li_2CO_3 joint caused by differences in the coefficient of thermal expansion with the surface to be joined prevented a good sealing.

Use of other salts such as lithium fluoride presented wetting difficulties. LiF wetted the lid but not the tube, leaving a gap between them. When the sealing temperature was increased, the lithium salt melted, and the tube hydrated or cracked. The eutectic compound of LiF and Li_2CO_3 must be avoided because of its low melting temperature. Sealing with silicates or cement failed due to reaction with lithium.

The joining and sintering of lithium yttrate proved to be more complex than transient-liquid-phase processes since several competitive mechanisms act simultaneously. This includes decomposition, hydration and carbonate formation at low temperature, lithium evaporation and LiYO₂ formation at the bonding temperature.

5.4 Lid preparation and stability against molten lithium

Yttrium oxide and MgO were chosen for lid materials, after trials with alumina, yttrium aluminum-garnet, magnesia, yttria and combinations of these materials. Also different fabrication methods were examined such as slip casting, dry pressing, ramming, impregnation or coating with slip. All those alternatives were evaluated qualitatively with respect to cold crushing, porosity and reactivy against lithium.

Isostatically pressed Y_2O_3 pellets heated at 1700°C for 12 h were used. A good cold crush strength was obtained but samples were brittle. Addition of magnesia to the yttrium oxide mix to prepare the pellets led to increased toughness.

The stability of the electrolyte and the lids against lithium attack was evaluated. Based on the experimental results of the three cells used in this work, there was no attack of the LiYO₂ tube by pure molten lithium until 500°C. One cell filled with pure lithium ran for 45 days and no sign of damage was observed. Another cell worked 60 days with no sign of damage at temperatures higher than 600°C. This result gives us confidence in the resistance of the lithium cell at high temperature. A micrograph of a section of tube used in the Li-Zn cell can be seen in Fig. 5.3. The cell was run for 42 days, working with concentrations up to 32 mol% Li and temperatures up to 610 °C.

The microstructure of an alumina lid showed intergranular penetration of molten lithium into the alumina after 84 hours of working with molten lithium up to 605°C (Fig.4.4). Yttria-magnesia lids worked in cells up to 45 and 60 days and showed no evidence of change in color, dimension or mechanical strength.

5.5 Thermodynamics

The accuracy of the literature data on lithium alloys is severely limited by the techniques used. For example, Moser stated that variation in the amounts of admixtures in circulating argon could have had some influence on the results of EMF obtained in their work on the Li-Zn system [15]. Grube et al. [46] used thermal analysis on samples

held in open crucibles under argon, and therefore some losses by vaporization and oxidation may be anticipated at high temperatures. Also in Grube's work, the absorption of Li into the graphite crucible could have introduced some errors into the data [46]. Resistometric measurements were performed on samples annealed for a day just below the solidus and reaction of Li with the glass tube probably occurred [46]. It is expected that those problems resulted in drift in the experimental values reported in these investigations.

In the experiment carried out in this thesis, the argon atmosphere reduced the extent of oxidation of lithium and zinc during the assembly of the cell. Because the cells were sealed, the oxidation of lithium at high temperature was negligible. Furthermore, there was no evaporation of lithium from the cell nor reaction with the sealing material.

The results presented in this work are the first set of thermodynamic data obtained by means of a $LiYO_2$ solid electrolyte. Although limited to only one cell, the data showed little scatter and results were consistent and reproducible during thermal cycling. Stability of the EMF under different conditions was corroborated by leaving the cell to equilibrate for more than 10 hours. Although there is obvious disagreement with Gasior and Moser's results up to 80 mV, variation of EMF with respect to temperature or concentration followed the expected thermodynamic relationship.

The EMF dependence on temperature obtained from the $LiYO_2$ electrolyte was fitted to the relation, $E = A + BT + CT \ln T$ for both solid and liquid phase. The solidus and liquidus points for the Li-Zn system were obtained through the plot of EMF versus temperature for mole fractions between 0.05 and 0.10 (Fig. 4.5). As expected, when the slope of the curve changes abruptly, a point of the liquidus or the solidus line is located. Results show a fair agreement with the binary diagram of Hansen. At 0.05 mole fraction, the solidus is at 403°C corresponding to the eutectic temperature. The liquidus and solidus for 0.10 mole fraction also match the temperature of the binary diagram as shown in Table 4.17.

At dilute concentrations, the Nernst slope between EMF and mole fraction of Li was -73.3 mV, slightly lower than the theoretical -75.6 mV, for the range between 5×10^{-4} and 1×10^{-3} at a temperature of 606°C (Fig. 4.7). The difference could be explained by impurities in the working electrode, possibly due to leaching of Li from the electrolyte.

At very low concentration, less than a mole fraction of 10^{-3} , cell stabilization was very slow and could last up to eight hours for a temperature perturbation of 20° C. At higher concentrations, EMF showed good stability and the time to reach equilibrium was less than two hours. It has been demonstrated that LiYO₂ functions well as a solid electrolyte for measuring thermodynamic data.

CHAPTER 6

CONCLUSIONS

In summary, the conclusions of this work are:

1) Slip casting of a suspension prepared with absolute ethanol in alumina powder molds showed to be an excellent technique to produce tubes of $LiYO_2$.

2) Conventional sintering techniques led to porous or hydrated LiYO_2 tubes. Only liquid phase sintering succeeded in producing impervious tubes. The critical parameter was the heating rate. At least 70°C/min for the first 700°C is required in order to achieve fully sintered pieces at 1390°C. The composition used was 6 mol% Li excess of stoichiometric. Micrographs showed round closed porosity typical of transient-liquidphase sintering.

3) Joining of LiYO₂ tubes and lids was achieved with the same liquid-phase as in sintering. In fact, both processes were carried out simultaneously. The bond was mechanically strong with lids made of Y_2O_3 , Y_2O_3 -MgO or Al_2O_3 . Leak tests showed that cells reached helium tightness of 1.3×10^{-8} atm or better. On the contrary, MgO lids were inert to this process and did not bond the tubes.

4) The final composition of the tubes had more than one phase. LiYO₂ and Y₂O₃ were identified by XRD. It is assumed than other lithium phases are present, such as Li₂CO₃, LiOH or Li₂O. This did not affect the cell performance according to the experimental results. The multiphase structure was found to be a result of the decomposition of LiYO₂
5) LiYO₂ functioned well as a Li ion conductor resistant to molten Li. Coulometric titration and measurements of EMF were performed with good stability and reproducibility for the system Li-Zn up to 0.10 mole fraction. Liquidus and solidus lines were determined in this range. Published phase diagrams and experimental data are in agreement.

6) It was found that the Li-Zn system exhibited the Nernst slope according to equation (2.10) in the mole fraction range of 5×10^{-4} to 1×10^{-3} . The activity coefficient of Zn and integral thermodynamic properties for the liquid phase including Gibbs energy, enthalpy and entropy were calculated.

7) At more than 600°C, yttrium oxide and yttria-magnesia (88:12) lids showed excellent chemical resistance to molten lithium as well as good mechanical properties.

8) Recommendation for future work includes assessment of Li-Zn and other lithium binary alloys; testing $LiYO_2$ as sensors to measure Li content in molten alloys; evaluation in lithium batteries for high temperatures, using cathodes such as FeS_2 , TiS_2 , $LiCoO_2$ or $LiNiO_2$; and examination of effects of second phases in the $LiYO_2$.

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