

High Energy Lithium-air Batteries for Soldier Power

D. L. Foster, J. R. Read and M. Shichtman
U. S. Army Research Laboratory
Adelphi, MD 20783-1197

S. Balagopal, J. Watkins and J. Gordon
Ceramatec Inc.
2425 South 900 West
Salt Lake City, UT 84119

ABSTRACT

High energy lithium-air cells are being developed with the use of LISICON membranes (a dense lithium ion conductor). The LISICON membrane allows cells to be divided into separate compartments, one containing the anode and the other the cathode, each with a different electrolyte. This is particularly important for the lithium/air cell where a LISICON membrane can be used to separate an organic non-aqueous anolyte from an aqueous catholyte. The LISICON membranes were evaluated for Li^+ ion conductivity. The construction and performance testing of laboratory type Li-air cells was conducted to determine rate capability, stability, and impedance characteristics of the Li-air cell.

1. INTRODUCTION

Army Research Laboratory is seeking lighter, higher energy power sources for longer dismounted missions where presently fielded lithium primary batteries or rechargeable lithium-ion batteries alone are not sufficient. In order to complete these long dismounted missions, multiple batteries must be carried by the troops. Metal-air batteries are an attractive choice for dismounted soldier power because of the very high specific energy afforded by the air positive electrode. Zinc-air batteries have been under development for this application. Lithium-air has the highest specific energy of any of the metal-air chemistries and fully developed could provide as much as 1000 Wh/kg (Visco et al., 2006) for soldier missions which is three fold the present state of the art Zn-air battery specific energy.

The development of high energy lithium-air batteries presents some difficult materials compatibility problems. The reactivity of the negative electrode with the electrolyte and other battery components has always been a problem in lithium battery development. In the case of most lithium batteries with lithium salt dissolved in an organic or inorganic solvent, a protective film or solid electrolyte interface (SEI) is formed on the anode surface from the reduction of the electrolyte by the

lithium anode. Lithium batteries with very aggressive electrolytes that do not form a protective film on lithium such as the aqueous electrolytes used with the air cathode are very limited in their application because of the rapid reaction of the aqueous electrolyte with the negative lithium electrode.

The goal of this work was to determine the feasibility of using a Li^+ ion conducting ceramic membrane (LISICON) for the construction of a Li/Air cell that uses aqueous catholyte and non-aqueous anolyte. The ceramic membrane was evaluated in order to establish chemical stability towards lithium metal, Li^+ ion conductivity, and stability towards both aqueous and non-aqueous electrolyte. The construction and performance testing of laboratory type Li/Air cells was conducted to determine rate capability, stability, and impedance characteristics of the Li/Air cell. The overall cell reaction is



2. EXPERIMENTAL

Several first generation Li^+ -ion conducting membranes of type composition $(\text{Li}_{3+x}\text{ZrSi}_{3-y}\text{P}_{1-y}\text{O}_{12-x})$ were prepared from a proprietary mixture of the starting precursors. The mixed precursor oxides were dried at 60 °C to evolve the solvent. The dried powder or material was calcined at 900 °C, to form the intended composition. The calcined material was wet ball milled with zirconium oxide media to achieve the prerequisite particle size distribution. Green membranes with 1-inch diameter size (after sintering) were pressed by compaction in a die and punch assembly and then sintered in air at temperatures between 1100 °C and 1200 °C to make dense membranes. The sintered membranes were surface ground to achieve thickness in the range of 0.90 mm and 1mm. X-ray diffraction analysis of LISICON compositions was performed to identify the crystal structure and phase purity before they were used in chemical and electrochemical testing.

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 NOV 2006		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE High Energy Lithium-air Batteries for Soldier Power				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U. S. Army Research Laboratory Adelphi, MD 20783-1197				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002075., The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

The second-generation membrane compositions based on the $\text{LiM}_2(\text{PO}_4)_3$ type structures with substitution of $+3$ or $+4$ elements at M site were synthesized by techniques similar to the techniques for the first generation membranes.

The conductivity of LiSICON compositions was measured in various cell configurations. A. C. (alternating current) impedance measurements were made with a Solartron SI 1260 Impedance Gain-Phase Analyzer and a Solartron SI 1287 Electrochemical Interface. By one method, non-woven polypropylene separator was soaked with organic electrolyte and placed between the LiSICON membrane and electrodes. Measurements were made this way with either lithium or blocking electrodes. The organic electrolyte used was either 1 M lithium hexafluorophosphate or lithium trifluoromethylsulfonate in propylene carbonate. Conductivity measurements were also made with aqueous electrolyte between blocking electrodes and membranes. A conductivity test fixture was constructed to seal the membranes and prevent leakage of liquid electrolyte around the membrane. For the conductivity experiments using organic electrolyte, the conductivity cell was prepared with organic electrolyte and sealed in an argon filled dry box. The impedance of the organic electrolyte was subtracted from the overall bulk impedance to get the membrane impedance

The Li-air cells had an active area of 3.88 cm^2 . The cell fixture is similar to the Li ion conductivity test fixture where one of the conductivity cell compartments was replaced with an air-cathode compartment. The cells were designed such that the membrane seal could be helium leak tested prior to transfer into an argon filled glove box where the anode compartment was assembled. After anode side assembly, the cells could be removed from the glove box for catholyte (aqueous electrolyte) filling and testing on the bench top.

The fabrication of air electrodes consisted of four primary steps:

- Catalyst synthesis
- Preparation of gas diffusion layer powder
- Preparation of reaction layer powder
- Cathode pressing

3. MEMBRANE CONDUCTIVITY

The conductivity of Li ion conducting LiSICON membranes reported in the literature (Dissanayake et al, 1993, Dissanayake et al., 1995, Sumathipala, et. al. 1995) of general formula $\text{Li}_{3+x}\text{AB}_{3-y}\text{C}_{1-y}\text{O}_{12-x}$ with substitution of $+3$, $+4$, and $+5$ valence elements at A, B, and C sites are in the range of 10^{-4} - 10^{-5} S/cm at ambient temperature. Our focus was to develop LISICON type

membranes iso-structural to the the Na^+ conducting NASICON type of membranes developed at Ceramtec, Inc. (Balagopal, et al., 1999) for commercial electrochemical applications with Li^+ conductivity in the range of 10^{-2} - 10^{-3} S/cm at ambient temperatures.

The conductivity of the second generation membranes, when measured by the same technique as the first generation membranes, showed remarkable improvement in conductivity. The conductivity, as measured by this technique, was found to be as high as 3.3×10^{-3} S/cm at room temperature.

Figure 1 shows the a. c. impedance plot of a second generation LISICON membrane. Although the membrane has excellent conductivity, there is a large interfacial impedance between the membrane and organic electrolyte. For these very conductive membranes this interface impedance can be higher than the impedance of the membrane.

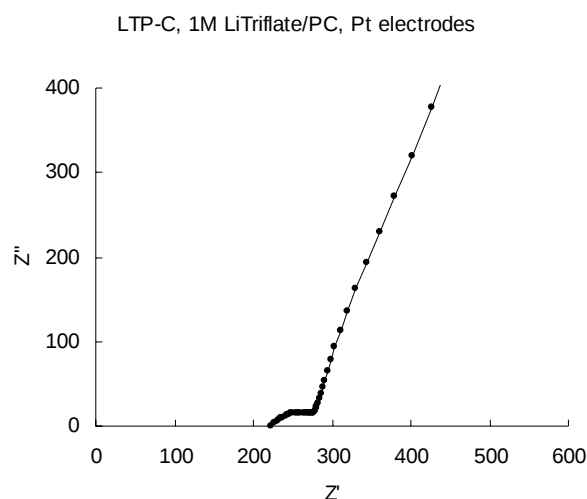


Fig 1. AC impedance of a second generation LISICON membrane in organic electrolyte.

4. LITHIUM-AIR CELLS

The lithium air cells with first generation LISICON membranes were discharged at 0.1 mA. The discharge curve for one of the cells was shown in Fig 2.

The open circuit potential was 2.98 V and it remained steady at 2.85 V during majority of the discharge cycle. Disassembly of the cell revealed that the anode face had turned white in color indicating leakage in the cell and formation of LiOH in the anode

compartment. LiPF_6 in propylene carbonate was used as the anolyte in this test.

Three additional cells were assembled and tested. In each case an attempt was made to improve the handling of lithium and sealing of the cell. It was clear from the nature of discharge curves that additional reactions were occurring in the cell to cause degradation in performance. Only a small potential drop was measured across the air cathode, eliminating the cathode as the major contributor to impedance in the Li/Air cell. Disassembly of the cell confirmed the presence of a layer of LiOH on the Li anode side facing the membrane. The majority of cells, which degraded in performance, showed leakage of the organic electrolyte from the cell during discharge.

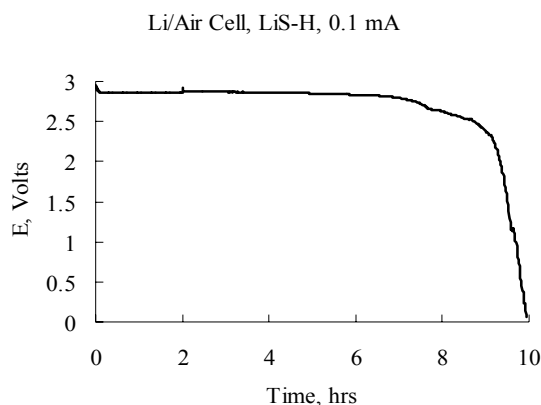


Fig 2. Discharge curve of a first generation membrane Li/Air cell

Alternative techniques to improve the sealing and assembly of cell were employed at this stage of the project for subsequent cells.

Fig. 3 shows the discharge curves for a Li/air cell assembled using more conductive second generation membranes and improved sealing techniques. In these tests, the cells were discharged at constant current of 0.5 mA. This rate is 5 times larger than what was accomplished with first generation membrane cells. The OCP of the cells was 3.1 volts. The discharge voltage ranged from 2.5 to 3 volts and this difference can be explained by the fact that the thickness of the membranes used in these tests was 2 to 3 mm. The cell with the longest discharge at 0.5 mA in Fig. 3..

A considerable effort was made to improve the procedures for assembly and the sealing methodology of

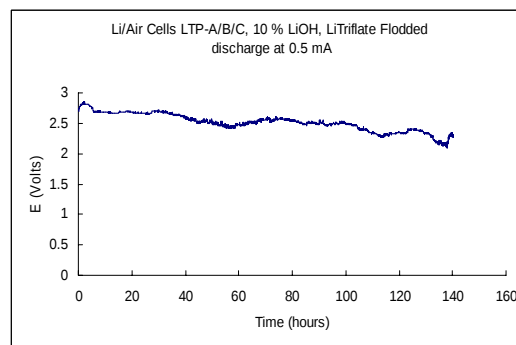


Fig 3. Discharge curve of a second generation membrane based Li/Air cell at 0.5 mA current

cells. Handling and storage of the organic electrolyte was improved, as was storage of the Li metal. A second gasket was used to improve sealing of the anode compartment and cell body components. The increased discharge rates and cell life times can be attributed to higher conductivity of the new second generation LISICON membrane compositions developed at Ceramtec.

To improve the cell performance, second generation membranes were fabricated with high surface area to decrease the interfacial impedance. Fig. 4 shows the AC impedance spectrum for the assembled cell with the high surface area membrane prior to testing. Comparison of Fig. 4 and Fig. 1 illustrates the qualitative improvement in lowering the impedance response by tailoring the surface properties of the membrane. Fig 5 also shows the discharge curve of the high surface area cell at 2 mA for greater than 24 hrs. This result indicates the project goals are attainable with further development and optimization of the performance of membrane and the battery cells.

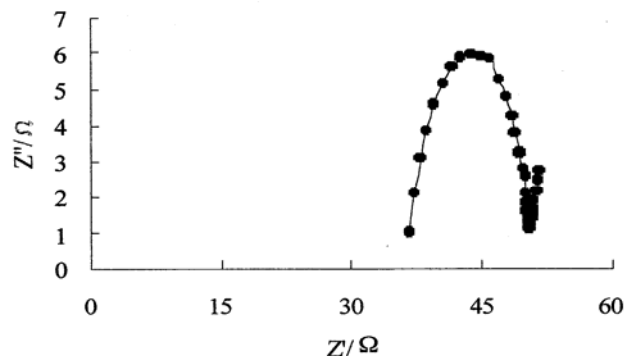


Fig. 4. A. C. impedance of high surface area, second generation LISICON membrane.

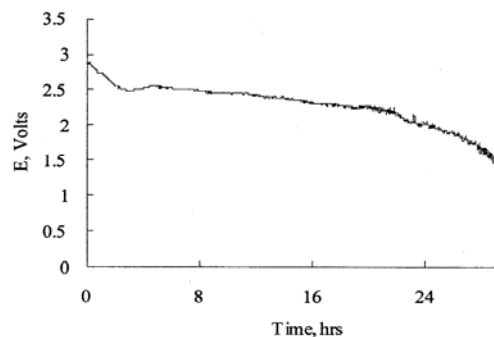


Fig. 5. 2 mA constant current discharge curve of Li/Air cell using the high surface area membrane.

5. CONCLUSION

The successful operation of Li-air batteries using second generation LISICON membranes with ionic conductivity in the 10^{-3} S/cm range has been demonstrated. The development of these membranes has resulted in over a ten fold improvement in the rate capability of the lithium-air cell. Our results agree with recent work (Sagane et al, 2005) which showed a large interfacial impedance for Li-cation transfer between the organic electrolyte in PC and the separator solid membrane electrolyte. Using a higher surface area membrane reduced the interfacial impedance which allowed the cell to be discharged at a higher rate.

Further improvements in performance are anticipated with the development of improved sealing and thinner membranes. When finally developed, lithium-air batteries could provide an ultra-high energy

primary battery that could power multiple devices in an integrated power source for soldier power.

REFERENCES

- Balogopal, S., Landro, T., Zecevic, S., Sutija, D., Elangovan, S and Khandkar, A, 1999: Selective Sodium Removal from Aqueous Waste Streams with NASICON Ceramics, *Separation and Purification Technology*, **15**, 231-237.
- Dissanayake, M. A. K. L., Gunawardane, R. P. Sumathipala, H. H., and West A. R. 1995: New Solid Electrolytes and Mixed Conductors: $\text{Li}_{3+x}\text{Cr}_{1-x}\text{M}_x\text{O}_4$: M= Ge, Ti, *Solid State Ionics* **76**, 215-220.
- Dissanayake, M. A. K. L., Gunawardane, R. P, West, A. R., Senadeera, G. K. R., Bandaranayake, P. W. S. K., and M. A. Caeem, 1993: Lithium Ion Conducting $\text{Li}_{4-2x}\text{Ge}_{1-x}\text{S}_x\text{O}_4$ Solid Electrolytes, *Solid State Ionics*, **62**, 217-223.
- Sange, F., Takeshi A., Yasutoshi I., Ogumi, Z., 2005: Li^+ and Na^+ Transfer Through Interfaces between Inorganic Solid Electrolytes and Polymer or Liquid Electrolytes, *J. Power Sources*, **146**, 749-752.
- Sumathipala, H. H., Dissanayake, M. A. K. L., West, A. R., 1995: Novel Li^+ Ion Conductors and Mixed Conductors, $\text{Li}_{3+x}\text{Si}_x\text{Cr}_{1-x}\text{O}_4$ and a Simple Method for Estimating Li^+/e^- Transport Numbers, *J. Electrochem. Soc.*, **142**, 2138-2143.
- Visco, S. J., Nimon, E., Katz, B., Chu, M., and De Jonghe, L. C., 2006: High Energy Density Lithium-Air Batteries with No Self Discharge, *Proceedings of the 42nd Power Sources Conference*, 201-203.