CONF-941063--13

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To be submitted for publication in *Proceedings of the 186th Meeting of the Electrochemical Society*, Miami Beach, Florida, October 9–14, 1994

# CATHODE LIMITED CHARGE TRANSPORT AND PERFORMANCE OF THIN-FILM RECHARGEABLE LITHIUM BATTERIES

J. B. Bates, F. X. Hart, D. Lubben, B. S. Kwak, and A. van Zomeren
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6030

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with the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee 37831-6030

November 1994

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J. B. Bates, F. X. Hart, D. Lubben, B. S. Kwak, and A. van Zomeren
Solid State Division, Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, Tennessee 37831-6030

## INTRODUCTION

Several types of thin-film rechargeable batteries based on lithium metal anodes and amorphous $V_2O_5$ ($aV_2O_5$), $LiMn_2O_4$, and $LiCoO_2$ cathodes have been investigated in this laboratory. In all cases, the current density of these cells is limited by lithium ion transport in the cathodes. In this paper, we discuss the sources of this impedance in Li-$aV_2O_5$ and Li-$LiMn_2O_4$ thin-film cells and their effect on cell performance.

## EXPERIMENTAL PROCEDURES

Thin-film batteries were fabricated using the methods described previously.[1,2] The cathodes had areas of about 1 cm$^2$ and were 0.13 µm to 4 µm thick. For the Li-$aV_2O_5$ cells, the amorphous $V_2O_5$ cathodes were deposited at ambient temperature over V current collectors on alumina substrates by dc magnetron sputtering of V in Ar + 14% $O_2$. For the Li-$LiMn_2O_4$ cells, the cathode films were deposited over Pt current collectors on alumina substrates by electron beam evaporation of $LiMn_2O_4$ in $10^{-5}$ Torr $O_2$ at ambient temperature. The source material was made by reacting $Li_2CO_3$ and $Mn_2O_3$ at 1000°C in air. The as-deposited amorphous $LiMn_2O_4$ films were annealed at 700°C to 800°C in $O_2$ in order to form the crystalline spinel phase. The thicknesses of the $aV_2O_5$ and crystalline $LiMn_2O_4$ films were measured with a profilometer, and their microstructure was examined in a scanning electron microscope. X-ray diffraction measurements also were made on the crystalline $LiMn_2O_4$ films. Following these experiments, the cathode films were covered with about 1 µm of the amorphous lithium phosphorus oxynitride electrolyte[1] deposited by rf magnetron sputtering of $Li_3PO_4$ in $N_2$, and the lithium anode films, about 3-µm thick, were deposited by evaporation of lithium metal at $10^{-6}$ Torr. In a few cases, the cells were sealed with a multilayer protective coating, but usually they were encapsulated in vacuum-tight weighing bottles.

Constant current cycle testing of the cells was performed using 1mA, 5 V channels of a Maccor Series 2000 battery test system. The impedance of the cells was measured with a Solartron 1250 frequency response analyzer and an HP 3577A Network Analyzer at frequencies between 10 mHz and 10 MHz using ac signals of 10 to 50 mV. A dc bias equal to the open circuit cell voltage (OCV) was applied during these measurements.

## RESULTS AND DISCUSSION

Examples of constant current discharge curves at 25°C for a Li-$aV_2O_5$ cell with an 0.13-µm-thick cathode and a Li-$LiMn_2O_4$ cell with a 0.3-µm-thick cathode are shown in Figs. 1 and 2, respectively. The Li-$aV_2O_5$ cell, fabricated in the fully charged state, was discharged to 1.5 V and cycled several times between 3.5 V and 1.5 V prior to measuring the discharge curves in Fig. 1. On the first discharge, about 3 Li/$V_2O_5$ is inserted into the cathode, but on the following charge and subsequent discharge-charge cycles, about 2.8 Li/$V_2O_5$ is inserted/removed from the cathode. For the Li-$LiMn_2O_4$ cell, the as-deposited OCV was about 3 V. The cell was first charged to 4.5 V and cycled several times prior to measuring the discharge curves of Fig. 2. For both cells, the voltage on the charge cycle was held fixed at the respective cutoff values until the current decreased to 1 μA.

Based on the iR loss for the second and third pair of curves near the midpoint of the discharge in Figs. 1 and 2, the resistance of the Li-a$V_2O_5$ cell with the 0.13-μm-thick cathode was about 7 KΩ whereas that of the Li-$LiMn_2O_4$ cell with the 0.3-μm-thick cathode was about 200 Ω. The corresponding resistivities based on the areas and thicknesses of the cathodes are $6 \times 10^8$ Ω-cm and $8 \times 10^6$ Ω-cm, respectively. These results show that the cell resistance is dominated by the cathode since the electrolyte, the lithium-electrolyte interface, and the lithium anode are the same in both cases. This conclusion is supported by the analyses of ac impedance data summarized below.

An example of an impedance spectrum of the Li-$LiMn_2O_4$ cell of Fig. 2 plotted in a Cole-Cole form is shown in Fig. 3. Similar results were obtained for the Li-a$V_2O_5$ cell. The solid line through the data points was obtained by a least squares fit of the parameters of the circuit model shown in Fig. 4. The constant phase angle elements $Z = A(j\omega)^{-n}$, where $\omega$ is the frequency in radians and A and n are parameters. The parallel RZ elements with subscripts $l$ and $w$ represent the low frequency capacitive and Warburg regimes, respectively, of the cathode. Both terms are evident in the measured impedance in Fig. 3 in which the transition from diffusive to blocking behavior occurs near Re(Z) = 400 Ω. The small contribution from the thin-film electrolyte is represented by the parallel $R_{el}Z_{el}$ element, where typically $R_{el}$ = 50 to 100 Ω. The $R_iZ_i$ element represents an interface impedance and is required in order to achieve a good fit to the data. The term $R_e$ represents a constant resistance which appears at high frequencies in all of the impedance data and is possibly due to the resistance between the semiconducting cathode and the metal current collector. Further discussion of the model and data analysis will be presented elsewhere.

The important parameters of the model that impact battery performance are those of the two cathode terms and the interface term. Examples for the two cells discussed above are given in Table 1. These parameters and Equations 1–3 below, taken from[3] Ho et. al.'s finite diffusion model, were used to calculate the change in OCV with respect to the lithium composition, dV/dx, the chemical diffusion coefficients, and the intrinsic diffusion coefficients for the two cathodes:

Table 1. Parameters obtained from the analysis of impedance spectra of the two cells discussed in the text

| | OCV (V) | $A_\ell$ | $n_\ell$ | $A_w$ | $n_w$ | $R_i(\Omega)$ | $R_e\Omega)$ |
|---|---|---|---|---|---|---|---|
| Li-a$V_2O_5$ | 3.33 | 1506 | 0.99 | 8790 | 0.5 | 3976 | 61 |
| Li-$LiMn_2O_4$ | 4.27 | 40 | 0.99 | 128 | 0.5 | 225 | 67 |

$$\frac{dV}{dx} = \frac{Fal}{V_m} A_l \quad (1)$$

$$D_c = \frac{l^2}{2}\left(\frac{A_\ell}{A_w}\right)^2 \quad (2)$$

$$D_i = \frac{RT}{F}\left(x\frac{dV}{dx}\right)^{-1} D_c \qquad (3)$$

where a and l are the area and thickness of the cathode film, respectively, F is Faraday's constant, and $V_m$ is the molar volume. The lithium composition, x, in $Li_xV_2O_5$ and $Li_xMn_2O_4$, used in Eq. (3), was estimated from the respective low current discharge curves, the measured cathode mass, and the measured charge.

Table 2. Lithium stoichiometry, x, dV/dx, and lithium ion diffusivities from the parameters in Table 1

| | x | dV/dx (volts) | $D_c$ ($cm^2/s$) | $D_i$ ($cm^2/s$) |
|---|---|---|---|---|
| Li-$Li_xV_2O_5$ | 0.25 | 37.7 | $2.5 \times 10^{-12}$ | $7.2 \times 10^{-15}$ |
| Li-$Li_xMn_2O_4$ | 0.65 | 2.0 | $1.2 \times 10^{-11}$ | $2.6 \times 10^{-13}$ |

The stoichiometry parameter x was obtained from the respective discharge curves, as described in the text. $D_c$ and $D_i$ are the chemical and intrinsic diffusion coefficients, respectively.

The calculated results from Eqs. 1-3 are given in Table 2. The large difference in the diffusivity of $Li^+$ ions between the two cathodes is responsible for most of the difference in the performance of the Li-a$V_2O_5$ and Li-$LiMn_2O_4$ thin-film cells (Figs. 1 and 2). The interface resistance $R_i$ (Table 1) is also important because, as the thickness of the a$V_2O_5$ or $LiMn_2O_4$ cathode film is reduced, this term becomes the dominant source of resistance in the cell. In all cases we have examined to date, the magnitude of $R_i$ is inversely related to the lithium ion mobility in the cathode, suggesting that $R_i$ is due to the resistance to lithium ion transport across the electrolyte-cathode interface. However, it is not possible at this time to exclude electron transfer at the cathode-current collector interface as the origin of this term.

## ACKNOWLEDGMENTS

Research was supported by the Office of Transportation Technologies, Division of Chemical Sciences, Office of Energy Research Technology Transfer Program, and the U.S. Department of Energy Division of Materials Sciences under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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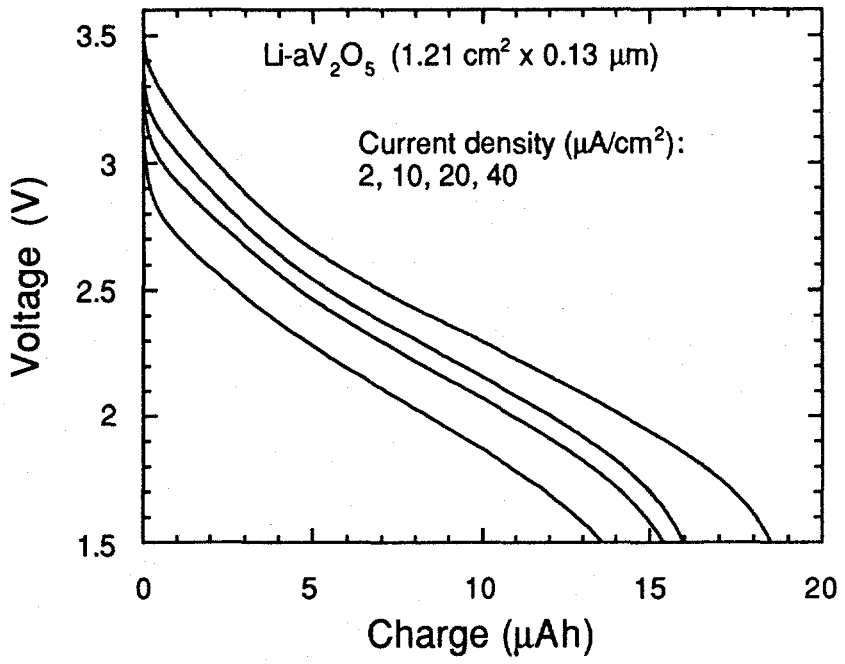

Figure. 1. Constant current discharge curves for a Li-a$V_2O_5$ cell at 25°C.

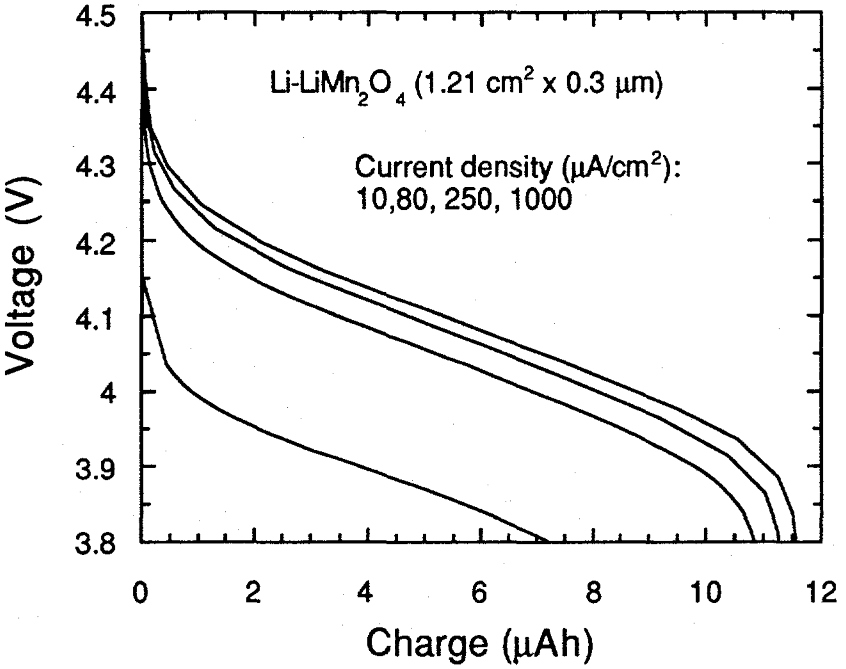

Figure 2. Constant current discharge curves for a Li-$LiMn_2O_4$ cell measured at 25°C. Cathode deposited by e-beam evaporation and annealed at 800°C in $O_2$.

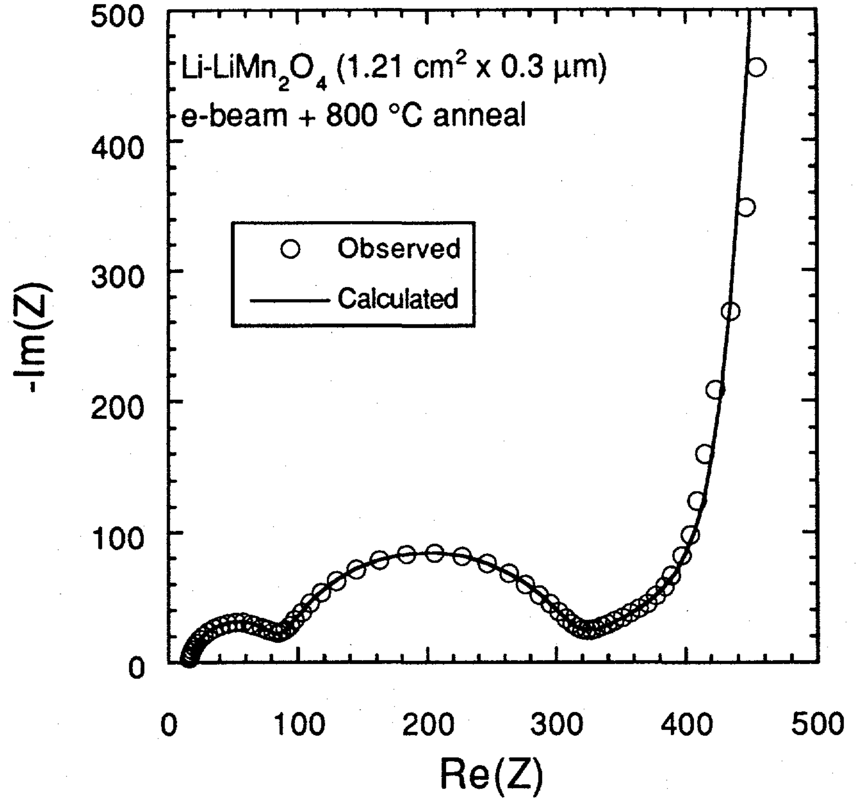

Figure 3. Cole-Cole graph of ac impedance at 25°C of a Li-LiMn$_2$O$_4$ cell measured at an OCV of 4.3 V.

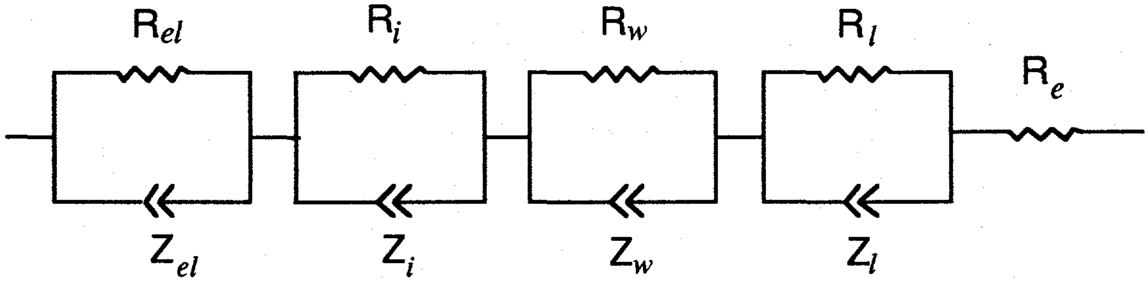

Figure 4. Equivalent circuit used in analyzing the impedance of thin film cells.