Electrochemical impedance spectroscopy studies of lithium diffusion in doped manganese oxide

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Abstract

The electrochemical properties of $LiMn_2O_4$ and $LiAl_xMn_{2-x}O_4$ (where $x = 0.125, 0.25, 0.375$) were studied for variations in lithium-ion diffusion. The largest diffusion coefficient was shown for the undoped material, $D_{Li+} = 2.7 \times 10^{-11}$ cm^2/s. As the level of dopant was increased a concurrent decrease in diffusion coefficient is shown. This effect was attributed to a decrease in the lattice parameter caused by dopant addition. © 1997 Published by Elsevier Science S.A.

1. Introduction

Cathode performance is critical to overall lithium-ion rechargeable battery performance and impacts some of the most important challenges in the development of commercial lithium-ion rechargeable batteries, namely energy density, cycle life, and rate capability. We are investigating the influence of doping lithium manganese oxide cathode materials on the fundamental properties that control cathode performance.

The goal of our studies was to develop an improved understanding of the chemical and physical properties that determine the performance of manganese oxide cathodes as well as to produce improved materials and preparation techniques for cathodes. We have developed an atomistic model of structures of various manganese oxide and lithium manganese oxide compounds [1]. Results from rigid ion and shell models allow a systematic analysis of changes in lattice parameter, lattice energy, cell volume, strain, and the relative stability of doped structures using ions such as aluminum, cobalt, nickel, and titanium.

To complement our modeling effort, we have developed a non-aqueous co-precipitation process to prepare controlled stoichiometry lithium manganese oxalate precipitates which form high purity $Li_xMn_yO_z$ powders when calcined [2]. The process involves mixing an $LiNO_3$ and $Mn(NO_3)_2$ methanolic solution with dehydrated tetramethylammonium oxalate

to form an off-white precipitate. A variety of transition-metal dopants have been incorporated by this process. The resulting precipitated oxalates were readily converted to a number of phase-pure lithium manganese oxides at moderate temperatures (≤ 600 °C) with the phase formed being dependent on the initial Li/Mn ratio in the starting solution. Our results are in general agreement with recent publications by Bito et al. [3] and Tarascon et al. [4].

This communication continues the electrochemical characterization and demonstrates that lithium diffusion rates in manganese oxide can be controlled by the quantity of dopant. This result is attributed to the dopant affecting the lattice parameter of the lithium manganese oxide unit cell. Lithium diffusion in bulk $LiMn_2O_4$ is thought to occur through the one-dimensional channels in the spinel structure. We took a representative dopant, aluminum, which decreases the lattice parameter with increasing levels of dopant, and studied the effect on electrode diffusion characteristics.

2. Experimental

The doped lithium manganese dioxide materials were prepared at Sandia National Laboratories per the reported synthetic method [2]. Cathodes were manufactured using 82 wt.% $LiAl_xMn_{2-x}O_4$, 10 wt.% Shawinigan acetylene black (SAB) and 8 wt.% Teflon. The electrolyte was a 50:50 (v/v) ethylene carbonate/dimethyl carbonate (EC/DMC), 1 M $LiPF_6$ solution. Electrochemical measurements employed a standard three-electrode configuration with lithium
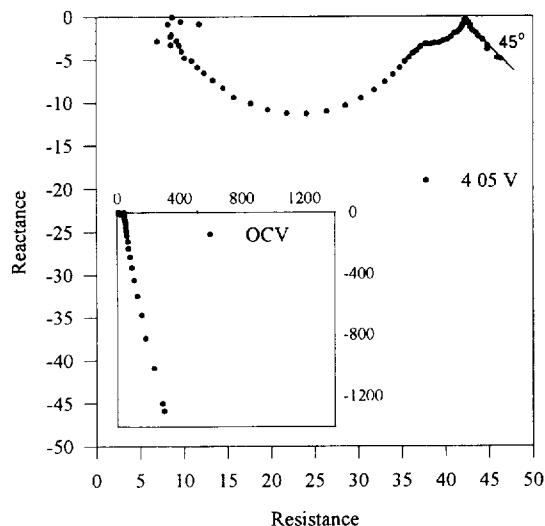
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Fig. 1. Impedance response of $Li_xAl_{0.125}Mn_{1.875}O_4$ at open-circuit voltage and 4.05 V vs. Li/Li$^+$.

counter and reference electrodes. The electrochemical cycling employed an Arbin Battery Test System (ABTS) operating at 0.5 mA/cm^2. Electrochemical impedance spectroscopy (EIS) measurements were taken at open-circuit potential (OCV) and 4.05 V versus the Li/Li$^+$ couple using a Solartron EIS configuration. The frequency was swept from 65 kHz to 0.01 Hz with an amplitude modulation of 10 mV p–p.

3. Results

The representative EIS response for an aluminum-doped manganese oxide, $LiAl_{0.125}Mn_{1.875}O_4$, is shown in Fig. 1. Measurements were made at OCV and 4.05 V versus Li/Li$^+$. The inset figure shows the OCV impedance response. This response is typical of a porous electrode [5]. This was modeled by a resistor in series with a capacitor, simulating the solution resistance in series with the porous electrode response, i.e. double-layer capacitance. The electrode was then galvanostatically charged to 4.05 V. The impedance response at this potential was controlled by a charge-transfer (high-frequency) region and a diffusion-controlled (low-frequency) region. The high-frequency response was attributed to charge transfer at the electrode-current collector

interface. The low-frequency region was attributed to a lithium-ion diffusion limited reaction. This low-frequency region was modeled by a series resistor and Warburg element in parallel with a double-layer capacitor.

The determination of diffusion characteristics is dependent on the solution of the Warburg impedance response [5–7]

$$Z_W = A_W\omega^{-0.5} - jA_W\omega^{-0.5} \tag{1}$$

where

$$A_W = \frac{V_M(dE/dx)}{Fa(2D_{Li})^{1/2}} \tag{2}$$

and ω is the frequency dependence, in radians, F is the Faraday constant, V_M is the molar volume of the electrode, a is the electrochemical surface area, dE/dx is the slope of the coulometric titration curve, and D_{Li} is the chemical diffusion coefficient. The least assessable variable is the electrochemical surface area a [6,7]. The surface area was determined by relating the porous electrode double-layer capacitance, Fig. 1 (inset), to the measured capacitance of a known sample [8]. The resultant surface area is shown as a_{DL}. The variable, A_W, can be determined by measuring the slope of the plot of either resistance ($A_W^{-0.5}$) or reactance ($-A_W^{-0.5}$) versus $\omega^{-0.5}$.

Table 1 shows the variation in V_M, dE/dx, a_{DL} and A_W as the level of aluminum dopant was increased from level 0 ($LiMn_2O_4$) to level 3 ($LiAl_{0.375}Mn_{1.625}O_4$). The dopant levels were $LiAl_xMn_{2-x}O_4$ where x is 0, 0.125, 0.25, and 0.375 corresponding to 0, 1, 2, and 3 dopant atoms per unit cell.

The variation in measured chemical diffusion coefficient, D_{Li+}, is shown in Fig. 2. As the dopant level was increased, a concurrent decrease in diffusion rate occurred. The measured diffusion coefficient for the undoped oxide was 2.7×10^{-11} cm^2/s. Dickens and Reynold [9] reported a similar value 4×10^{-11} cm^2/s, though Guyomard and Tarascon [10] have reported a higher value of around 10^{-9} cm^2/s for their material. Within our family of materials, as the aluminum dopant was increased, Fig. 2, a decrease in the measured diffusion coefficient was noted. At the highest level of aluminum dopant, $LiAl_{0.375}Mn_{1.625}O_4$, the measured lithium diffusion coefficient was 4.4×10^{-12} cm^2/s.

Table 1

Variations of V_M (molar volume), dE/dx (slope of the voltage vs. concentration curve), a_{DL} (electrochemical surface area) and A_w (slope of the reactance vs. $\omega^{-1/2}$ curve) with aluminum dopant level. All values were measured or calculated at 4.05 V vs. Li/Li$^+$

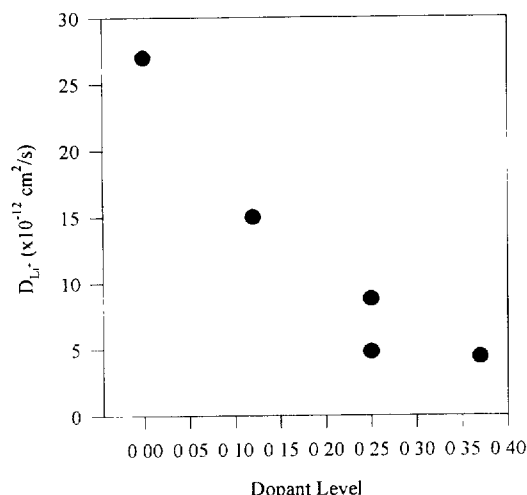|	V_M (cm^3/mol)	dE/dx (CΩ/s)	a_{DL} (cm^2/g, cm^2)	A_w (Ω/s$^{1/2}$)
$LiMn_2O_4$	140	0.49	9418, 78.0	1.23
$LiAl_{0.125}Mn_{1.875}O_4$	142	0.50	14147, 127.4	1.05
$LiAl_{0.25}Mn_{1.75}O_4$	166	0.62	12334, 82.4	3.09
	171	0.60	12573, 83.2	4.12
$LiAl_{0.375}Mn_{1.625}O_4$	161	1.06	11195, 61.7	9.67

Fig. 2. Variation in lithium-ion diffusion coefficient on increasing levels of aluminum dopant. Determination of lithium diffusion coefficient at 4.05 V vs. Li/Li$^+$.

4. Discussion

Bito et al. [3] and Tarascon et al. [4] have previously shown that as spinel lithium manganese oxide is doped, the cubic lattice parameter and unit cell volume changes. This change was dependent on the dopant atom. Tarascon et al. [4] showed an increase in lattice parameter with each dopant of titanium, germanium, nickel, zinc and iron. Whereas, Bito et al. [3] showed a lattice parameter increase with titanium, but a lattice parameter decrease with nickel, and a similar decrease with cobalt and aluminum. A computer modeling study of the doped lithium manganese oxide system by Cygan et al. [1] has supported the Bito observation. Cygan and Tarascon also showed that as the amount of dopant is increased, additional change in the lattice parameter occurs. In the case of aluminum dopant, as the amount of aluminum is increased the lattice parameter decreases. This decrease could be viewed as a contraction of the spinel crystal structure. If one assumes lithium transport is through this structure, this contraction would be a limitation on diffusion. In this work we have shown that as the level of aluminum dopant was increased, a resultant decrease in diffusion coefficient occurred. This would support the hypothesis that crystal cell contraction, due to doping, is affecting lithium mobility.

Further studies with other dopant systems are planned. An especially important case would be the addition of a dopant which would increase the lattice parameter.

5. Conclusions

We have shown that the chemical diffusion coefficient is altered on doping lithium manganese oxide with various levels of aluminum dopant. The highest diffusion rate was measured for the undoped oxide, $D_{Li^+} = 2.7 \times 10^{-11}$ cm^2/s. Subsequent increases in dopant level decreased the diffusion rate. This effect was attributed to a decrease in the lattice parameter of the oxide's crystal structure.

Acknowledgements

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