



Kinetics and thermodynamics of the lithium insertion reaction in spinel phase $\text{Li}_x\text{Mn}_2\text{O}_4$

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Abstract

Electrochemical measurements in the voltage range from 3.0 to 4.0 V versus Li/Li^+ have demonstrated the excellent reversibility of the lithium insertion reactions in the spinel phase $\text{Li}_x\text{Mn}_2\text{O}_4$. Electrochemical voltage spectroscopy studies indicate the formation of ordering of the inserted lithium ions over the available sites, the ordered phases corresponding to approximate compositions $x=0.5$ and $x=1.0$. Cell cycling experiments at various rates show that greater than 1 Li per Mn_2O_4 can be cycled. This performance corresponds to a material utilization of better than 150 mAh/g. Coupled to the low cell impedance and the relatively facile reaction kinetics, the spinel material is considered a viable material for incorporation into lithium-ion-type battery technology.

Keywords: Lithium intercalation; Manganese oxide; Spinel

1. Introduction

Several high voltage compound materials have been investigated recently with a view to their incorporation as cathode active materials in the so-called 'rocking-chair' or 'lithium ion' technology [1]. Candidate materials include Li_xCoO_2 [2], $\text{Li}_x\text{Mn}_2\text{O}_4$ [3], Li_xNiO_2 [4] and $\text{Li}_x\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_2$ [5]. For practical application $\text{Li}_x\text{Mn}_2\text{O}_4$ has some distinct advantages, such as low cost and low toxicity.

The possibility of lithium extraction/insertion from the spinel compound $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x < 1$) has been reported since the early 1980s [6]. To date, commercial exploitation of the $\text{Li}_x\text{Mn}_2\text{O}_4$ as a cathode material in secondary lithium batteries has been limited due the lack of a suitable electrolyte system with an upper voltage stability limit in excess of 4 V versus Li/Li^+ . $\text{Li}-\text{Li}_x\text{Mn}_2\text{O}_4$ electrochemical cells employing a lithium metal anode in a suitable non-aqueous electrolyte should allow the effective electrochemical characterization of the spinel phase.

This paper concerns the thermodynamic, interfacial and kinetic properties of the lithium insertion reaction in crystalline $\text{Li}_x\text{Mn}_2\text{O}_4$. The thermodynamic and kinetic properties have been studied using electrochemical voltage spectroscopy (EVS), constant-current cycling

and electrochemical pulse techniques. The interfacial properties of the system have been investigated by a.c. impedance methods.

2. Experimental

The $\text{Li}_x\text{Mn}_2\text{O}_4$ was supplied from a commercial source. It was used as received. The phase purity of the compound was confirmed by powder X-ray diffraction (XRD) using a Siemens D5000 powder diffractometer. All XRD lines were identified as belonging to the $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel phase.

Typical electrode compositions and preparations have been previously described [7]. The cell construction consisted of an $\text{Li}_x\text{Mn}_2\text{O}_4$ containing cathode and metallic lithium anode separated by a polymeric electrolyte. The entire assembly was placed in a flexible encapsulation which was heat-sealed under vacuum. Some of the cycling data were obtained from a smaller cell design which used an essentially identical electrochemical arrangement.

For long-term cycling experiments the cells were cycled between preset voltage limits using constant discharge and charge currents as depicted in the relevant figures. EVS is a voltage-step technique [8], which

provides a high resolution approximation to the open-circuit voltage (OCV) curve for the insertion system. The technique also provides a measurement of the differential capacity, which has been demonstrated to allow effective characterization of order/disorder and structural ordering phenomena in insertion systems. Kinetic properties such as the solid-state lithium-ion diffusion may be estimated by analyzing the decay of the cell current following each voltage step. This, then is proportional to $t^{-1/2}$ for linear diffusion in a semi-infinite system [9]. This treatment is essentially a solution of the current–time response from the well-known Cottrell equation [10]. Separate experiments were performed to verify the diffusional data using the so-called galvanostatic intermittent titration technique (GITT) [11]. In this method a small constant-current pulse is applied across a cell, while the transient voltage is measured as a function of time. The change of the steady-state voltage following the pulse then determines the dependence of the cell voltage on the concentration of the electroactive species.

The electrode interfacial properties were followed by a.c. impedance measurements on two electrode cells using a Solartron 1286 electrochemical interface coupled to a Solartron 1255 frequency response analyzer. The a.c. perturbation was ± 10 mV and the frequency range was typically from 65 kHz to 0.1 Hz.

3. Results and discussion

Fig. 1 shows a voltage profile for a typical discharge/charge cycle of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ system. The cell was cycled between voltage limits of 3.0 and 4.3 V versus Li/Li^+ at 23 °C under normal EVS conditions. Subsequent cycles give essentially identical response to that shown in the Figure. The system is demonstrated to be highly reversible and allow around 1 Li per Mn_2O_4

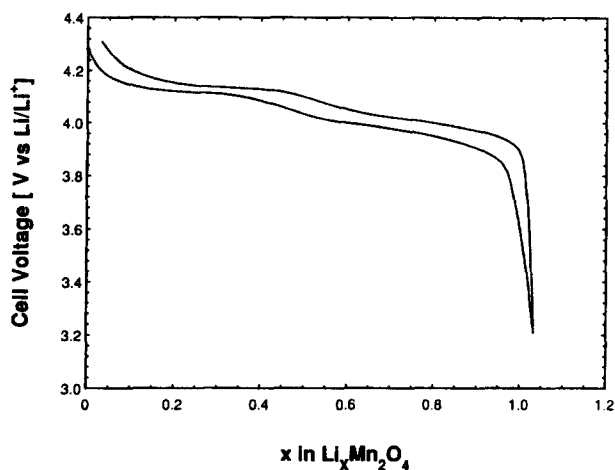


Fig. 1. Electrochemical voltage spectroscopy profile of the $\text{Li}/\text{LiMn}_2\text{O}_4$ system.

unit cell to be cycled. This Figure corresponds to an active material utilization of around 150 mAh/g. This is an extremely encouraging result for this material. The small amount of hysteresis between the discharge/charge curves is indicative of the low overvoltage associated with the insertion reactions within this voltage range.

The differential capacity plot in Fig. 2 shows two sharp peaks, with only small overlap between the anodic (above the x-axis) and the cathodic waves. This behaviour is indicative of ordering of the inserted lithium ions over the tetrahedral ($8a$) sites that are occupied during the 4 V plateau. The ordering is driven by guest–host interactions, and at low concentrations these interactions are strong enough to separate the inserted ions in two co-existing phases with different lithium occupancies. The ordered lattice has a composition approximating to $x=0.5$ in $\text{Li}_x\text{Mn}_2\text{O}_4$. The transition from $x=0.5$ to $x=1.0$ occurs with only small changes of electrode voltage. The assumption of an ordered superstructure around $x=0.5$ is in accordance with the discontinuity observed for the cubic lattice constants during the lithium extraction from LiMn_2O_4 [12]. Cells cycled to cell voltages in excess of 4.3 V versus Li/Li^+ show no additional reversible charge retention. At voltages approaching 5 V significant electrolyte degradation is observed.

Complementary chemical diffusion coefficient measurements determined by the two electrochemical pulse methods described in Section 2, indicate the relatively fast reaction kinetics for the lithium insertion process. Effective diffusion coefficients for the electrodes composites were calculated from these measurements based on the geometric surface areas of the electrodes. These values will be dependent on the intrinsic diffusion coefficients for the electrode materials in question. It should be noted, however, that other electrode parameters will also affect the magnitudes. As these factors

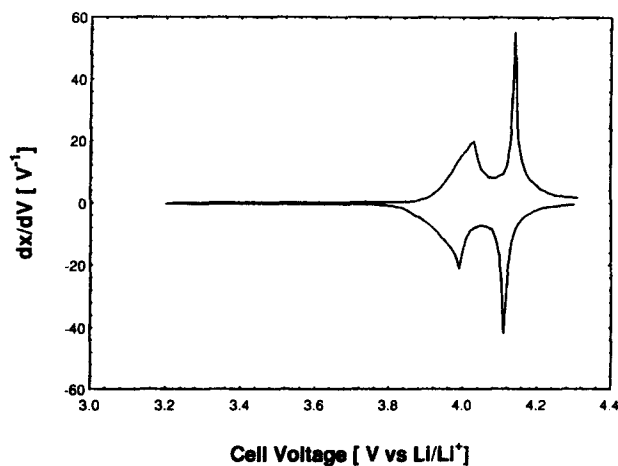


Fig. 2. Differential capacity of the $\text{Li}/\text{LiMn}_2\text{O}_4$ system. The trace is derived from the voltage curve shown in Fig. 1.

do not depend on the state-of-charge of the electrode, the variation in the measured effective diffusion coefficients are expected to directly reflect the compositional variation of the intrinsic diffusion coefficient for lithium in the electrode material.

Fig. 3 shows the variation of the chemical diffusion coefficient with x in $\text{Li}_x\text{Mn}_2\text{O}_4$ for cell discharge derived from the EVS measurements. The corresponding data for cell charge is shown in Fig. 4. The mean diffusion coefficient for the system is between 10^{-9} and 10^{-8} $\text{cm}^2 \text{ s}^{-1}$. Two distinct minima are discernible in each plot corresponding directly to the filling/removing of lithium from the two lattice sites in the $\text{Li}_x\text{Mn}_2\text{O}_4$. The observation of the minima is predicted due to the increasing lithium-lithium coulombic repulsion effects which will be present as each lattice site is filled. The magnitude of the diffusion coefficients and their variation with composition was also measured by the GITT method. Prior to each measurement the cells were held potentiostatically for 5 h to ensure uniformity of the

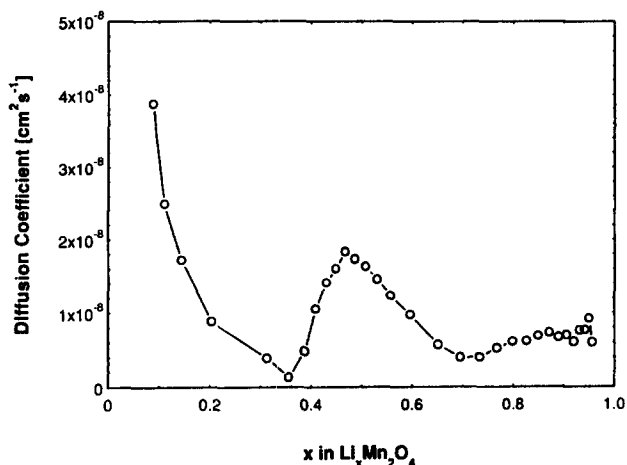


Fig. 3. Diffusion coefficient as function of x in $\text{Li}_x\text{Mn}_2\text{O}_4$ during discharge under conditions of electrochemical voltage spectroscopy.

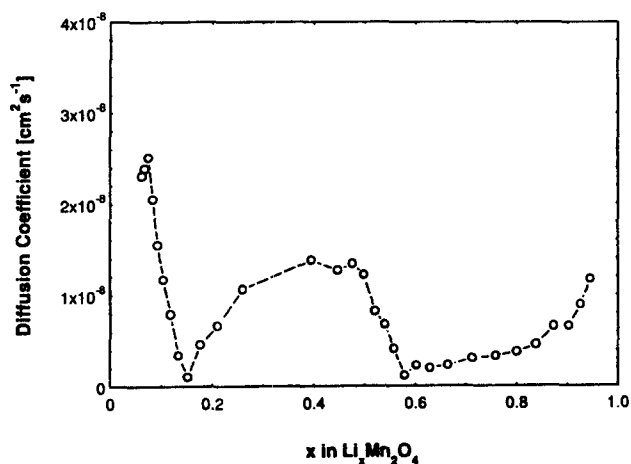


Fig. 4. Diffusion coefficient as function of x in $\text{Li}_x\text{Mn}_2\text{O}_4$ during charge under conditions of electrochemical voltage spectroscopy.

lithium ion concentration in the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode. The comparison of the two pulse techniques is summarized in Table 1. In summary, the GITT measurements accurately confirm the diffusional data derived from the EVS technique.

The a.c. impedance data for an uncycled and a charged cell are summarized in Fig. 5. The initial relatively high cell impedance is predominantly caused by the presence of the oxide layer on the pristine lithium foil electrode. In the charged state the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ system generates a low cell impedance consistent with the low overvoltage found during cell cycling.

The cell cycling data at different discharge/charge rates are shown in Fig. 6. As a consequence of the good thermodynamics, low impedance and reasonable reaction kinetics the system demonstrates very high active material utilization. Indeed, initially around 1 Li per LiMn_2O_4 is cycled regardless of the rate. This confirms the findings from the EVS experiments. The decaying capacity is ascribed to degradation of the

Table 1

Comparative diffusion coefficient measurements at 23 °C derived from electrochemical voltage spectroscopy (EVS) and galvanostatic intermittent titration technique (GITT) techniques: upper data for cell discharge, lower for cell charge

	D (GITT) ($\text{cm}^2 \text{ s}^{-1}$)	D (EVS) ($\text{cm}^2 \text{ s}^{-1}$)
a) x in $\text{Li}_x\text{Mn}_2\text{O}_4$ (cell discharge)		
0.2	1.1×10^{-8}	8.9×10^{-9}
0.4	1.1×10^{-8}	9.0×10^{-9}
0.6	1.3×10^{-8}	9.8×10^{-9}
0.8	8.4×10^{-9}	6.1×10^{-9}
b) x in $\text{Li}_x\text{Mn}_2\text{O}_4$ (cell charge)		
0.2	5.2×10^{-9}	6.7×10^{-9}
0.4	3.0×10^{-9}	1.4×10^{-9}
0.6	2.1×10^{-9}	2.3×10^{-9}
0.8	5.1×10^{-9}	3.8×10^{-9}

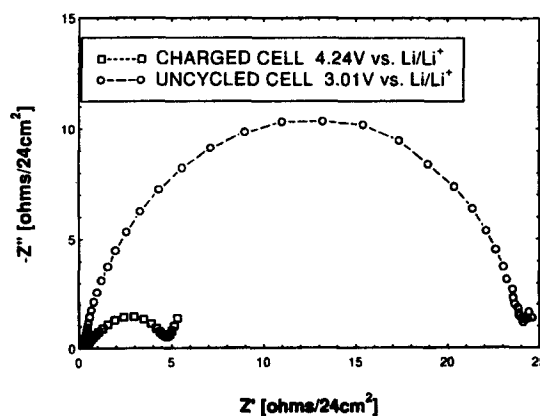


Fig. 5. A.c. impedance of the $\text{Li}/\text{LiMn}_2\text{O}_4$ system.

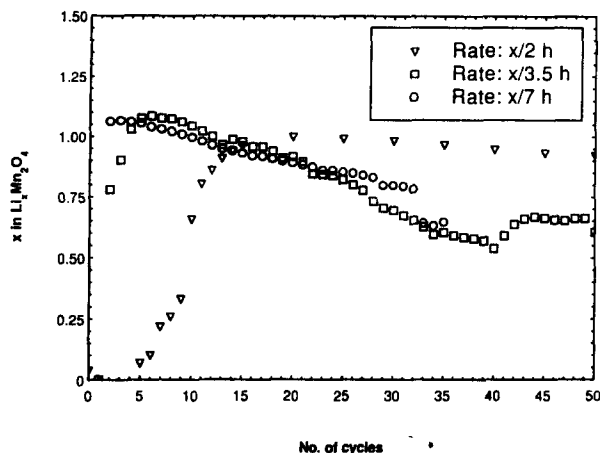


Fig. 6. Cycling capacities of Li/LiMn₂O₄ cells cycled at different rates as indicated in the Figure.

lithium foil counter electrode since the electrolyte used for these experiments was optimized for non-lithium electrodes and for high voltage application.

4. Conclusions

The results presented here demonstrate the excellent reversibility of the Li-Li_xMn₂O₄ insertion system. The EVS data indicate the formation of ordering of the lithium ions over the available lattice sites in Li_xMn₂O₄ system, the ordered phase having approximate compositions $x=0.5$ and $x=1.0$. The hysteresis between charge/discharge curves also shows the low overvoltage associated with the insertion reactions. This low overvoltage is confirmed by a.c. impedance studies on a charged cell. Complementary kinetic data collected using two different electrochemical pulse methods, also

demonstrate the relatively fast solid-state diffusion of lithium ions within the Li_xMn₂O₄ electrodes (effective diffusion coefficients between 10^{-9} and 10^{-8} cm² s⁻¹).

The cell cycling data conducted at various rates, confirm the EVS findings and show that in the initial stages greater than 1 Li per Mn₂O₄ could be cycled. This corresponds to a material utilization of greater than 150 mAh/g. The gradual decrease in the discharge capacity is related to changes occurring at the lithium electrode rather than at the insertion electrode.

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