

Self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ batteries in relation to corrosion of aluminum cathode substrates

Shengshui Zhang^{*}, Michael S. Ding, T. Richard Jow

Army Research Laboratory, AMSRL-SE-DC, 2800 Power Mill Road, Adelphi, MD 20783, USA

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Abstract

We studied the self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells in relation to the corrosion of aluminum cathode substrates. We determined the self-discharge of the cells from the decline of their open-circuit voltage, observed aluminum corrosion with use of voltammetry on electrochemical corrosion cells with an aluminum working electrode, and detected the existence and change of passivation films on the aluminum substrates with ac impedance measurement. The results showed that for the two salts LiPF_6 and LiClO_4 that formed the electrolytes with a binary solvent of ethylene carbonate–dimethoxyethane, the presence of LiPF_6 reduced the self-discharge of the battery cells, retarded the corrosion of aluminum, and assisted the formation of a passivation film on aluminum. On the other hand, pre-treating aluminum to 480°C seemed to have similar but weaker effects. We therefore concluded that corrosion of aluminum played a significant role in the self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ batteries with an aluminum cathode substrate, but the corrosion could be greatly reduced by the formation of protection films on the aluminum. Such films could be formed by either having LiPF_6 salt in the electrolyte in contact with the aluminum or by pre-treating the aluminum to a high temperature. However, films formed in the former fashion seemed much more stable when the aluminum was carrying an $\text{Li}_x\text{Mn}_2\text{O}_4$ material. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The purpose of this work was to investigate the self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ batteries in relation to the corrosion of aluminum substrates of the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathodes. Such a substrate provides mechanical strength to the overlaying cathode film and acts as the current collector for the cathode. The active cathode material we employed in our experiment, the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$, is an oxide compound with a 3D framework structure capable of reversible intercalation of lithium [1]. Due to its non-toxicity, low cost, and high stability, it has been among the most extensively studied and widely used cathode materials for lithium and lithium ion batteries [1,2]. It is also considered one of the safest to use in lithium batteries, as compared to the other common cathode materials with layered structures, such as Li_xNiO_2 and Li_xCoO_2 [3]. Papers covering this material range from materials synthesis and preparation [4,5] to structural stabilization through doping [5–7]. However, shortcomings still exist in this material as a cathode, which include fast

capacity fading, low specific capacity, and high self-discharge. The capacity fading has been variously ascribed to the irreversible Jahn–Teller distortion upon deep discharge [8], dissolution of manganese ions into the electrolyte [9–11], and oxidative decomposition of the electrolyte solvents [10,11]. The self-discharge of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells has also been intensively studied, but the results are not yet conclusive. In this work, we focused our attention on the corrosion of aluminum and its effects on the self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ batteries that employed aluminum material for their cathode substrates.

Aluminum has long been established as the most suitable material for $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode substrates, as its naturally occurring oxide surface layer helps it resist corrosion at the high potentials at which the cathode materials operate. However, despite this protection layer, corrosion of aluminum substrates still occurs in the batteries with such a cathode [12,13]. We therefore set out to find out how this corrosion was correlated with the self-discharge and ac impedance of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells at different conditions. The difference in cell condition was effected by using different salts in the electrolytes and by pre-treating to a high temperature some of the aluminum materials. For salts, we

^{*} Corresponding author. Tel.: +1-301-394-0046; fax: +1-301-394-0273.
E-mail address: szhang@mail.com (S. Zhang).

chose LiClO_4 and LiPF_6 , two of the most commonly used in lithium and lithium ion batteries, which we dissolved in a binary solvent of ethylene carbonate (EC)–dimethoxyethane (DME) in 1:1 weight ratio to a concentration of 1 mol of salt per kg of solvent ($1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$). For the heat-treatment, aluminum substrates and aluminum electrodes were kept at 480°C for 24 h before use. The purpose was to find out whether the different salts would alter the corrosion rate of aluminum by forming different passivation films on the aluminum, and whether the pre-treatment would reduce the corrosion by strengthening the naturally occurring oxide films on the aluminum.

2. Experimental

All starting materials were from commercial sources, except spinel $\text{Li}_x\text{Mn}_2\text{O}_4$, which was prepared in our laboratory. LiClO_4 and LiPF_6 of purities 99.99 and 99.9% were from Aldrich and Stella Chemifa Co., respectively. EC of purity 99.95% was from Grant Chemical. DME of purity 99% was from TCI America, which was further purified by distilling over lithium metal chips. Aluminum foil for the substrates and aluminum wire for the electrodes were both of purity 99.999% from Aldrich. The spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ was prepared by firing a mixture of Mn_2O_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ in 1.00:1.05 mole ratio at 650°C for 24 h; the stoichiometric formula of the resulting spinel should thus be $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$.

Cathodes with the spinel as the active material were made by pressing a mixture of 90% of the spinel, 9% of an acetylene black, and 1% of Teflon onto an aluminum foil. Electrolytes were made by dissolving either LiClO_4 or LiPF_6 salt in a binary solvent of EC–DME in 1:1 weight ratio to a concentration of $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$. Battery cells of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ were of dip-type, consisting of an $8 \text{ mm} \times 8 \text{ mm}$ cathode film of 2.0 mg loading of active material and a square of lithium foil of a similar size as the anode. Electrochemical corrosion cells were made with an aluminum wire, a strip of lithium metal foil, and a piece of lithium metal foil as the working, reference, and counter electrodes, respectively. Impedance of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells was measured with a three-electrode configuration, with a lithium reference electrode introduced into the electrolyte to isolate the impedance of the cathode from that of the anode.

We used a potentiostat/galvanostat (EG&G 283, Princeton Applied Research) to charge up a battery cell to a specific voltage and then record the decline of its open-circuit voltage (OCV). We used the same instrument to perform linear scan voltammetry on the corrosion cells with a scan rate of 5 mV/s. Impedance of the battery cells was measured with a Solartron impedance system consisting of an SI 1287 Electrochemical Interface, an SI 1260 Impedance/Gain-Phase Analyzer, and a Pentium PC running a Zplot software by Scribner and Associates, Inc. The impedance measurement covered a frequency range from 0.1 Hz to 100 kHz with a perturbation level of 10 mV and with the

dc bias voltage matching the OCV of the battery cell whose impedance was to be measured.

3. Results

3.1. OCV decline of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells

To study the self-discharge of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells, we monitored the decline of OCV of a number of freshly prepared cells after charging them to certain voltages at a rate of $0.5 \text{ mA}/\text{cm}^2$. The results are shown in Fig. 1, where curves of OCV decline of four different $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells are plotted. Curve 1 is the OCV decline of a cell with LiClO_4 as the electrolyte salt and with untreated aluminum foil as the cathode substrate. Starting from 4.4 V, to which the fresh cell had been charged up, the OCV declined through two plateaus to stabilize at about 2.8 V in about 25 h. The two-plateau shape in this self-discharge curve is typical of the discharge of battery cells with $\text{Li}_x\text{Mn}_2\text{O}_4$ as the cathode material, with its mechanisms extensively studied and elucidated [14]. Curve 4 is the OCV decline of a cell of the same type, except that the fresh cell was charged to 4.2 instead of 4.4 V before the start of the OCV monitoring. We can see that the lower starting voltage slowed down the OCV decline of the cell, with the final drop to 2.8 V occurring at about 60 h. Curve 2 represents the OCV decline of a cell with the same conditions as for curve 1 but with LiPF_6 as its electrolyte salt instead of LiClO_4 . Compared to the first two curves, the decline of OCV in this case is almost negligible, pointing to a very low rate of self-discharge. Finally, curve 3 of Fig. 1 traces the OCV decline of a cell of the same type as for curve 1, except that its aluminum substrate had been pre-treated to 480°C for 24 h. It can be seen that as with the replacement of LiClO_4 with LiPF_6 for the electrolyte salt, replacing an untreated aluminum substrate with a pre-treated one can also slow down the decline of OCV of the cell, but only to a more limited extent. Additionally, we point out that after the cells were discharged, we took the cells apart, and were able to visually observe clear signs of corrosion on the surface of the aluminum substrates.

3.2. Corrosion of aluminum as observed with electrochemical cells

To establish in a more quantitative fashion the correlation between the self-discharge of the battery cells and the corrosion of their aluminum substrates, we applied linear scan voltammetry to electrochemical corrosion cells with conditions corresponding to those of the self-discharge experiments. During a voltammetric linear scan, the aluminum working electrode was set to progressively more positive potentials, and the anodic current due to aluminum dissolution increased rapidly around a particular potential. This is the characteristic potential for the corrosion of the

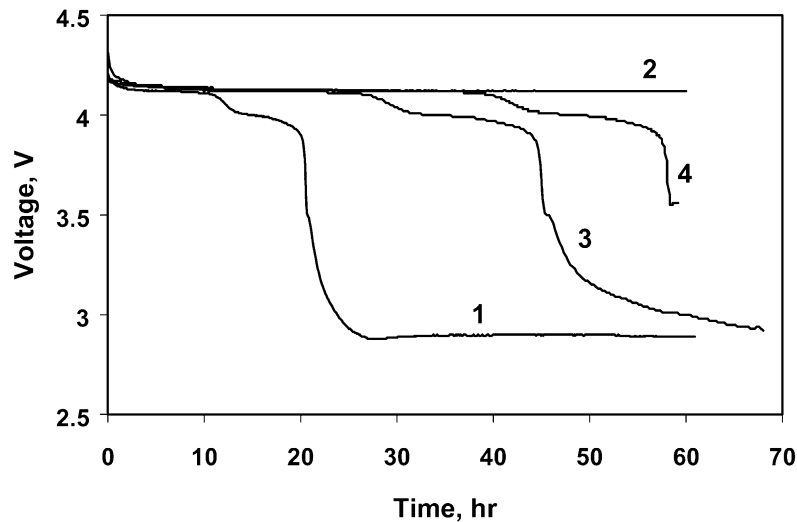


Fig. 1. Decline of OCV of $\text{Li/Li}_x\text{Mn}_2\text{O}_4$ battery cells after they had been freshly prepared and then charged to 4.4 V (except curve 4) at a rate of 0.5 mA/cm^2 . Curve 1 describes a cell with an EC–DME (1:1 w/w) solution of $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$ LiClO_4 as its electrolyte and untreated aluminum foil as its substrate. Curve 2 is the same as for curve 1 except the use of LiPF_6 in the place of LiClO_4 . Curve 3 is the same as for curve 1 except the pre-treatment of the aluminum foil to 480°C for 24 h before its use as the substrate. Curve 4 is the same as for curve 1 except that the fresh cell had been charged to 4.2 instead of 4.4 V.

aluminum, also known as the pitting potential of the aluminum. Results of this set of experiments are summarized in Fig. 2. It can be seen that although the pitting potentials of the different curves are about the same, specific features differ substantially. Curve 1 shows a corrosion curve under the conditions corresponding to those of curve 1 of Fig. 1, with an EC–DME solution of $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$ LiPF_6 as the electrolyte and an untreated aluminum wire as the working electrode. As can be seen from the curve, the corrosion current started at around 3.4 V and continued to increase as the potential of the working electrode was made more

positive. In the same fashion, curve 2 of Fig. 2 corresponds to curve 2 of Fig. 1, with LiPF_6 as the electrolyte salt instead of LiClO_4 . In this case, corrosion started at around the same potential as for curve 1, but the subsequent increase of the corrosion current at higher potentials stopped at around 6 V and then reversed. Finally, curve 3 of Fig. 2 corresponds to curve 3 of Fig. 1, with an aluminum wire pre-treated to 480°C for 24 h as the working electrode. As shown by the curve, corrosion of the aluminum electrode in this case was almost negligible as compared to the other two curves. But a close inspection of the curve still revealed the

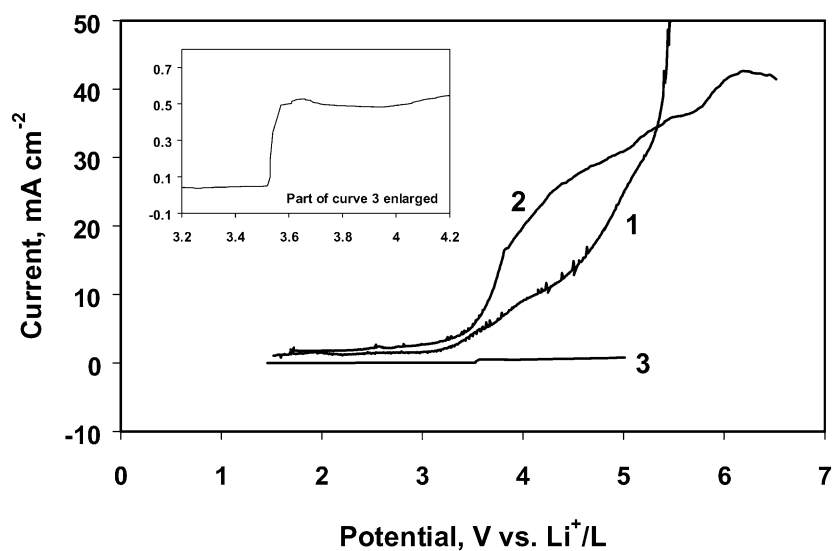


Fig. 2. Linear scan voltammograms of electrochemical corrosion cells with aluminum as the working electrode and with lithium as both the reference and counter electrodes. The scan rate was 5 mV/s . Curve 1 represents a cell with an EC–DME (1:1 w/w) solution of $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$ LiClO_4 as its electrolyte. Curve 2 is the same as for curve 1 except the use of LiPF_6 in the place of LiClO_4 . Curve 3 is the same as for curve 1 except the pre-treatment of the aluminum wire to 480°C for 24 h before its use as the working electrode.

onset of the corrosion at about 3.5 V, as indicated by the insert of Fig. 2.

3.3. The ac impedance of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells

To further confirm the existence of a passivation layer on the aluminum substrates and to observe its change with the cell condition, we measured ac impedance of battery cells corresponding to curves 1 and 2 in Figs. 1 and 2. Fig. 3a shows three impedance curves for the cathode of a cell with LiClO_4 as the electrolyte salt and untreated aluminum foil as the substrate. It can be seen that compared to the impedance curve of the fresh cell (curve 1), that for the cell charged to 4.4 V from its initial condition had an additional semicircle (curve 2), which we believe was due to the formation of a passivation layer on the aluminum substrate. Furthermore, this semicircle disappeared when the cell was subsequently self-discharged to 2.8 V (curve 3), indicating the loss of the passivation layer. Fig. 3b shows another set of four impedance curves for a cell with LiPF_6 as the electrolyte salt and untreated aluminum as the substrate. The results were similar to those of Fig. 3a, with the generation of a semicircle after the cell had been charged to 4.4 V from its initial state (curves 1 and 2). However, the passivation layer in this case seemed more stable, as another measurement at 4.12 V

OCV 60 h after the charge-up indicated a thickening of the passivation layer with an enlarged semicircle (curve 3). However, this layer was eventually lost as the cell was further discharged to 3.32 V, accompanied by the disappearance of the semicircle (curve 4). We can see from Fig. 3 the correlation between a discharged battery cell and the disappearance of the semicircle from its impedance curve, and therefore infer the effects of a passivation film on the prevention of the self-discharge of a cell.

4. Discussion

From the above results, we can see that the corrosion of aluminum substrates of the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode material played a significant, possibly dominant, role in the self-discharge of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells. A direct evidence of this came from the observation that the aluminum substrates of the cathodes of the discharged battery cells showed clear sign of corrosion under visual inspection after the cells were taken apart. More support can be obtained by correlating the results shown in all the figures. For a battery cell with LiClO_4 as the electrolyte salt and untreated aluminum foil as the substrate, the self-discharge was rapid (curve 1 of Fig. 1), and the impedance of the cathode indicated the formation of a passivation layer during charge-up and its rapid loss when the cell was subsequently self-discharged (Fig. 3a). Correspondingly, corrosion of untreated aluminum in such an electrolyte in a corrosion cell was rapid, with no indication for the formation of a passivation layer (curve 1 of Fig. 2). These results seemed to indicate that the electrolyte with LiClO_4 salt would form a passivation layer on the surface of the aluminum substrate during the charge-up of such a battery. However, this layer was not very stable and would be quickly lost if the cell was left standing, resulting in a fully discharged cell in a short period of time. In contrast, when LiPF_6 was used in the place of LiClO_4 , the self-discharge of the battery cell was significantly slowed down (curve 2 of Fig. 1), and the impedance indicated the existence of a passivation film that persisted much longer in the self-discharge experiment (Fig. 3b). Correspondingly, corrosion current of untreated aluminum in a corrosion cell with such an electrolyte grew to a plateau and then decreased as the driving potential on the aluminum working electrode was made progressively more positive (curve 2 of Fig. 2). These results, as compared to those with LiClO_4 , indicated that the passivation film formed on aluminum with the participation of LiPF_6 was much more stable. Such a film slowed down the self-discharge of the battery cells by retarding the corrosion of the aluminum substrates. Finally, comparison of curves 3 of Figs. 1 and 2 indicates that pre-treating the aluminum material to a high temperature before its use for cathode substrates or working electrodes could also have the same effects of protecting the aluminum from corrosion. This is likely the result of the heat-treatment strengthening

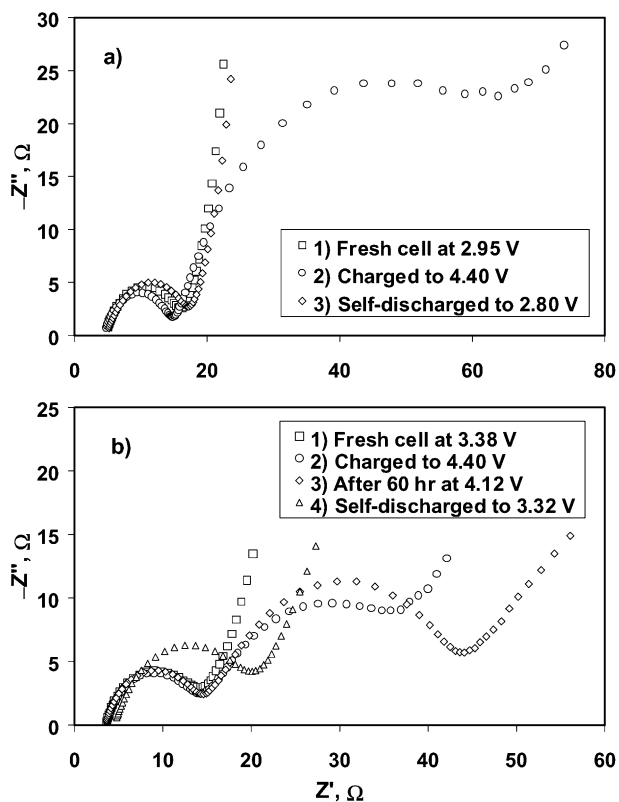


Fig. 3. Impedance curves of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells with untreated aluminum foil as the cathode substrate and with an EC–DME (1:1 w/w) solution of either (a) $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$ LiClO_4 or (b) $1 \text{ mol}_{\text{salt}}/\text{kg}_{\text{sol}}$ LiPF_6 as its electrolyte.

the naturally occurring oxide surface layer of the aluminum. Such an enforced layer was very stable and very effective in suppressing corrosion of aluminum in the corrosion cells (curve 3 of Fig. 2). However, the stability of such a layer was severely diminished in a battery cell where the aluminum was in direct contact with $\text{Li}_x\text{Mn}_2\text{O}_4$ (curve 3 of Fig. 1), possibly due to some reactions in which the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode material took part.

5. Conclusions

Corrosion of aluminum substrates played a significant role in the self-discharge of $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ battery cells that employed aluminum as their cathode substrates and current collectors. However, this corrosion, and with it the self-discharge, could be greatly reduced by the formation of protecting surface films on the aluminum substrates. Such films could be formed either by having LiPF_6 in the electrolyte in contact with the aluminum or by pre-treating the aluminum to high temperatures. But the films formed in the former fashion seemed much more stable when the aluminum was carrying an $\text{Li}_x\text{Mn}_2\text{O}_4$ material.

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