Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Power Sources 150 (2005) 1–10

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Rotating ring-disc electrode measurements of manganese dissolution and capacity loss of $Li_{1+x}Mn_{2-x}O_4$ and $Li_{1+x}Al_yMn_{2-x-y}O_4$ spinel electrodes for lithium-ion batteries

Li-Fang Wang [a], Bor-Jian Fang [a], Jenn-Shing Chen [b,*]

[a] School of Chemistry, Kaohsiung Medical University, Kaohsiung City 807, Taiwan, ROC
[b] Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung City 811, Taiwan, ROC

Received 17 November 2004; accepted 31 January 2005
Available online 16 March 2005

Abstract

Three types of spinel-based cathode powders, namely, $LiMn_2O_4$, $Li_{1.07}Mn_{1.93}O_4$, and $Li_{1.06}Al_{0.2}Mn_{1.74}O_4$, are examined with rotating ring-disc collection experiments to measure manganese dissolution and capacity losses in lithium-ion cells. The cyclic voltammograms are similar at high scan rates for all three electrodes. Initially, all electrodes rapidly lose capacity during cycling. After about 25 cycles, the electrodes start to exhibit capacity retention, and the performance matches that of the best spinels. The cation-substituted spinel electrodes experience a moderate capacity loss of 0.2% per cycle over 200 cycles, which is half that suffered by a typical spinel electrode ($LiMnO_4$). Manganese (Mn) dissolution from all the spinel-based samples is monitored in situ under various conditions. The ring cathodic currents for the cation-substituted spinel electrodes are similar to those for $LiMn_2O_4$, which shows that the Mn dissolution behaviour is the same for all spinel-based cathode powders. The ring currents reach maximum values at the end-of charge (EOC) and end-of discharge (EOD), with the largest peak at EOC. The results suggest that the dissolution of Mn from all spinel-based samples occurs during charge–discharge cycling, especially in a charged state at >4.0 V and in a discharged state at <3.1 V. In addition, lower ring cathodic currents are observed in the cation-substituted spinel cathodes and this indicates that the rate of dissolution of Mn has decreased in these materials.

Keywords: Lithium-ion cell; Spinel cathode ($LiMn_2O_4$); Cathode material; Rotating ring disc electrode; Manganese dissolution; Capacity loss

---

1. Introduction

In recent years, spinel $LiMn_2O_4$ has been studied extensively for lithium-ion (Li-ion) batteries as a cathode material because of its high voltage, low cost, and environmentally benign nature. These attractive characteristics make spinel $LiMn_2O_4$ a good candidate for use in large scale Li-ion batteries for electric vehicle (EV) and hybrid electric vehicle (HEV) applications [1]. Nevertheless, capacity fading during charge–discharge cycling is a problem for the spinel, particularly at elevated temperatures. It has been proposed that several factors contribute to capacity fading, namely: (i) electrochemical reaction with, the electrolyte at high voltage [2,3]; (ii) manganese dissolution into the electrolyte due to acid attack and a disproportionation reaction at the particle surface [4–7]: $2Mn^{3+}_{solid} \rightarrow Mn^{4+}_{solid} + Mn^{2+}_{solution}$; (iii) instability of the two-phase structure in the charged state leading to the loss of MnO and dissolution of Mn to a more stable single-phase structure [4,8,9]; (iv) formation of tetragonal $Li_2Mn_2O_4$ on the surface of spinel and the associated Jahn–Teller distortion at the end of discharge, especially under high current density, nonequilibrium conditions [5,10,11]; (v) formation of oxygen-deficient spinels [12]; (vi) cation mixing between the lithium and manganese sites in the spinel lattice [13]; (vii) loss of crystallinity during cycling [14,15].

Although many possible factors have been proposed that contribute to capacity fading of the spinel $LiMn_2O_4$ elec-

---

[*] Corresponding author. Tel.: +886 7 591 9463; fax: +886 7 591 9348.
E-mail address: jschen@nuk.edu.tw (J.-S. Chen).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.01.043

trode, most of the evidence reported so far points to manganese dissolution at the top of charge as the major cause. Thus, it is essential to investigate the dissolution behaviour of the spinel electrode in order to reduce the level of capacity fading. In our earlier paper [16], Mn dissolution from a thin porous spinel $LiMn_2O_4$ electrode was measured using rotating ring-disc collection experiments. The in situ monitoring of Mn dissolution from the spinel $LiMn_2O_4$ electrode was examined in terms of cycle number, temperature, overcharge and overdischarge. The finding, provided a clear understanding of the Mn dissolution behaviour and the variation in manganese concentration in the electrolyte during cycling.

In order to minimize the solubility of the spinel electrode, several strategies have been followed over the years through substituting other cations for manganese in $LiMn_{2-x}M_xO_4$ (M: Li, Al, Ni, Mg or Cr) [17–19] or using an electrolyte with a salt other than $LiPF_6$ and eliminating water contamination [19,20]. The present study examines further the Mn dissolution behaviour of substituted manganese spinels using the rotating ring-disc electrode (RRDE) technique.

2. Experimental

Composite disc cathodes were prepared by wet coating, and were made from spinel-based cathode powders with acetylene black, SFG-6 (Timcal), and polyvinylidene fluoride (PVDF) binder (MKB-212C, Elf Atochem) in a weight ratio of 86:2:4:6. The spinel-based active materials, acetylene black and SFG-6 were first added to a solution of poly (vinylidene fluoride) (PVDF) in *n*-methyl-2-pyrrolidone (NMP, Riedel-deHaen). The mixture was stirred for 20 min at room temperature with a magnetic bar, and then with a turbine for 5 min at 2000 rpm to form a slurry that had the appropriate viscosity. The resulting slurry was coated on to a stainless-steel disc (diameter: 6 mm) and dried at 120 °C for 40 min. The resulting coating had a thickness of ~100 μm and an active material mass of ~2.4 mg. The quantity of active materials on the disc electrodes was kept constant (±0.2 mg) The electrodes were dried overnight at 100 °C under vacuum before being transferred to an argon-filled glove box for cell assembly.

The RRDE system (AFMT134DCPTT, Pine Instruments) with interchangeable discs consisted of the above electrode and a Pt ring electrode (width: 1 mm) that were separated with a 0.5 mm gap. The collection efficiency when using this geometry was 0.24. The rotating ring-disk assembly was operated by means of a Pine AFMSRX rotator and a CH705 Bipotentiostat (CH Instruments) with a computerized interface. The manganese dissolved from the disc electrode was collected at the Pt ring. Lithium foil (Aldrich) was used for both the reference and the counter electrodes. A schematic of a glass-beaker cell containing the RRDE system was given in our earlier paper [16]. A solution of $LiPF_6$ (1.0 M) in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte (Ferro Corp.).

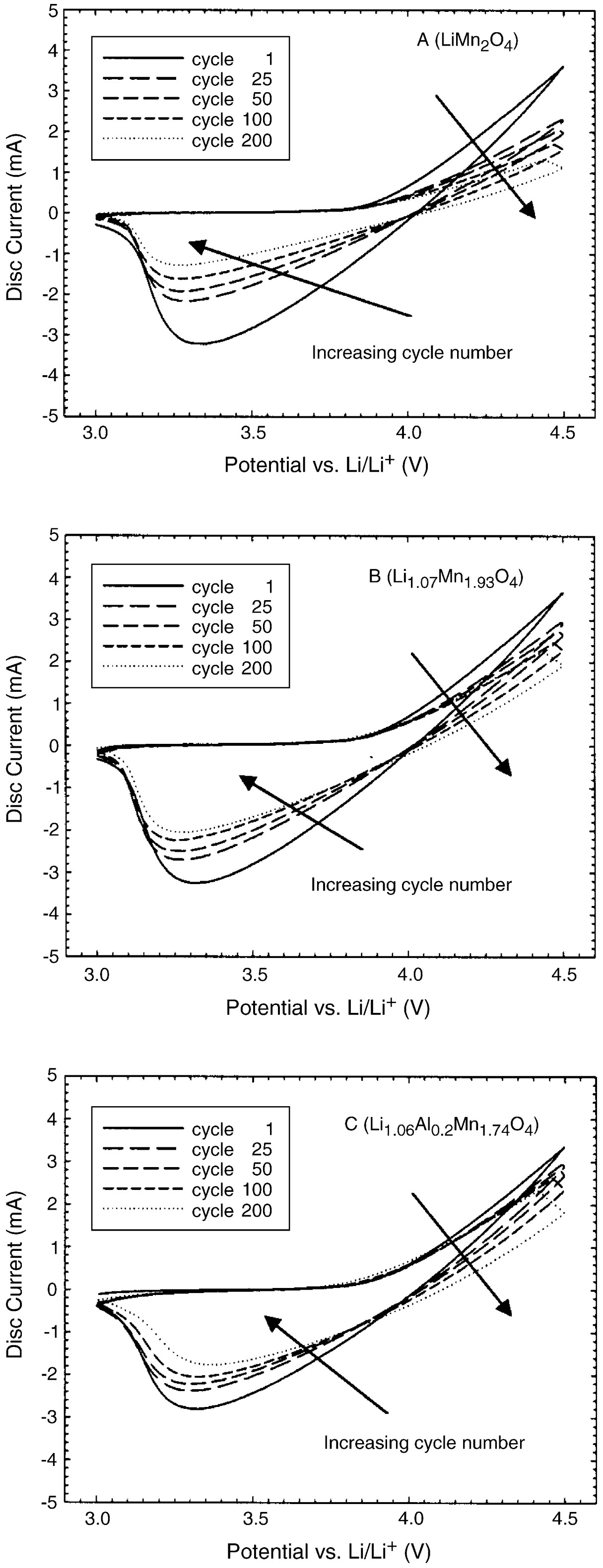

Fig. 1. Cyclic voltammograms for representative groups of spinel-based electrodes cycled between 3.0 and 4.5 V at 10 mV s^{-1} and 500 rpm with 1 M $LiPF_6$ + EC/DMC (1:1) at 1, 50, 100, 150 and 200 cycles at 30 °C.