

# An alternative method to improve the electrochemical performance of a lithium secondary battery with $\text{LiMn}_2\text{O}_4$

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## Abstract

The electrochemical properties of the Li-ion battery with a lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) cathode are improved by efficiently reducing the reaction between  $\text{LiMn}_2\text{O}_4$  and hydrofluoric acid (HF) produced in the electrolyte. By introducing fine  $\text{ZrO}_2$  particles in the slurry during fabrication, Mn dissolution of the cathode during the charge–discharge cycles is minimized by scavenging the HF produced in the cell. Results from galvanostatic experiments show that the capacity retention of the  $\text{LiMn}_2\text{O}_4$  fabricated with new method is maintained up to 92% after 50 cycles at room temperature and 76% at high temperature without losing initial capacity. The improvement in the electrochemical properties of the cathode prepared by this method is superior to other approaches in terms of fabrication process and it sheds light on the possibility of further improving the electrochemical properties of  $\text{LiMn}_2\text{O}_4$ .

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**Keywords:** Lithium manganese oxide; Lithium-ion battery; Capacity retention; Hydrofluoric acid; Zirconium oxide particles

## 1. Introduction

Lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) has been considered as a promising positive-electrode (cathode) material for lithium-ion batteries since it is non-toxic and cost-effective. Another advantage of using the  $\text{LiMn}_2\text{O}_4$  is based on its high cell voltage so that it has been considered as a cathode material for high-power battery applications. The material suffers, however, from insufficient cycling stability and structural instability for high-temperature applications. The instability of  $\text{LiMn}_2\text{O}_4$  is attributed to Mn dissolution into electrolyte due to hydrofluoric acid (HF) produced by the reaction of  $\text{LiPF}_6$  and  $\text{H}_2\text{O}$  in the electrolyte [1]. The Mn dissolution has been expressed in terms of Hunter's reaction [2];



and the dissolution of  $\text{MnO}_2$  and  $\text{Li}_2\text{O}$  into the electrolyte is known to give strong adverse effects on the performance of the  $\text{LiMn}_2\text{O}_4$  at elevated temperature (40–50 °C) [3–6].

To overcome the shortcomings of  $\text{LiMn}_2\text{O}_4$ , several approaches have been carried out [7–10]. One way to solve the problem is the substitution of mono-, di-, or trivalent cations in  $\text{LiMn}_2\text{O}_4$  to decrease  $\text{Mn}^{3+}$  ions which cause disproportion reactions. An alternative approach is to coat the  $\text{LiMn}_2\text{O}_4$  particles with various protective layers of  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  [3,4]. This is because these oxides can suppress Mn dissolution by scavenging HF from the electrolyte. Thackeray et al. [9] introduced colloidal nano-particles of  $\text{ZrO}_2$  on the surface of the spinel electrode and reported an improvement in cycle stability at 50 °C. Sun et al. [11] also used  $\text{ZnO}$  to coat  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles by means of a sol–gel method and successfully scavenged the HF produced in the cell.

Protecting the  $\text{LiMn}_2\text{O}_4$  particles from HF in the electrolyte appears successful in improving the structural stability of the cathode and maintaining the capacity of Li-ion batteries. The detailed mechanism of the successful treatments for better

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performance, however, has not been reported and has yet to be elucidated. In particular, the effect of the  $\text{ZrO}_2$  location in the cell has not been examined systematically despite the fact that it is crucial to understand the role of the oxides in providing better electrochemical performance.

This study focuses on the effectiveness of  $\text{ZrO}_2$  in protecting Mn dissolution by changing the location on the oxide at which the reaction takes place. In particular, the mechanism account for the improvement in the electrochemical properties by oxide addition is explored by comparing four different cells produced using bare  $\text{LiMn}_2\text{O}_4$ ,  $\text{ZrO}_2$  attached  $\text{LiMn}_2\text{O}_4$ , a slurry mixed with  $\text{ZrO}_2$ , and by directly introducing  $\text{ZrO}_2$  into the electrolyte.

## 2. Experimental

Bare  $\text{LiMn}_2\text{O}_4$  was synthesized by a sol–gel method. The 0.1 M  $(\text{CH}_3\text{COO})\text{Li}\cdot\text{H}_2\text{O}$  and 0.2 M  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  were dissolved in distilled water and acrylic acid was added to the solution to control the reaction kinetics. The remaining water and acrylic acid were removed in a rotary evaporator at  $80^\circ\text{C}$ . After drying, the product was heated for 12 h at  $600^\circ\text{C}$  in air followed by calcination at  $800^\circ\text{C}$  for 24 h under an oxygen flow. To produce  $\text{ZrO}_2$  attached  $\text{LiMn}_2\text{O}_4$  particles, 2 wt.%  $\text{ZrO}_2$  (zirconium(IV) oxide, nano-powder, Aldrich) was mixed with the  $\text{LiMn}_2\text{O}_4$  that was calcined for 18 h at  $800^\circ\text{C}$ , and the mixture was calcined for an additional 6 h at  $800^\circ\text{C}$  under an oxygen flow. The cathode was also prepared by adding 2 wt.% of  $\text{ZrO}_2$  directly into the slurry and by adding 2 wt.% of  $\text{ZrO}_2$  to the electrolyte.

The positive electrode was prepared by combining  $\text{LiMn}_2\text{O}_4$ , polyvinylidene difluoride (PVdF) (5 wt.% in 1-methyl-2-pyrrolinone (NMP)), and carbon. The ratio was 85:5:10 in wt.% and acetone was added to lower the viscosity before homogenizing the mixture at 5000 rpm. The cathode was cast by the doctor blade method on an Al foil. It was pressed using a rolling press at  $110^\circ\text{C}$  and dried in a vacuum oven for 24 h at  $80^\circ\text{C}$ . The

electrolyte was 1 M high purity  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume ratio). Cells were assembled in a dry room and poly-propylene (PP) was used for the separator.

The electrochemical properties of  $\text{LiMn}_2\text{O}_4$  were examined using coin cells with a lithium foil as a negative electrode. Charge–discharge experiments were carried out at room tem-

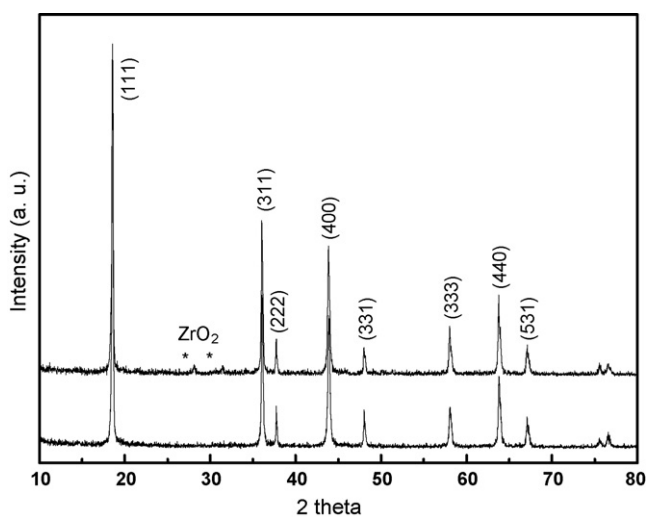


Fig. 1. X-Ray diffraction patterns obtained from (a)  $\text{LiMn}_2\text{O}_4$  and (b)  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ . Diffraction angles ( $2\theta$ ) from  $\text{ZrO}_2$  phases are indicated by asterisks.

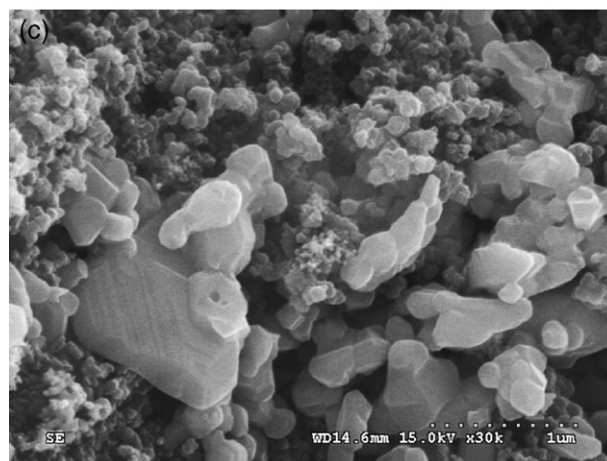
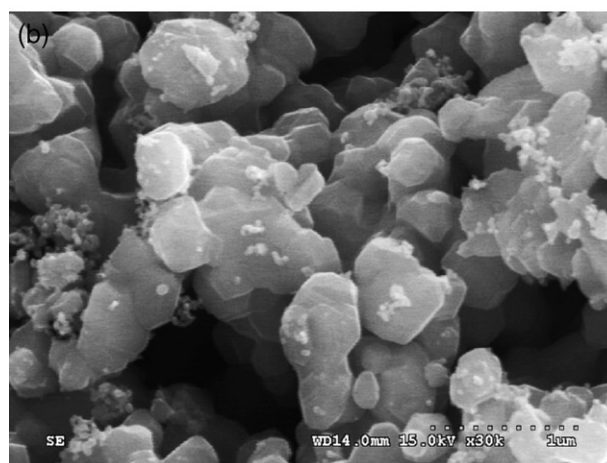


Fig. 2. Scanning electron micrographs of: (a) bare  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ , and (c)  $\text{ZrO}_2$  added slurry.

perature and 55 °C by means of a battery cycling system (Maccor4000, Maccor). The charge–discharge rate was set at 0.5 C and tests were conducted for 50 cycles at room temperature and 30 cycles at 55 °C. The crystal structure of the specimen was examined by X-ray diffraction (XRD; D/MAX-II A) and the morphology of the powder specimen was investigated with a scanning electron microscope (SEM; Hitachi, S-4300) and a transmission electron microscope (TEM; JEOL, JEM4010).

### 3. Results and discussion

#### 3.1. Crystal structure and surface morphology

The XRD patterns obtained from bare  $\text{LiMn}_2\text{O}_4$  and after  $\text{ZrO}_2$  attachment are given in Fig. 1. These indicate a well-crystallized spinel structure (space group  $Fd3m$ ) [12] without producing impurity phases since the patterns do not exhibit extra peaks. The  $\text{LiMn}_2\text{O}_4$  attached with  $\text{ZrO}_2$  particles shows small peaks in the XRD pattern that correspond to  $\text{ZrO}_2$ . The lattice parameters of bare and  $\text{ZrO}_2$ -modified material are 8.24 and 8.25 Å, respectively.

Scanning electron micrographs of the specimens are presented in Fig. 2. It is seen that the particle size of bare  $\text{LiMn}_2\text{O}_4$  is in the range of 0.1–0.5  $\mu\text{m}$  and that there is no size difference between the  $\text{ZrO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  and the bare particles after heat treatment (Fig. 2(a, b)). The  $\text{ZrO}_2$  particles are slightly larger than their initial size due to high-temperature heat treatment and are physically in contact with the  $\text{LiMn}_2\text{O}_4$  particles. The micrographs also show that the  $\text{ZrO}_2$  particles are aggregated on the  $\text{LiMn}_2\text{O}_4$  surface, and this reduces the specific surface-area for chemical reaction. The slurry with  $\text{ZrO}_2$  particles is shown in Fig. 2(c). All the ingredients used to prepare slurry are visible and the  $\text{LiMn}_2\text{O}_4$  surfaces are clean without any adherent  $\text{ZrO}_2$  particles.

Transmission electron micrographs in Fig. 3 show bare  $\text{LiMn}_2\text{O}_4$  particles and  $\text{ZrO}_2$  particles adhered to  $\text{LiMn}_2\text{O}_4$ . This suggests that the effective surface area of  $\text{ZrO}_2$ -attached  $\text{LiMn}_2\text{O}_4$  available for intercalation of Li is decreased. The attached  $\text{ZrO}_2$  particles also appear to reduce the effective surface area that participates in the chemical reaction to scavenge HF in the cell.

#### 3.2. Electrochemical properties

The charge–discharge characteristics of the four specimens investigated in this study are presented in Fig. 4. All specimens show two distinct discharge plateaux. These are attributed to orderly intercalating lithium ions in the tetrahedral (8a) sites at 4.1 V and disorderly intercalating lithium ions at 3.9 V [13]. The charge–discharge curve obtained at room temperature from bare  $\text{LiMn}_2\text{O}_4$  (Fig. 4(a)) shows a relatively large fading in capacity after 50 cycles. On the other hand, the capacity fading is worse in the case of using  $\text{LiMn}_2\text{O}_4$  attached with  $\text{ZrO}_2$  particles (Fig. 4(b)). This suggests that the mixing and subsequent heat treatment of fine  $\text{ZrO}_2$  particles with  $\text{LiMn}_2\text{O}_4$  is not effective in terms of an improvement in the electrochemical properties of  $\text{LiMn}_2\text{O}_4$ . This apparent harmful effect of  $\text{ZrO}_2$  attachment appears to be due to the adherent  $\text{ZrO}_2$  particles blocking the pathway for Li intercalation on the surface of the active material. The application of the  $\text{ZrO}_2$  to scavenge HF also seems to be inefficient in this case because of the reduced effective surface area of the  $\text{ZrO}_2$  particles for the chemical reaction with HF. This is contrary to the successful results from other workers [9,11,14] and the difference appears to rely on the resultant morphology of the coating layers on the  $\text{LiMn}_2\text{O}_4$  surface.

On the other hand, the charge–discharge curves from the cathode made from the slurry mixed with the same  $\text{ZrO}_2$  particles

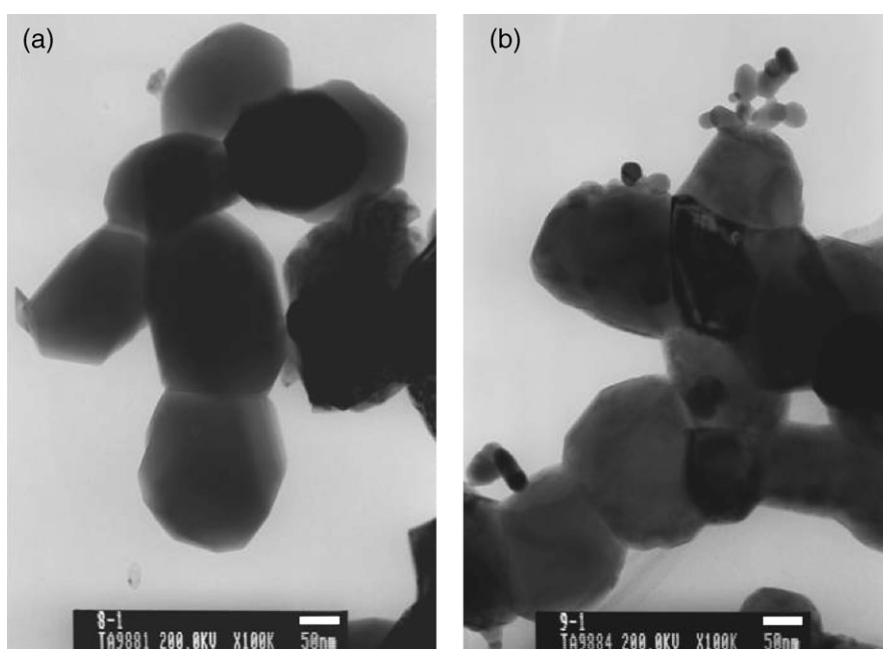


Fig. 3. Transmission electron micrographs of: (a) bare  $\text{LiMn}_2\text{O}_4$  and (b)  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ .

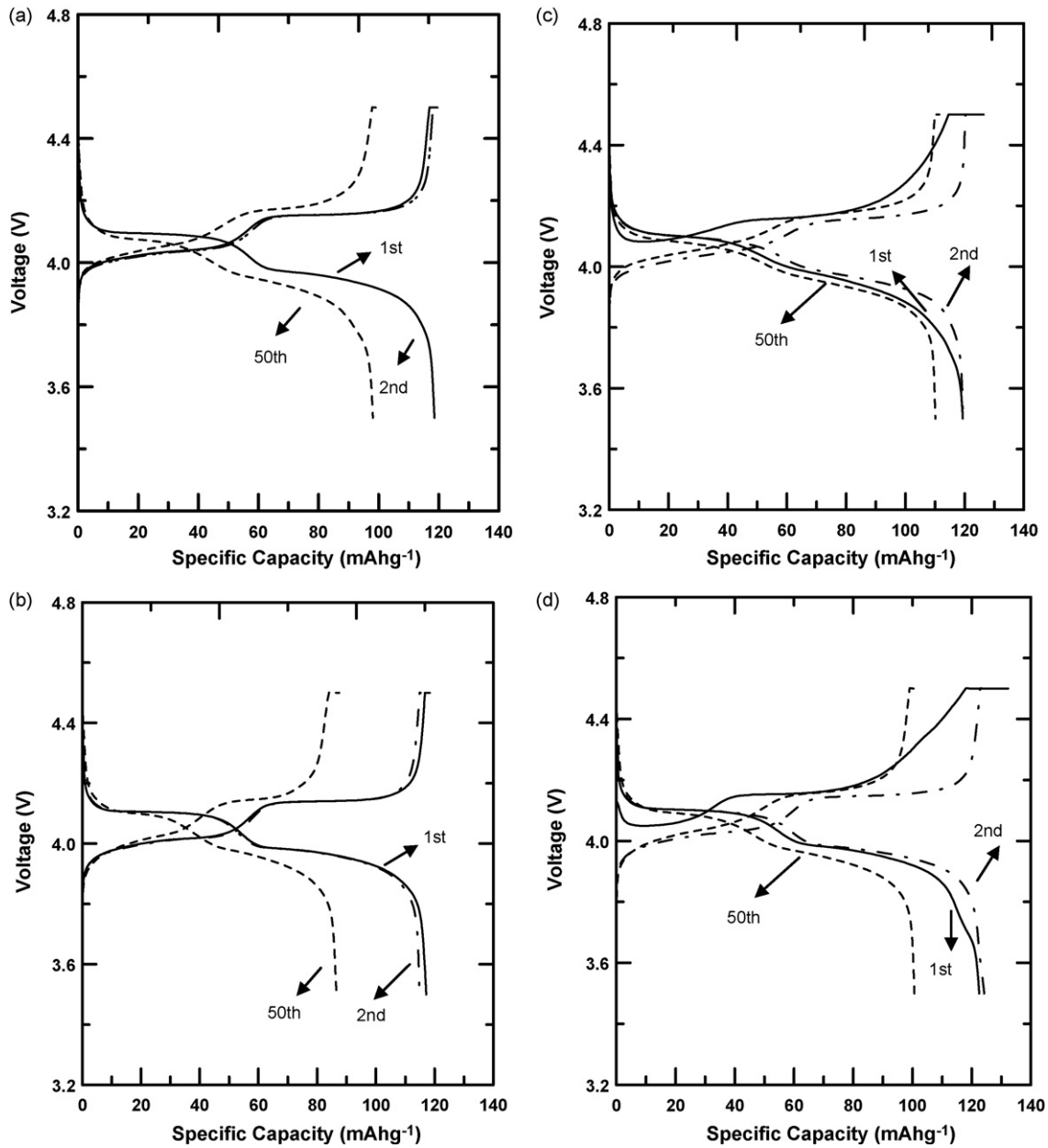


Fig. 4. Charge–discharge curves from cathodes at room temperature using: (a) bare  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ , (c)  $\text{ZrO}_2$  added slurry, and (d)  $\text{ZrO}_2$  in the electrolyte.

showed the best performance compared with other methods. It showed 92% capacity retention after 50 cycles (Fig. 4(c)). The beneficial effect of adding  $\text{ZrO}_2$  to the slurry appears due to the greater surface area that takes part in the chemical reaction than when  $\text{ZrO}_2$  is attached to  $\text{LiMn}_2\text{O}_4$ . This is a salient result and can provide a viable alternative to improve the electrochemical performance of the cathode for Li-ion batteries. This is because the mixing of  $\text{ZrO}_2$  into the slurry greatly simplifies the fabrication procedure compared with other coating methods. An attempt was also made to improve the performance of the cathode by inserting the same  $\text{ZrO}_2$  into the electrolyte, which is the source of the HF in the cell [1]. The effect of the  $\text{ZrO}_2$  in the electrolyte, however, is inferior to that of  $\text{ZrO}_2$  in

the slurry (Fig. 4(d)) but is similar to that of the cell with bare  $\text{LiMn}_2\text{O}_4$ .

High-temperature, charge–discharge experiments were performed because Mn dissolution is severe at high temperatures [15,16]. The test was carried out for up to 30 cycles due to fast reaction of  $\text{LiMn}_2\text{O}_4$  with HF (Fig. 5). The results show that the cathode with  $\text{ZrO}_2$  particles in the slurry protect the  $\text{LiMn}_2\text{O}_4$  from HF attack, which suggests that the contact and effective surface area of  $\text{ZrO}_2$  are again crucial factors at high temperatures. The curves in Fig. 5 indicate that the suppression of Mn dissolution is more pronounced by using a slurry with  $\text{ZrO}_2$  particles than the three other cases at high temperature. Improvement of the electrochemical properties of  $\text{LiMn}_2\text{O}_4$  at

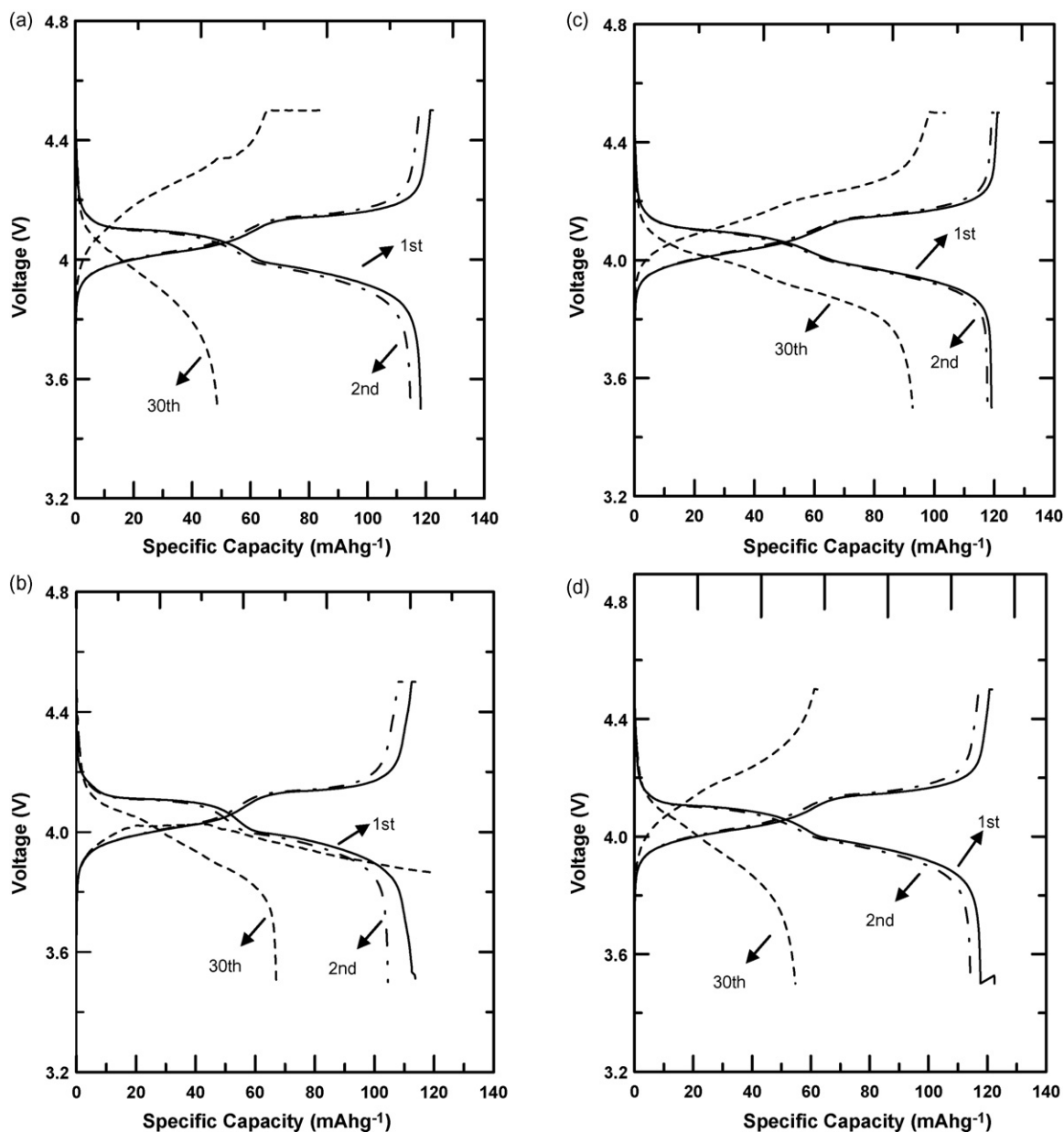


Fig. 5. Charge–discharge curves from cathodes at 55 °C using: (a) bare  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ , (c)  $\text{ZrO}_2$  added slurry, and (d)  $\text{ZrO}_2$  in electrolyte.

elevated temperatures has been reported by coating amphoteric oxides such as  $\text{ZrO}_2$  and  $\text{ZnO}$  on  $\text{LiMn}_2\text{O}_4$  particles [9,14]. Thackeray et al. [9] reported that  $\text{ZrO}_2$  or  $\text{LiZrO}_3$  coated on the surface of spinel or layered cathodes enhances the electrochemical performance by minimizing the solubility of  $\text{LiMn}_2\text{O}_4$  or by suppressing the reactivity of the layered electrodes. Sun et al. [14] also suggested that an amphoteric oxide such as  $\text{ZnO}$  scavenges HF in the electrolyte. The enhanced electrochemical properties of the  $\text{LiMn}_2\text{O}_4$  from these previous studies, however, were accomplished by coating the  $\text{LiMn}_2\text{O}_4$  surface by amphoteric oxides and protecting the surface from HF. On the other hand, the improvement observed in this present investigation is based on the addition of amphoteric powder to the slurry, which is much simpler from a manufacturer's point of view.

The cycling stability of the four different cells was examined by measuring the cell capacity at the 0.5 C rate. Cycling curves at room temperature and at high temperature are shown in Figs. 6 and 7. The bare  $\text{LiMn}_2\text{O}_4$  shows 85% capacity retention while the specimen with  $\text{ZrO}_2$  in the slurry reports 92% capacity retention after 50 cycles at room temperature without losing initial capacity. In general, coated cathodes have shown lower initial capacities than a bare cathode. Wu and co-workers [17] found that the initial capacity of the electrode containing bare  $\text{LiMn}_2\text{O}_4$  was about  $125 \text{ mA h g}^{-1}$  while the capacity after 5%  $\text{ZrO}_2$  coating was reduced to  $118 \text{ mA h g}^{-1}$ . Zheng et al. [18] obtained a similar result from a sol–gel coated cathode material. In this study, however, the cathode with  $\text{ZrO}_2$  in the slurry displays almost the same initial capacity compared with the bare electrode.

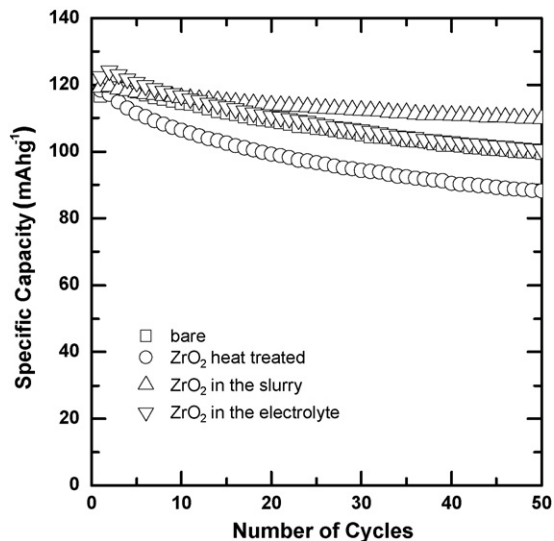


Fig. 6. Cycling stability curves at room temperature at 0.5C rate using bare  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ ,  $\text{ZrO}_2$  added slurry, and  $\text{ZrO}_2$  in electrolyte.

The cycling stability at 55 °C is presented in Fig. 7. The data show that the cathode with  $\text{ZrO}_2$  in the slurry exhibits good capacity retention in comparison with other cases. This is consistent with the results from Thackeray and co-workers [15]. These authors reported that a specimen with the high specific surface area of  $\text{ZrO}_2$  exhibited better capacity retention than a specimen coated with larger  $\text{ZrO}_2$ . They also found that the initial capacity was decreased while the capacity retention was improved after  $\text{ZrO}_2$  coating. On the other hand, the cycling stability curves in Fig. 7 show 76% capacity retention without loss in initial capacity when  $\text{ZrO}_2$  is added to the slurry.

A quantitative analysis of the role of  $\text{ZrO}_2$  in the cell is not provided in this paper. It appears that the  $\text{ZrO}_2$  particles evenly

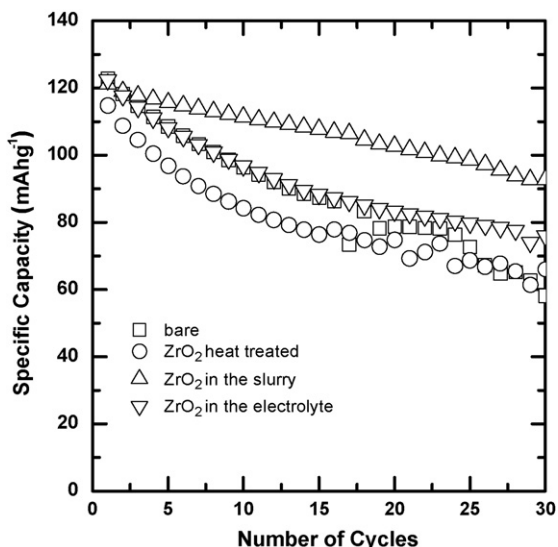


Fig. 7. Cycling stability curves at 55 °C at 0.5C rate using bare  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_2\text{O}_4$  with 2 wt.%  $\text{ZrO}_2$ ,  $\text{ZrO}_2$  added slurry, and  $\text{ZrO}_2$  in electrolyte.

distributed in the slurry are more effective in scavenging the HF than those in the electrolyte or on the  $\text{LiMn}_2\text{O}_4$  surface. Although this new method of manufacturing a cathode by mixing  $\text{ZrO}_2$  into the slurry is slightly inferior to other reported coating methods in terms of capacity retention during cycling, the maintenance of the initial capacity and the simple production route that sidesteps the elaborate procedure of oxide coating suggest that there is scope to improve the electrochemical properties of  $\text{LiMn}_2\text{O}_4$ .

#### 4. Conclusions

The effects of  $\text{ZrO}_2$  on the electrochemical properties of  $\text{LiMn}_2\text{O}_4$  have been studied using electrochemical tests and several analytical methods such as XRD, SEM, and TEM. The results can be summarized as follows:

- (i) The synthesized  $\text{LiMn}_2\text{O}_4$  does not show secondary phases, which indicates that  $\text{ZrO}_2$  does not react with  $\text{LiMn}_2\text{O}_4$ .
- (ii) A cathode with  $\text{ZrO}_2$  in the slurry does not affect the initial capacity compared with bare  $\text{LiMn}_2\text{O}_4$  and maintains a capacity retention of up to 92% at room temperature and 76% at high temperature.
- (iii)  $\text{ZrO}_2$  in the slurry is more effective than  $\text{ZrO}_2$  in the electrolyte since protection of the cathode from HF is enhanced by dispersed  $\text{ZrO}_2$  particles in the vicinity of the cathode materials but not in contact, with them.
- (iv) To reduce production time and cost, addition of  $\text{ZrO}_2$  to the slurry is recommended to improve the electrochemical properties of  $\text{LiMn}_2\text{O}_4$  cathodes.

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