

Electrochemical and structural studies of the composite MnO₂ cathode doped with metal oxides

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Abstract

The composite manganese dioxide made from heat-treated LiOH·MnO₂ (CDMO) was doped with various metal oxides and characterized by X-ray diffraction and differential thermal analysis. The results indicated that the doped CDMO kept the crystal structure of CDMO and had a reduced Li₂MnO₃ content. Cycling tests showed that the doped CDMO had superior cycleability and improved dischargeability than undoped CDMO.

Introduction

MnO₂ has for a long time attracted particular attention as a high-voltage and low-cost cathode material for secondary lithium batteries. A variety of structural forms of MnO₂ and related composite oxides of manganese has been investigated in order to improve the rechargeability and energy capacity of such materials. Though λ-MnO₂ has shown an excellent rechargeability [1], the existence of several voltage steps makes it discharge characteristic inconvenient for many applications. Spinel LiMn₂O₄ also exhibits good cycleability, but its capacity is somewhat too low and decreases rather rapidly with cycling, especially when subjected to deep discharge cycles [2]. On the other hand, the composite MnO₂ cathode (CDMO) has a moderately high capacity and satisfactory cycling behavior and seems to be a promising cathode material for secondary Li/MnO₂ batteries [3, 4]. However, its degradation during deep cycling is still a problem not yet well solved.

In order to improve the charge/discharge characteristics of CDMO, we tried to modify CDMO cathode by doping it with various metal cations. In this paper, we report the electrochemical and structural properties of the doped CDMO in comparison with undoped CDMO cathode.

Experimental

CDMO material was prepared as described in ref. 3 by heating a mixture of Li/Mn molar ratio at 400 °C for 24 h. The doping of CDMO was made by replacing a part of LiOH with other metal oxides and then heat-treated at the same condition. The cathode was prepared by calendering a mixture of CDMO (85 wt.%), acetylene black (8 wt.%) and polytetrafluoroethylene (PTFE) powder (7 wt.%) on to a 0.25 mm sheet. The electrolyte was 1.0 M LiClO₄ in 1:1 volume mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME). The charge/discharge characteristics

of the cathode were measured by cycling at constant current density of 15 mA/g cathode active material in a sandwich-type cell.

The powder samples of CDMO and doped CDMO were characterized by X-ray diffraction analysis (XRD, Rigaku D/DAX-RB), infrared spectrometry (IR, Nicolet FT-IR 170 SX), thermogravimetric and differential thermal analysis (TG and DTA, Rigaku TAG-100). Samples of the cycled cathodes taken from test cells were firstly vacuum dried and then analyzed by XRD and IR.

Results and discussion

Figure 1 shows the discharge profile of CDMO cathode with Li:Mn molar ratio = 0.3, prepared from $\text{LiOH} \cdot \text{MnO}_2$ heat-treated at 400 °C. The optimized Li:Mn ratio was found to lie between 0.20–0.35% as a compromise between the capacity and cycleability, in good agreement with previous results of Nohma *et al.* [3]. It can be seen from this Fig. that the capacity loss and cathode polarization increase quite rapidly with cycles. After 100th cycle, the capacity was about half of its initial capacity.

It has been proposed that CDMO is composed of $\gamma/\beta\text{-MnO}_2$ and Li_2MnO_3 [5], and Li_2MnO_3 is considered to have a poor dischargeability [3]. Since the content of Li_2MnO_3 increased with the increase of lithium in CDMO, we attempted to replace a part of the lithium by doping other metal cations to reduce the Li_2MnO_3 content and thereby to improve the discharge and cycling characteristics of CDMO.

Figure 2 shows the XRD patterns of doped CDMOs compared with that of CDMO. A main XRD feature of the doped CDMOs is the disappearance of the peaks previously assigned to Li_2MnO_3 , indicating a great reduction in the content of Li_2MnO_3 . Instead, the doping metal oxides showed quite distinctive peaks. Since the doped CDMO has very poor crystalline structure we can not exactly determine whether the doping process produced a new composite oxide or did not change the crystal structure of CDMO. However, the observation of strong XRD peak at 2.4 and 2.17 Å, a characteristic feature of $\gamma/\beta\text{-MnO}_2$, suggest that $\gamma/\beta\text{-MnO}_2$ exists predominately in doped CDMOs.

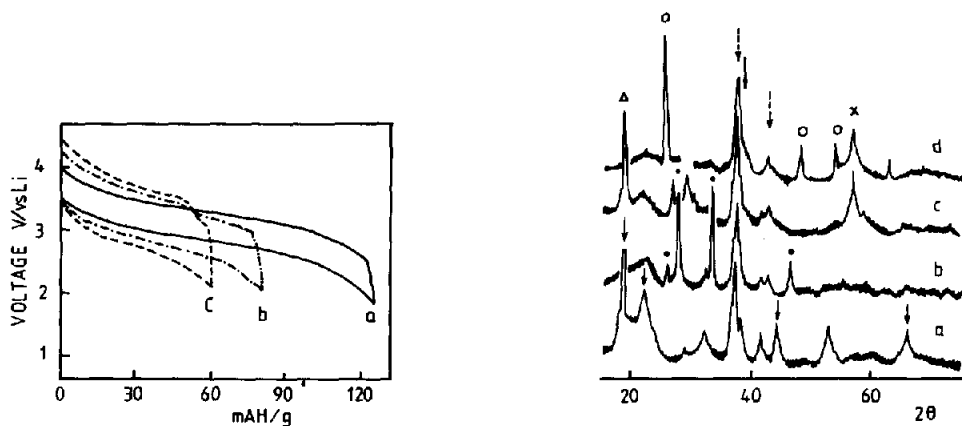


Fig. 1. Discharge/charge curves of a heat-treated $\text{LiOH} \cdot \text{MnO}_2$ cathode with Li:Mn molar ratio = 0.3: (a) 1st; (b) 50th, and (c) 100th cycle. DOD = 38% (45 mA h/g) of its initial capacity.

Fig. 2. XRD patterns of (a) CDMO, (b) Bi_2O_3 -doped CDMO, (c) V_2O_5 , and (d) TiO_2 . (↓) Li_2MnO_3 ; (↓) $\gamma/\beta\text{-MnO}_2$; (●) Bi_2O_3 ; (Δ) LiVO_3 ; (○) TiO_2 , and (x) $\gamma\text{-MnO}_2$.

IR, TG and DTA measurements support this suggestion. Figure 3 compares the TG and DTA curves of CDMO and Bi(III)-doped CDMO. A main difference in DTA curves of these two composites is the observation of four additional endothermic peaks at 556, 918, 726 and 819 °C for Bi-doped CDMO. Parallel DTA study of manganese oxides and bismuth oxides indicated that the 556 and 918 °C peaks were due to electrochemically manganese dioxide (EMD) and the latter two peaks were given rise by Bi_2O_3 . Except for this, the DTA and TG data for Bi-doped CDMO and CDMO are almost the same. IR spectra of the two compounds are shown in Fig. 4. The band number and the band shape of these two oxides resemble very well, indicating that they have the same crystal structure. Since the doping process can only reduce the Li_2MnO_3 content but not destroy the basic structure of CDMO, it is expected that the doped CDMO possesses a good rechargeability as CDMO, but improved dischargeability.

The discharge curves of CDMO samples doped with a variety of metal cations is given in Fig. 5. The discharge capacities of CDMO doped with Co, V, Pb, Ti and Bi cation were all around 180 mA h/g, about 20% higher than that of the undoped CDMO cathode in our experiments. However, the cycling properties of the doped CDMO cathode varied significantly with the nature of doping metal cations. For Sn(IV), Pb(IV) and Ti(IV)-doped CDMO cathodes, the rechargeability became poorer while Bi(III) and V(V)-doped CDMO showed better discharge and cycling performances. The optimum Bi content in doped CDMO was evaluated to lie between 1 to 3 mol%, seen the discharge capacity and cycleability.

Figure 6 shows the cycling curves of the Bi-doped CDMO cathode. The discharge capacity of the Bi-doped CDMO cathode decreases only 25% after 100 cycles. It was also found that the cycling efficiency of the Bi-doped CDMO cathode was high (>90%) and the cathode polarization did not vary significantly from cycle to cycle after a few tens of cycles. After 100 cycles, the cathode polarizations of the doped CDMO (Fig. 5(c)) during charge or discharge were obviously smaller than CDMO.

Figures 7 and 8 are the XRD diffractograms and IR spectra of cycled Bi-doped cathodes. It can be seen that after 10 cycles the XRD patterns of the cathodes were almost the same and exhibited a slight and reversible shift during charge and discharge. This is usually considered to be due to the expansion and contraction of the crystal lattice caused by lithium insertion and deintercalation. IR results in Fig. 8 are consistent

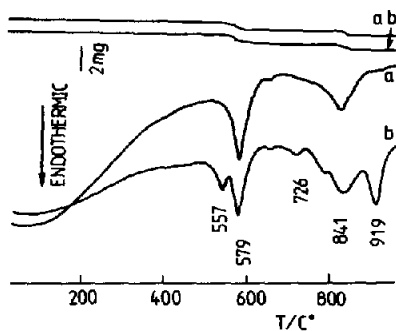


Fig. 3. TG and DTA curves of (a) CDMO and (b) Bi(III)-doped CDMO.

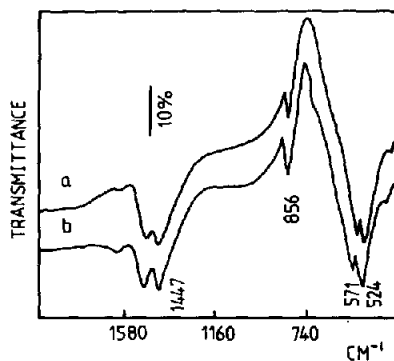


Fig. 4. IR spectra of (a) CDMO compared with (b) Bi-doped CDMO.

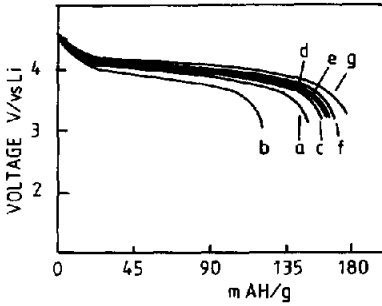


Fig. 5. Discharge profiles of (a) CDMO and the doped CDMO with: 0.05 M (b) SnO_2 ; (c) CoCl_2 ; (d) V_2O_5 ; (e) TiO_2 ; (f) Bi_2O_3 , and (g) PbO_2 .

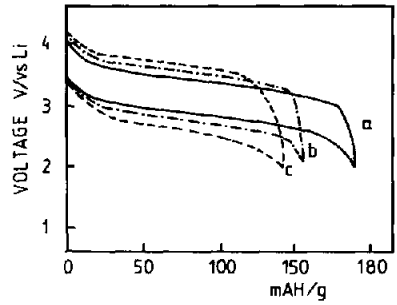


Fig. 6. The cycling curve of Bi(III)-doped CDMO with Li:Bi:Mn molar ratio: 0.27:0.02:1. (a) 1st; (b) 50th, and (c) 100th cycle. DOD=50% (90 mA h/g) of its initial capacity.

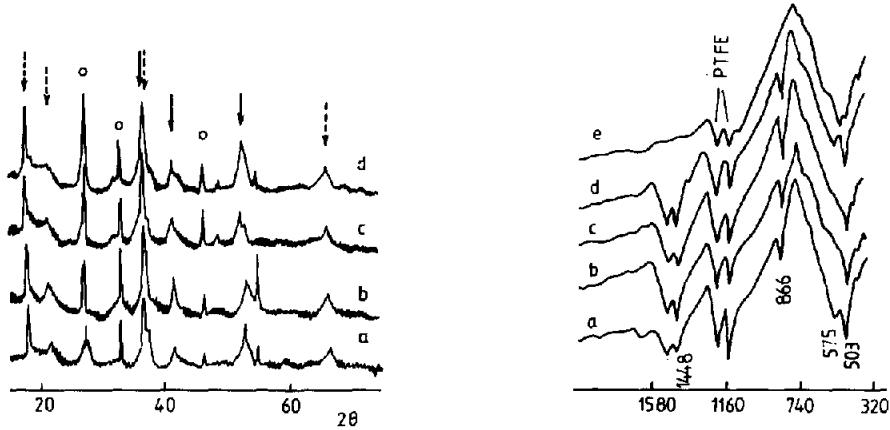


Fig. 7. X-ray diffractograms of the Bi-doped CDMO cathodes taken after (a) 1st discharge; (b) 1st charge; (c) 10th discharge, and (d) 10th charge. (↓) Li_2MnO_3 , (↓) $\gamma/\beta\text{-MnO}_2$, and (○) Bi_2O_3 .

Fig. 8. IR spectra of the Bi-doped CDMO cathode: (a) at open-circuit voltage; (b), (c), (d) after 1st, 10th and 150th discharge, and (e) after 1st charge.

with the XRD measurements. Even after 150 cycles the spectra did not show any significant distortion in the band shape and position, indicating a structural stability of the cathode. Though the detailed assignments of XRD and IR peaks for the CDMO are inconclusive at present [6] it is obvious from the results that the doped CDMO kept its parent crystal structure and it has good reversibilities for the insertion and removal of lithium.

Conclusion

The discharge performances and cycling properties of CDMO can be improved by doping with a number of metal oxides to replace a part of lithium. Bi_2O_3 -doped CDMO cathode was evaluated to have the best rechargeability and rate capacity.

XRD, IR, DTA analysis showed that the doping of CDMO did not change its crystal structure but inhibited the formation of Li_2MnO_3 in CDMO.

References

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