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Effects of conducting carbon on the electrochemical performance of LiCoO₂ and LiMn₂O₄ cathodes

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Abstract

The effects of conducting carbon additive on the performance of LiCoO₂ and LiMn₂O₄ cathodes in lithium-ion batteries have been investigated. While 2–5 wt.% of carbon are adequate for the LiMn₂O₄ cathode to deliver good rate capability and maintain cyclability, the LiCoO₂ cathode requires more carbon (10 wt.%) to achieve likewise. The sensitivity of the LiCoO₂ electrode for carbon content is particularly pronounced in high rate charging. Cyclic voltammetry and electrochemical impedance spectroscopy measurements indicate that deteriorating particle contacts leading to the incomplete charging of the active materials is the primary cause of material non-performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Conducting carbon; Cathodes; Rechargeable lithium-ion batteries

1. Introduction

Since the successful launch of the lithium-ion batteries by Sony in 1990 [1], layered oxides such as LiCoO₂, LiNiO₂, and LiMn₂O₄ spinels have served as very effective cathode materials. Rechargeability is based on the reversibility of Li⁺ extraction and reinsertion into the host matrix, which is excellent for a LiCoO₂ cathode cycled over the limited composition range of $0 < x < 0.5$. The inexpensive LiMn₂O₄ cathode has a lower specific capacity and suffers from a progressive capacity loss upon cycling that can be attributed to several causes [2].

As LiCoO₂ and LiMn₂O₄ have low electronic conductivities, they have to be blended with a conductivity agent such as carbon black to form a working cathode. Jang et al. [3] have reported severe capacity losses in LiMn₂O₄ cathodes with low carbon contents. While the addition of excess carbon may seem to be the solution, it also reduces the energy and power densities of the resulting batteries. The carbon loading in a working cathode must therefore, be optimized.

In this paper, we report our findings on the effects of carbon loading on polarization losses and capacity fading in LiCoO₂ and LiMn₂O₄ cathodes. Electrochemical impedance

spectroscopy was used to determine the dominant factor for the capacity loss on cycling.

2. Experimental

LiCoO₂ was prepared by calcinating a pressed stoichiometric mixture of CoCO₃ and Li₂CO₃ in air at 850°C for 24 h. Spinel LiMn₂O₄ was likewise prepared from heating a pressed stoichiometric mixture of Li₂CO₃ and MnCO₃ in air at 450°C for 24 h, followed by another 24 h at 750°C. The reaction products were ground in an automated mortar with agate balls to 200 mesh and below (<75 μm in particle size), and stored in a desiccator with blue silica-gels. The particle size distributions of the samples were measured by Elzone 5380 Analyzers (Micromeritics Instrument Corporation). The *d*₅₀ of LiCoO₂ and LiMn₂O₄ are approximately 10 and 23 μm, respectively. The crystal structures of the lithiated oxides were determined by powder X-ray diffraction (XRD) on a Philips PW1877 diffractometer, using Cu Kα radiation and a graphite monochromator.

LiCoO₂ and LiMn₂O₄ were mixed with 2–10 wt.% of carbon black and 10 wt.% of PVDF in 1-methyl-2-pyrrolidone (NMP). The slurry was used to coat 20 μm thick Al disks of 16 mm diameters to a mass loading of 40–50 mg cm⁻² after drying (at 120°C) and compaction (at 2.0 × 10⁶ Pa). Each coated electrode was assembled into

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a 2016 coin cell using a Li counter electrode, a microporous polypropylene separator, and an electrolyte of 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Cell assembly was carried out in an Ar filled glove box with less than 1 ppm each of oxygen and moisture.

The cells were charged and discharged at 25°C on a Bitrode life cycle tester. Cyclic voltammetry was carried out on an EG&G model 273 potentiostat/galvonostat using the system software from the vender. Cell impedances were measured in the frequency range of 1 mHz to 100 kHz by connecting the EG&G 273 to a EG&G model 5210 lock-in amplifier, and using an ac modulation voltage of ±10 mV. Impedance readings were taken under open-circuit conditions after the cell was charged to predetermined levels. All measurements were carried out at 25°C.

3. Results and discussion

3.1. XRD patterns of LiCoO₂ and LiMn₂O₄

The XRD patterns of the as-synthesized LiCoO₂ and LiMn₂O₄ are pure phase products without any discernable impurity. The diffraction peaks of the LiCoO₂ powder can be indexed by a α-NaFeO₂ type hexagonal structure with the lattice parameters $a = 2.816 \text{ \AA}$, and $c = 14.056 \text{ \AA}$. The lattice parameter of the LiMn₂O₄ cubic spinel as calculated from the diffraction pattern is 8.245 \AA .

3.2. Effects of carbon loading on charge and discharge capacities

Table 1 indicates succinctly the dependence of the cathode charge and discharge capacities on carbon loadings and charging rates. The capacities of LiCoO₂ and LiMn₂O₄ at the low charging rate of 0.4 mA cm^{-2} are not affected as much by the carbon content as they do at the higher rates of

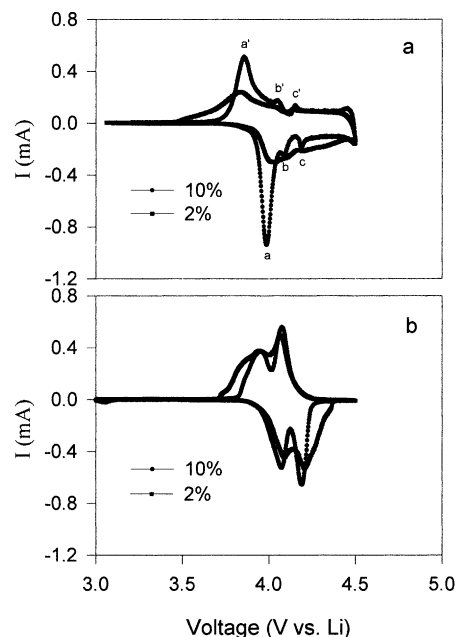


Fig. 1. Cyclic voltammograms (at 0.03 mV s^{-1}) for (a) LiCoO₂; (b) LiMn₂O₄ cathodes of different carbon loadings.

charging (1 mA cm^{-2} and above). LiCoO₂ cathode charged at the highest rate (2 mA cm^{-2}) can still deliver good capacity if it is loaded with 10% of carbon. The LiMn₂O₄ cathodes are generally less sensitive to the carbon content. However, they do show a more drastic decrease in capacity with increasing rate of charging.

3.3. Slow-scan cyclic voltammetry

Typical cyclic voltammograms of the LiCoO₂ electrodes at 0.03 mV s^{-1} are shown in Fig. 1a. Three pairs of well-separated peaks are found. The peaks at 3.98 V (a, largest), 4.08 V (b), and at 4.18 V (c) due to Li⁺ intercalation, and the corresponding peaks at 3.85 V (a'), 4.07 V (b'), and 4.17 V (c') due to Li⁺ de-intercalation, are in good agreement with

Table 1

Charge and discharge capacities per gram of active material at three different carbon loadings and different charging rates^a

Carbon (wt.%)	0.4 mA cm ⁻² to 4.3 V		1 mA cm ⁻² to 4.3 V		2 mA cm ⁻² to 4.3 V	
	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)
LiCoO ₂						
2	146.9	140.6	129.2	127.1	116.4	115
5	156.1	147.0	137.3	133.7	127.2	125.9
10	158.3	150.0	148.4	146.3	144.6	142.9
Carbon (wt.%)	0.4 mA cm ⁻² to 4.5 V		1 mA cm ⁻² to 4.5 V		2 mA cm ⁻² to 4.5 V	
	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)	Q _c (mAh g ⁻¹)	Q _d (mAh g ⁻¹)
LiMn ₂ O ₄						
2	120.0	118.4	111.4	109.8	96.8	95.7
5	124.0	121.1	112.5	110.3	101.0	100.0
10	128.9	127.0	117.4	115.0	105.1	104.0

^a Discharge was carried out at the constant rate of 0.4 mA cm^{-2} (26.7 mA g^{-1}).

the published data of Plichta [4], Dahn [5] and Uchida [6]. The peaks are stronger and sharper in the LiCoO₂ cathode with 10% carbon. At 2% of carbon loading, the peaks are generally broader and the voltammetric response is typical of a frustrated electrochemical system. Since the pasted-electrode is resistive and porous with a high surface area, the diffusion of Li⁺ in low carbon electrodes may be rate limited by inter-particle transfer of electrons. The voltammetric features can be greatly distorted even at very slow-scan rates. Adequate amount of carbon (e.g. 10% carbon) has to be used to obtain a truer electrochemical response.

The cyclic voltammograms of the LiMn₂O₄ cathodes are shown in Fig. 1b. According to Tarascon and Guyomard [7,8], the two peaks seen for both the reduction and oxidation reactions are indications of Li⁺ insertion and extraction occurring in stages. The accumulated charges of the two redox pairs are essentially equal, suggesting that in each stage lithium-ions occupy about half of the total available crystallographic sites. The separation between the redox pairs is more distinct at the higher (10%) carbon loading, even though the influence of carbon loading on the voltammetric features is not as pronounced as in the case of LiCoO₂.

3.4. Effect of carbon loading on cathode cyclability

Fig. 2 shows the cyclability of the LiCoO₂ and LiMn₂O₄ cathodes at three different carbon loadings. The LiCoO₂ electrodes were charged at different rates (0.4 and

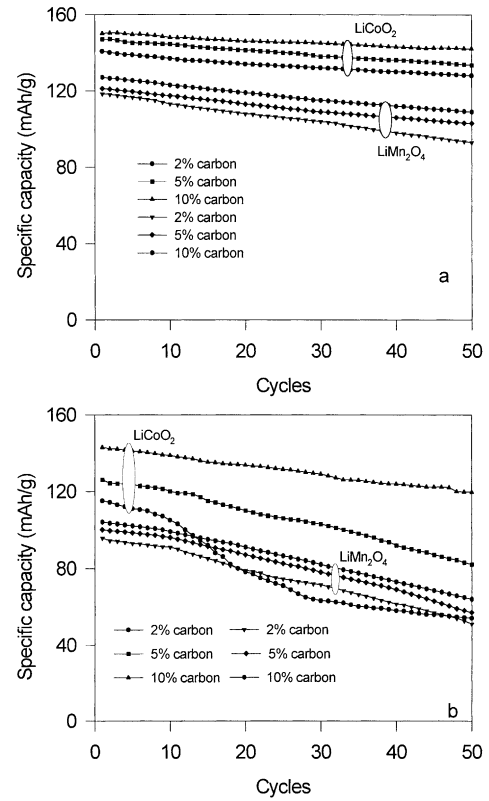


Fig. 2. Dependence of cyclability of LiCoO₂ and LiMn₂O₄ cathodes on carbon contents: (a) charging at 0.4 mA cm⁻²; (b) charging at 2 mA cm⁻².

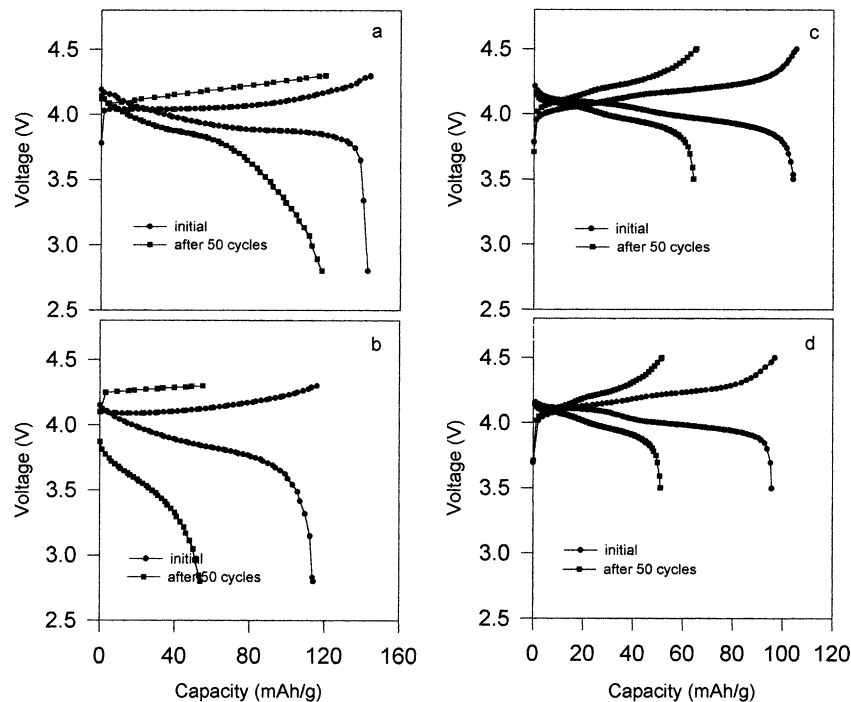


Fig. 3. Charge and discharge profiles in the 1st and the 50th cycles of LiCoO₂ cathodes: (a) with 10% carbon; (b) with 2% carbon, and LiMn₂O₄ cathodes; (c) with 10% carbon; (d) with 2% carbon.

2 mA cm^{-2}) to 4.3 V and discharged at the same rate (0.4 mA cm^{-2}) to 2.8 V. It is apparent that a low charging rate benefits all three LiCoO_2 electrodes in terms of acceptable capacity fades. Capacity fades are accelerated after charging at 2 mA cm^{-2} , with the 2 and 5% carbon loaded cathodes showing higher degrees of deterioration compared to the 10% carbon loaded cathode. For the LiMn_2O_4 cathodes which were charged and discharged in a likewise manner (0.4 or 2 mA cm^{-2} to 4.5 V and 0.4 mA cm^{-2} to 3.5 V), the effect of carbon loading at the low charging rate is similar to that in the LiCoO_2 electrodes. The discharge capacities of LiMn_2O_4 are noticeably lowered by increasing the charging rate, but the cyclability of the electrodes is not as dramatically reduced by a lower carbon content as in the case of LiCoO_2 . These results indicate the importance of carbon content on cyclability, particularly for the LiCoO_2 cathode. Good capacity retention for cathodes charged at a high current density (2 mA cm^{-2}) may be obtained in

practice with 5–10% of carbon for the LiCoO_2 cathode, and 2–5% of carbon for the LiMn_2O_4 cathode. This advantage is however, realized at the expense of lower energy and power contents of the resulting cells, as electrically conductive but electrochemically inactive carbon necessarily adds weight and volume to the cells.

The rapid loss of capacity in electrodes with low carbon contents charged at the higher rate (2 mA cm^{-2}) comes primarily from incomplete charging. Fig. 3 compares the charge and discharge profiles in the 1st and the 50th cycles of LiCoO_2 and LiMn_2O_4 cathodes containing 10 and 2% of carbon black, respectively. The inability of the latter electrode to be adequately charged in the 50th cycle is rather eminent. Consequently, the discharge capacity, which scales with the charged capacity, is correspondingly lower. Incomplete charging was caused by high cathode polarization resulting from deteriorating electrical contacts between oxide and carbon particles.

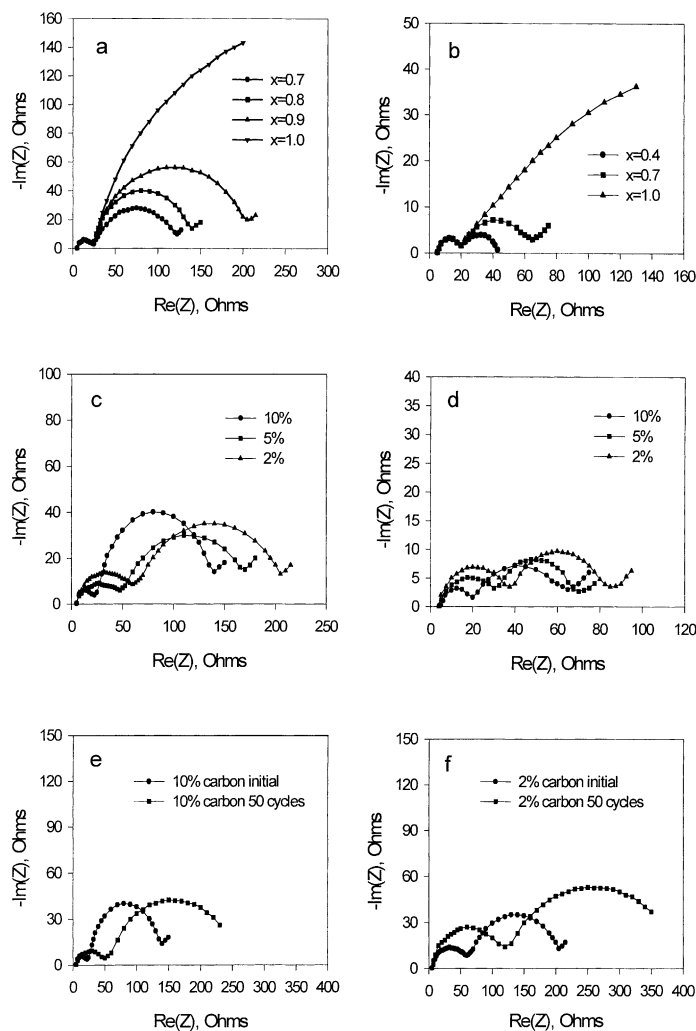


Fig. 4. Nyquist plots of (a) LiCoO_2 cathode with 10% of carbon at different x values; (b) LiMn_2O_4 cathode with 10% of carbon at different x values; (c) $\text{Li}_{0.8}\text{CoO}_2$ cathode for different carbon loadings; (d) $\text{Li}_{0.7}\text{Mn}_2\text{O}_4$ cathode for different carbon loadings; (e) LiCoO_2 cathode with 10% carbon in the 1st and the 50th cycle; (f) LiCoO_2 cathode with 2% carbon in the 1st and the 50th cycle.

3.5. Electrochemical impedance spectroscopy

The electrochemical impedance of the Li_xCoO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes was examined for various x values. Fig. 4a and b show the corresponding Nyquist plots. The impedance spectra of Li_xCoO_2 for $x < 0.9$ and that of $\text{Li}_x\text{Mn}_2\text{O}_4$ for $x < 0.7$ contain two clearly separated semi-circular arcs and a spur at approximately 45° to the real axis occurring in the frequency range of 0.01–0.001 Hz. The (smaller) high frequency arc can be categorically attributed to the impedance at the cathode/electrolyte interface, the mid frequency arc to the impedance from charge-transfer reactions, and the spur to a Warburg-like impedance from the diffusional transport of electroactive species [9]. As the magnitude of the high frequency arc remains nearly constant when the lithium content in the oxide cathodes varies, the high frequency arc is a manifestation of the resistance and capacitance at the particle-to-particle contacts in the cathode. It is noted that the semicircle at medium frequencies becomes smaller when more lithium-ions are extracted from the oxide lattice.

Fig. 4c and d show the impedance spectra of $\text{Li}_{0.8}\text{CoO}_2$ and $\text{Li}_{0.7}\text{Mn}_2\text{O}_4$ at three different carbon loadings. The magnitudes of the high frequency arcs in both figures increase with the decrease in carbon contents. This illustrates that the oxide and carbon particles are in good contact in the densely loaded (10%) cathode, but are not contacted as satisfactorily in the lightly loaded (2%) cathode. In contrast, the magnitude of the middle frequency arc is almost not affected by the carbon content, confirming that the latter arise mainly from intra-particle charge-transfer reactions.

The impedance spectra of LiCoO_2 electrodes with 2 and 10% of carbon were also measured after repeated cycling (Fig. 4e and f). The initial diameters of the high frequency arcs are nearly the same for these cathodes. The diameters increase steadily with cycling but the rate of increase is faster for the electrode with 2% carbon, indicating a more substantial increase in the cathode resistance. The change in the diameters of the mid frequency arcs also follows a similar trend. The increase in the size of both arcs can be interpreted as an increase in contact resistance and the increasing difficulty in Li^+ intercalation and de-intercalation reactions over time. The combined effect leads to an overall high cell polarization, resulting in incomplete charging of the electrodes and hence the apparent capacity loss.

4. Conclusions

The effects of conducting carbon loading on the electrochemical performance of LiCoO_2 and LiMn_2O_4 cathodes were investigated by constant current charging and discharging, cyclic voltammetry and electrochemical impedance spectroscopy. In general the LiCoO_2 electrode is more sensitive to the amount of carbon, particularly at high charging current densities where good charge and discharge capacities can only be obtained with an excess of carbon. In cyclic voltammetry, the LiCoO_2 electrode with 10% carbon displays stronger and sharper redox peaks, whereas broad voltammetric features typical of a frustrated electrochemical system are obtained from an electrode with 2% of carbon. The sequential insertion and extraction reactions of Li^+ in LiMn_2O_4 are also more distinct in the presence of 10% of carbon. Good capacity retention at high charging rate (2 mA cm^{-2}) may be obtained in practice with 5–10% of carbon for the LiCoO_2 cathodes, and 2–5% of carbon for the LiMn_2O_4 cathodes. The large capacity loss of low carbon cathodes at the high charging rate comes primarily from incomplete charging caused by cathode polarization resulting from the resistive electrical contacts between oxide and carbon particles.

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