

The role of carbon black distribution in cathodes for Li ion batteries

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Abstract

The influence of carbon black distribution/arrangement in cathode composite on cathode performance is studied using three types of active materials: LiMn_2O_2 -spinel, LiCoO_2 , and LiFePO_4 . To the active materials, carbon black is added in two different ways: (a) using a conventional mixing procedure and (b) using a novel coating technology (NCT) invented in our laboratory. Different technologies yield different arrangement (distribution) of carbon black around active particles. It is shown that the uniformity of carbon black distribution affects significantly the cathode kinetics, regardless of the type of active particles used. A simple model explaining the influence of carbon black distribution on cathode kinetics is presented.

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Keywords: Li ion batteries; Cathode; Carbon black; Kinetics

1. Introduction

To increase the poor electronic conductivity of oxide cathodes, a certain amount of electronic conductor, such as carbon black, is usually added to the active particles. Ideally, the particles of electronic conductor should be available at every spot on the surface of active particle in order to allow for simultaneous insertion/deinsertion on the whole surface (Fig. 1), thus maximizing the current density and minimizing the local stress and heating due to inhomogeneous mass and electrical transport.

In practice, it turns out that it is very difficult to control and design the carbon black arrangement in cathode composites. Actually, the problem seems to be underestimated or even ignored. Recently, as the particles size is decreasing to sub-micron dimensions, these problems are becoming even more relevant. For example, we have shown in a previous paper [1] that the conventional technology of cathode preparation, in which the constituents are simply mixed together, yields quite non-uniform distribution of carbon black in the final cathode composite. Consequently, the polarisation is much higher than if the active particles surface is pre-treated to induce a very uniform distribution of carbon black around active particles (we patented such a

procedure as a novel coating technology (NCT) [1]). In our case, the pre-treating agent has been gelatin. After pre-treatment, the thin film of gelatin around each active particle serves as a sort of glue which, in dispersions, catches smaller particles, such as carbon black. At the end of the procedure, carbon black is uniformly deposited all over the surface of each active particle. Hence, the arrangement of carbon black becomes close to the ideal one.

In the present paper, we investigate the impact of carbon black distribution on cathode kinetics using three different active materials: LiMn_2O_2 -spinel, LiCoO_2 , and LiFePO_4 . These materials are not only different in composition but also in particle geometry, size and surface morphology. We expected that the diversity of active materials would help us evaluate (a) if NCT is generally applicable to various cathode active materials and (b) if a more uniform carbon black distribution always—i.e. regardless of the type of active material—leads to a faster electrochemical kinetics.

2. Experimental

(a) Conventional procedure of cathode preparation:

The active materials were Merck SP30 LiMn_2O_4 (average particle size 30 μm), Merck SC20 LiCoO_2 (average particle size 7 μm), and LiFePO_4 (particle size 0.5–1.0 μm) delivered kindly by M. Armand, J. Thomas and N. Ravet. Each active material was mixed with a Teflon dispersion and

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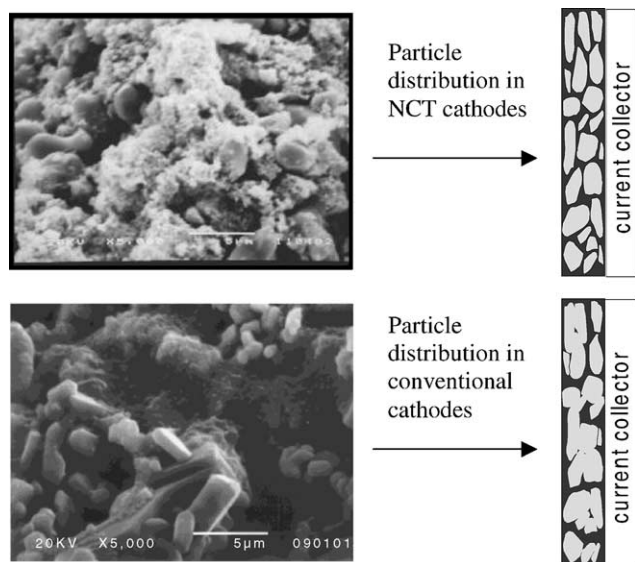


Fig. 1. SEM micrographs of cathode materials and sketches of cathodes obtained via the novel coating technology (NCT) (above) and via a conventional mixing procedure (below). On SEM micrographs, carbon black is visible as powder dispersed among the larger LiCoO_2 crystals. The grey particles on the sketches represent active particles and the black areas correspond to a mixture of carbon black and binder.

carbon black (Printex XE2). The slurry was then deposited on an aluminium substrate to obtain an electrode of a thickness of $80\ \mu\text{m}$ ($5\text{--}7\ \text{mg}$ of active material).

(b) *NCT procedure:*

The same active materials as in procedure (a) were used. Gelatin (Fluka) was dissolved in water and the solution was modified using NaOH, KOH or LiOH to set pH to a pre-selected value. The active particles were immersed into the modified gelatin solution. Then, a dispersion of carbon black particles (Degussa, Printex XE2) was added to the gelatin-pre-treated active particles. To the obtained mixture, an additional amount of gelatin solution was added to bind the carbon black-covered active particles. The amount of gelatin in the final composite material did not exceed 2 wt.%. The electrodes were prepared in the same way as in procedure (a).

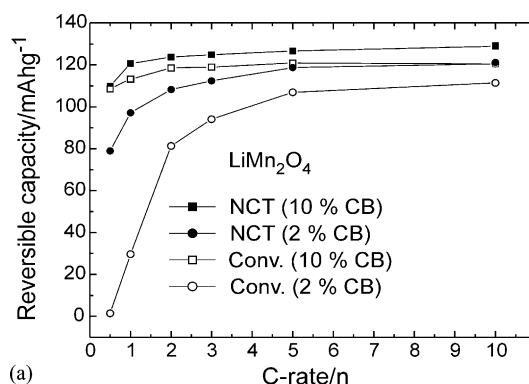
A laboratory-made three-electrode test cell was used to carry out the electrochemical tests. The cell construction is described elsewhere [2,3]. The working and the counter (lithium) electrodes were held apart with two separators (Celgard No. 2402) between which a thin strip of lithium serving as a reference electrode was positioned. In all cases, the electrolyte used was a 1 M solution of LiPF_6 in EC:DMC (1:1 ratio by volume), as received from Merck.

Charge–discharge curves were recorded using a Solartron 1286 Electrochemical Interface or EG&G Model 283. The constant current during cell cycling was set to a value between $25\ \mu\text{A}$ and $1\ \text{mA}$ (corresponding roughly to $C/20$ to $2C$), and the geometric surface area of the working electrode was always $0.5\ \text{cm}^2$. Scanning electron micrographs were

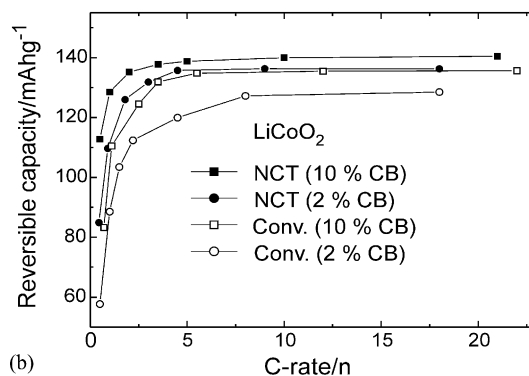
obtained using a JEOL JSM-T220 Scanning Electron Microscope. Before that, the samples were sputtered by gold using a Balzers SCD 050 Sputter Coater.

3. Results and discussion

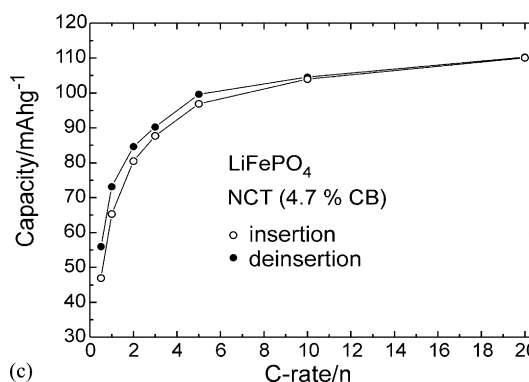
SEM micrographs show that the novel coating technology (NCT) gives much more uniform distribution of carbon



(a)



(b)



(c)

Fig. 2. Capacity as a function of C-rate for (a) LiMn_2O_4 , (b) LiCoO_2 and (c) LiFePO_4 . C-rate is the inverse of time expressed in hours needed to reach the theoretical capacity of the given electrode at selected constant current. The geometric surface area of the working electrode was always $0.5\ \text{cm}^2$, while the typical mass of active material was $3 \pm 0.5\ \text{mg}$. A given C-rate curve was obtained by measuring charge/discharge curves of selected electrode at various values of constant current. Prior to that each electrode was cycled in order to avoid the artefacts associated with initial cycles.

black in the cathode material when compared to the distribution obtained using the conventional mixing procedure (Fig. 1). This feature was observed with all three types of active materials, indicating that NCT is an effective procedure, which quite generally leads to a more uniform carbon black distribution, i.e. regardless of the type of active material used. A more uniform carbon black distribution, in turn, always leads to a lower polarisation and, consequently, to a higher reversible capacity at given carbon black content and given current density (Fig. 2). Some examples even show that a much lower content (e.g. 2 wt.%) of uniformly distributed carbon black gives better kinetics than a higher content (e.g. 10 wt.%) of non-uniformly distributed carbon black (Fig. 2b). The effect of uniformity of carbon black distribution is most expressed in the case of largest active particles (LiMn_2O_4). This result is more or less expected. In the case of smaller particles, the size of carbon black particles (ca. $0.2\ \mu\text{m}$) becomes comparable to the size of active particles ($0.5\ \mu\text{m}$ in the case of LiFePO_4), so arranging of the former around the latter becomes more difficult than when the size ratio is more extreme. Nevertheless, also in this inconvenient case, NCT procedure gives significantly better results than simple mixing. For example,

the result of Fig. 2c is comparable to the result of reference [4] where the same type of active material was used but the content of carbon black (acetylene black) was much higher, i.e. 25% while the present cathodes contain only 4.7 wt.% of carbon black.

In the last series of experiments, we wanted to make additional tests if it is really only carbon black distribution, which affects the electrochemical properties. Namely, one might speculate that, beside the particle arrangement, there are other procedure-specific parameters, which can have effect on electrochemical features of cathodes. For example, NCT involves gelatin while the conventional simple mixing does not. So we prepared two sets of cathodes, both via NCT and with the same carbon black and gelatin contents, but with different carbon black arrangement. This was possible by simply using gelatin solutions of different pH values. As shown in our previous papers [5–7] and elsewhere in literature [8], pH has an important effect on the shape of gelatin molecules, which affects the adsorption properties of gelatin and, hence, the uniformity of subsequent carbon black deposition. For example, at isoelectric point (pH 9) a large amount of gelatin is adsorbed on substrate—however, the adsorption is quite non-uniform

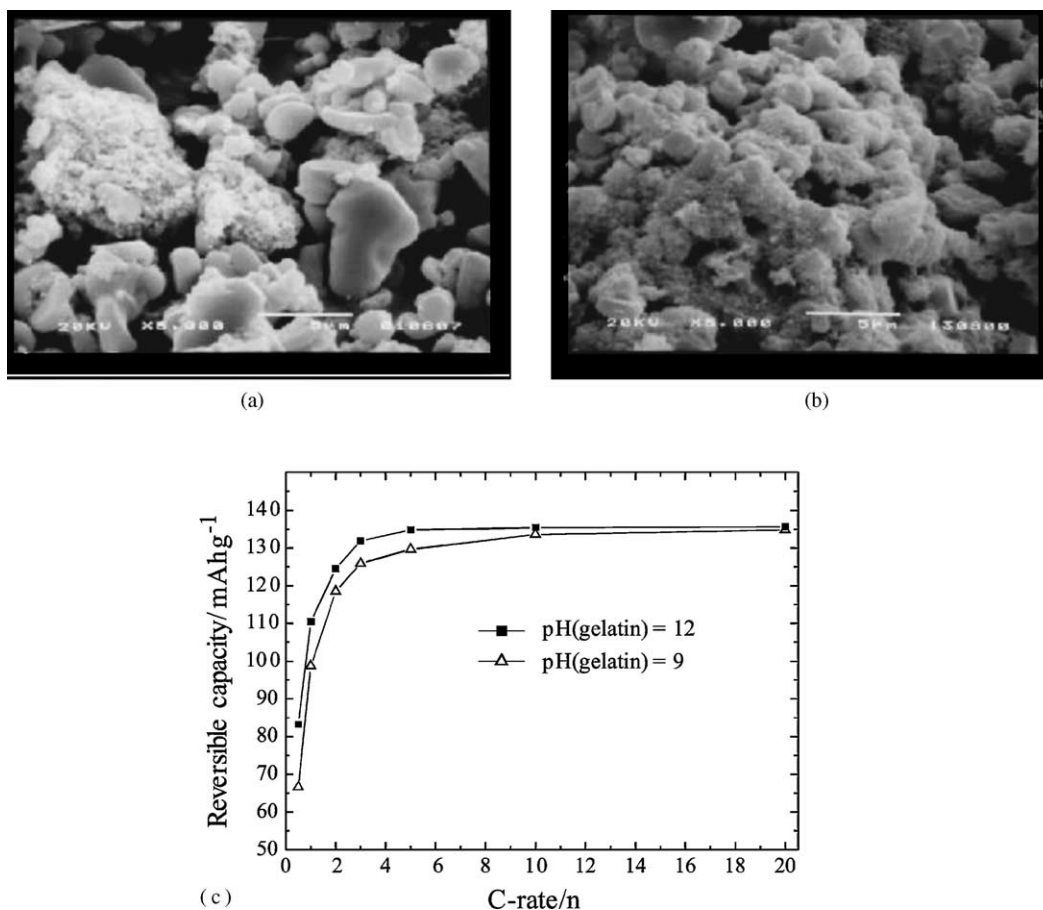


Fig. 3. Distribution of carbon black among LiCoO_2 in the case when gelatin solution had a pH of (a) 9 and (b) 12. (c) Reversible capacity as a function of C-rate for cathode materials under (a) and (b). The cycling conditions were the same as those described in Fig. 2.

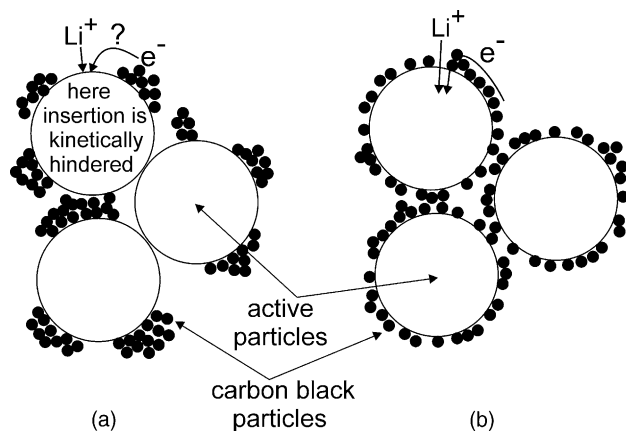


Fig. 4. A sketch indicating the possible impact of carbon black (electron conductor) on kinetics of Li^+ /electron electrochemical insertion into active particles.

(gelatin tends to form agglomerates). Conversely, at pH 12 much less gelatin is adsorbed (at least five times less), however, in this case the adsorption is very uniform resulting in a few nm thin gelatin layer. Once gelatin is adsorbed on active particles, it attracts gelatin-free particles in the surroundings, in our case carbon black which is added to the gelatin-treated active particles. Now, it seems reasonable to assume that the distribution of gelatin on the active particles will determine the distribution of consequently deposited carbon black which is directly attracted and bonded by gelatin molecules. We checked this hypothesis in experiments shown in Fig. 3a and b. It can be seen that carbon black is more uniformly deposited if gelatin has a pH value 12 than if the value is 9. Again, the electrochemical performance (Fig. 3c) is clearly correlated to the uniformity of carbon black distribution.

The results of Figs. 3 and 4 can be explained with the mechanism proposed in Fig. 4. In order for insertion to occur without excessive polarisation, both the Li^+ ion and the electron have to be available at the same spot (Fig. 4b). By contrast, if a part of active material is not in contact with an electronic conductor (Fig. 4a), the supply of electrons to this spot will be reflected in additional polarisation and, hence, in a lower reversible capacity.

4. Conclusions

Using three different active materials, we have shown that the distribution of carbon black in cathode composites is a crucial parameter determining the cathode performance. A simple model has shown that in order to minimize the polarisation due to insertion, carbon black (or alternative electron conductor) must be uniformly distributed around each active particle. In terms of cathode performance, the lower polarisation leads to a higher reversible capacity at all C-rates and at all cycle numbers investigated. For example, in the case of LiCoO_2 , even a much lower content (2 wt.%) of uniformly distributed carbon black gives better kinetics than a higher content (10 wt.%) of non-uniformly distributed carbon black.

Acknowledgements

This research was sponsored by NATO's Scientific Affairs Division in the framework of the Science for Peace Programme. The financial support from the Ministry of Science and Technology of Slovenia is also fully acknowledged. The authors thank to Profs. M. Armand and J. Thomas and Dr. N. Ravet for providing LiFePO_4 .

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