Structure of Polyaniline and Its Influences on the Electrochemical Performance of LiCoO₂ Cathode for Lithium Ion Batteries

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Polyaniline synthesized by chemical polymerization is replace acetylene black to be used as the conductive additive of LiCoO₂ cathode. FTIR shows that polyaniline prepared possesses the typical features of conductive emeraldine salts. The conductivity of polyaniline is 15.29 S cm⁻¹ which is more than that of acetylene black. Polyaniline has some discharge capacity in the potential range of cathode, so it can be used as the cathode material. The conductivity changes of LiCoO₂ cathode film with the increase of the content of conductive additive conform to the percolation theory. The conductivity of cathode reaches its maximum value of 4.02×10^{-1} S cm⁻¹ when the content of polyaniline reaches 15 wt. %, which is much bigger than that of acetylene black. The electrochemical performances of LiCoO₂ cathode is improved remarkably. The discharge capacity of LiCoO₂ cathode is 95.9 mAh g⁻¹ at the current density of 170 mA g⁻¹. Its charge transfer resistance is much lower than that of acetylene black in the 20 cycle. The resilience of polyaniline reduces the expansion and contraction of LiCoO₂, which keeps the conductive network integrity.

Key Words: Lithium ion batteries, Polyaniline, LiCoO₂, Percolation theory, Electrochemical performances.

INTRODUCTION

Because of the high potential platform and the good electrochemical performances of LiCoO₂, this is widely used as the cathode of lithium ion batteries. As a semiconductor, its low conductivity will deteriorate its rate performances.

The surface of LiCoO₂ is coated with conductive materials such as silver[1], carbon black[2], carbon nanolayer[3], multi-walled carbon nanotubes[4] and ionic liquids[5], which can enhance the electric conductivity of the active materials.

Adding conductive additives to the cathode film can strengthen its electrochemical performance. Besides the use of acetylene black as a conductive additive, super phosphorus[6], vapour growth carbon fiber[7], multi-walled carbon nanotubes[8,9] and nano composite conductive additive[10] which is composed of multi-walled carbon nanotubes and acetylene black can be used as the conductive additives of cathode. These materials can improve the electrochemical performances of cathode to some degree. But there are some drawbacks, which lead to the fact that it has not been widely used. First, the aspect ratio of carbon fibers or multi-walled carbon nanotubes is too big, so it is difficult to make them mixed with active materials homogeneously in the preparation of an electrode. Besides, their price is much higher than that of acetylene black, the best

conductive additive should be cheap and isotropic powder particles with high electric conductivity and small aspect ratio.

Conductive polymer has drawn great attention since the electric conductivity of polyacetylene can be turned out to be 10^3 S cm⁻¹ in the research[11]. Polyaniline has some striking features such as cheap materials, simple synthesis, high electric conductivity and good environmental stability. There are few reports on the application of polyaniline in the LiCoO₂ cathode.

In this paper, polyaniline synthesized with the high conductivity of 15.29 S cm⁻¹ was used to replace acetylene black in LiCoO₂ cathode. Percolation theory was applied to discuss the relationships between the conductivity of LiCoO₂ cathode film and the content of conductive additives acetylene black and polyaniline. The electrochemical performances of LiCoO₂ cathode film using polyaniline were systematically investigated.

EXPERIMENTAL

Preparation of samples: Conductive polymer polyaniline was synthesized by a chemical oxidative method as described elsewhere[12]. It was prepared in the media of hydrochloric acid and ammonium persulfate was used as oxidant.

Sample characterization: X-ray diffraction was performed on D-MAX2500VB diffractometer (Rigaku Co. Japan). The morphology was investigated by JSM-6700F scanning electron microscopy (SEM, Japan electronic Co. Japan). Fourier transform infrared spectroscopy (FTIR) was determined with a Nicolet 6700 (Thermo Fisher Scientific Co., USA). The electronic conductivity of powder and film samples was determined at the pressure of 4.90 MPa by the connection of a GM-II resistivity tester (Coal Chemistry Institute, China) and a 34401A type 6 1/2 Digit multimeter (Agilent Co., USA).

Characterization of electrochemical performances: Cathode films were prepared by mixing $LiMn_{1.95}Al_{0.05}O_4$ with acetylene black or polyaniline and binder polytetrafluoroethylene. The charge and discharge performances were examined by a BT2000 battery testing system (Arbin Co. USA) at various current densities in the range of 3.300-4.300 V (*vs.* Li+/Li). Electrochemical impedance spectra and cyclic voltammetry were performed by using a CHI 660c electrochemical workstation (Chenhua Co., China). The amplitude of potential was 5 mV and the frequency was from 100 kHz to 0.01 Hz. The potential scan rate of cyclic voltammetry was 0.1 mV s^{-1}.

RESULTS AND DISCUSSION

Structure and performance of polyaniline: Conductive polymer polyaniline is synthesized with the optimal conditions of chemical oxidative method. Its FTIR spectrum is illustrated in Fig. 1. The peaks at 1573 and 1493 cm^{-1} belong to quinonoid and benzenoid ring-stretching deformations, respectively. The absorption bands at 1373 and 1301 cm^{-1} are assigned to π-electron delocalization in polyaniline induced by the protonation. The characteristic peak of protonated polyaniline is at 1240 cm^{-1} and can be looked as a C-N$^{+\cdot}$ stretching vibration in the polaron structure. The 1134 cm^{-1} peak corresponds to a vibration of -NH$^{+\cdot}$= structure. The out-of-plane deformations of C-H on rings are located at 800 cm^{-1}. Therefore, polyaniline prepared possesses the typical features of conductive emeraldine salts.
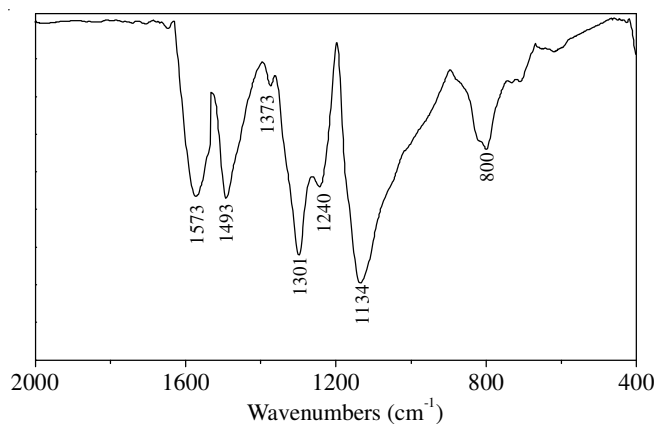

Fig. 1. FTIR spectrum of polyaniline in 2000-400 cm^{-1} region

The conductivity of polyaniline prepared under the optimal conditions[12] is 15.29 S cm^{-1}, which is much larger than that of acetylene black (7.77 S cm^{-1}).

The cyclic voltammograms of polyaniline in the 1st and 20th cycle are given in Fig. 2. It shows that polyaniline possesses the charge and discharge capacity in potential range of cathode. Note that the carriers are PF$_6^-$ but not Li$^+$. When polyaniline is used as a cathode active material, its charge capacity is associated with the doping and de-doping of PF$_6^-$ in electrolyte on the polymer chain as shown below.

$$[PAn^0]^{-e} + PF_6^- \leftrightarrow [PAn^+] PF_6^-$$
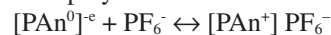
After the integration of discharge curve in the 1st cycle, we know that its discharge capacity is 45.6 mAh g^{-1}. The capacity declines very slowly in 20 cycles. Therefore, polyaniline can be used as not only conductive additive, but also cathode.
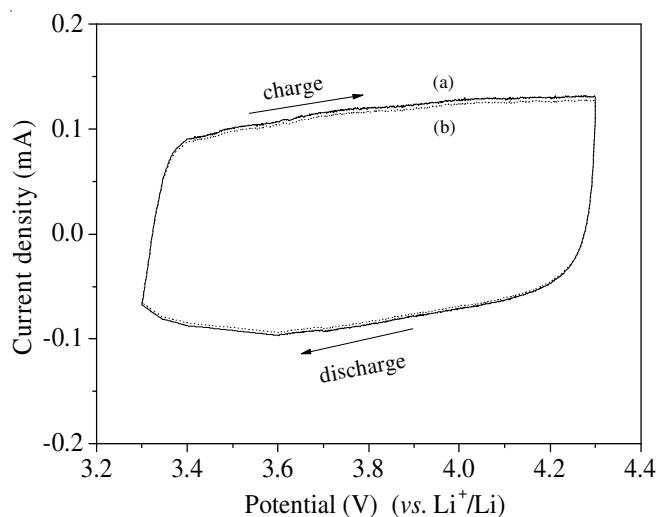

Fig. 2. Cyclic voltammograms of polyaniline in the 1st cycle (a) and 20th cycle (b)

Structure and performance of LiCoO₂: XRD patterns of $LiCoO_2$ and standard $LiCoO_2$ are presented in Fig. 3. The lattice parameters are given in Table-1. In comparison, the peak and relative intensity of every diffraction peak is in tune with the standard spectra. The sharp peak and the good symmetry reveal that crystals of $LiCoO_2$ powder samples are perfect. Diffraction peaks (006) and (012) or (108) and (110) are well separated, which proves the stability of their layer structures. The c/a of $LiCoO_2$ powder samples is quite the same as standard powders, which shows that there is no disorder arrangement of cations in $LiCoO_2$ powder samples.
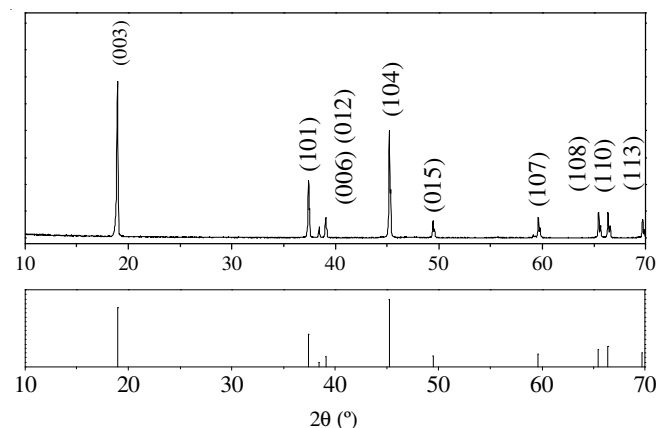

Fig. 3. XRD pattern of $LiCoO_2$

TABLE-1
LATTICE PARAMETERS OF LiCoO₂ SAMPLES

Samples	a (nm)	b (nm)	c (nm)	c/a
LiCoO₂	0.28142	0.28142	1.40421	4.990
Standard LiCoO₂	0.28149	0.28149	1.40493	4.991

Fig. 4 gives the morphology image of LiCoO₂. From the Fig. 4, it is noted that the surface of LiCoO₂ powder is smooth, their boundary is clear and no impurities exist in LiCoO₂ powders. In addition, their particle sizes are in uniform distribution.
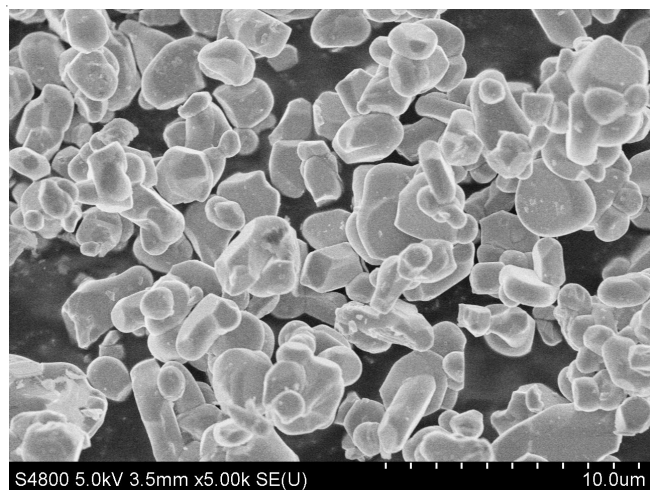

S4800 5.0kV 3.5mm x5.00k SE(U)   10.0um

Fig. 4. SEM image of LiCoO₂

Percolation theory analysis: The electric conductivity of LiCoO₂ cathode films is changed with the volume percentage of polyaniline and acetylene black (Fig. 5). From the Fig. 5, we can see that when the volume percentage of polyaniline in the LiCoO₂ cathode films is 2.50 %, the electric conductivity of LiCoO₂ cathode films stays $ca.$ 10^{-6} S cm^{-1}, but polyaniline particles in the LiCoO₂ anode films are reducing, which makes the effective link difficult. When the volume percentage of polyaniline in the LiCoO₂ cathode films adds up to 5 %, the electric conductivity rises rapidly and the volume percentage of conductive additives is its percolation threshold. When the conductive additive particles of cathode films reach a certain number, the effective conductive contact comes into being. When the volume percentage of polyaniline and acetylene black rises to 26.11 % and 28.54 % and each responding quality percentage is 15 wt.%, the electric conductivities of LiCoO₂ cathode films can get to the peak 4.02×10^{-1} S cm^{-1} and 3.21×10^{-1} S cm^{-1} respectively. But on increasing the volume percentage of the conductive additives, the electric conductivity of LiCoO₂ cathode films stays nearly the same. Experiments show when polyaniline is used as conductive additive, the electric conductivity of LiCoO₂ cathode films rises by 25.23 %, compared with acetylene black which has the same content and volume as polyaniline.

The scaling law, $\sigma(P-P_c)^t$, is often employed to analyze the percolation behaviour of conductive polymer composite[13,14]. σ in the equation represents the conductivity of LiCoO₂ cathode. P_c and P are the critical and actual content of conductive additive. t is the conductivity exponent and its value generally

reflects the dimensionality of the filler network in conductive composite. The value of t is between 1.6 and 2.0 for three dimensions composite. The results in Fig. 5 is be fitted after calculation. The exponent t of LiCoO₂ cathode are 1.10 and 1.03 according to the variation of log σ with log(P-P$_c$) when polyaniline and acetylene black is used.
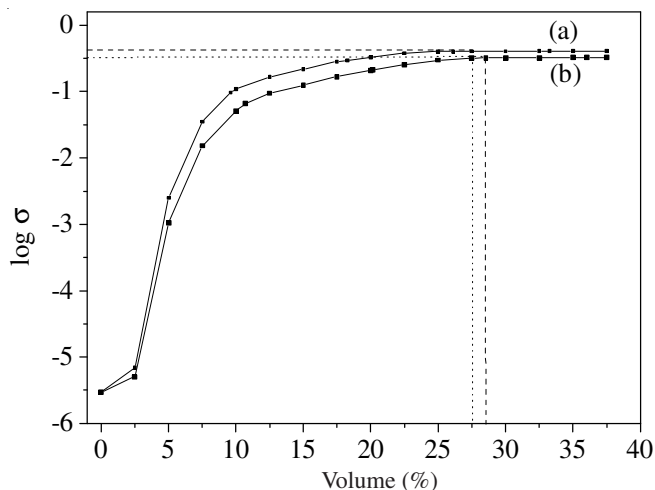

Fig. 5. Relationships between the conductivities of LiCoO₂ cathode film and the volume percentages of polyaniline (a) and acetyl black (b)

It should be noted that the LiCoO₂ cathode discussed here is different from conductive polymer composite in literature[13]. The content of polymer in the latter is more than 80 wt.%. However, the content of polymer polytetrafluoroethylene in cathode is only 5 wt.%. Hence, it is reasonable that difference exists between the t value obtained here and the typical value.

Rate performances: Fig. 6 gives the discharge curves of LiCoO₂ cathode under different current densities in the 3rd cycle when 15 wt.% polyaniline and acetylene black are used as conductive additives. When acetylene black is used as conductive additive, the discharge capacity of LiCoO₂ cathode decreases obviously and its potential profile drops quickly with the increase of current density. There is no platform and the discharge curve is an oblique line. The discharge capacity is only 66.3 mAh g^{-1} when current density reaches 170 mA g^{-1}.

However, the discharge curve of LiCoO₂ cathode decreases slowly with the increase of the current density when polyaniline is used. But its discharge curve still stays a high potential platform under the condition of 120 mA g^{-1}. Discharge capacity of LiCoO₂ cathode is more than that of acetylene black as a conductive additive. Compared with acetylene black, the discharge capacity of LiCoO₂ cathode containing polyaniline increases by 29.5 mAh g^{-1} when current density is 340 mA g^{-1}. This is because when polyaniline is used as conductive additive, the electric conductivity of LiCoO₂ cathode films rises by 25.23 % in comparison with acetylene black as a conductive additive. As the polarization of LiCoO₂ cathode reduces and the utilization of active materials increases, the ratio performance has been improved greatly.

Electrochemical impedance spectra: Fig. 7 shows that the electrochemical impedance spectra of LiCoO₂ cathode after 20 cycles when polyaniline and acetylene black with the content of 15 wt. % are used. Fig. 7 shows that when
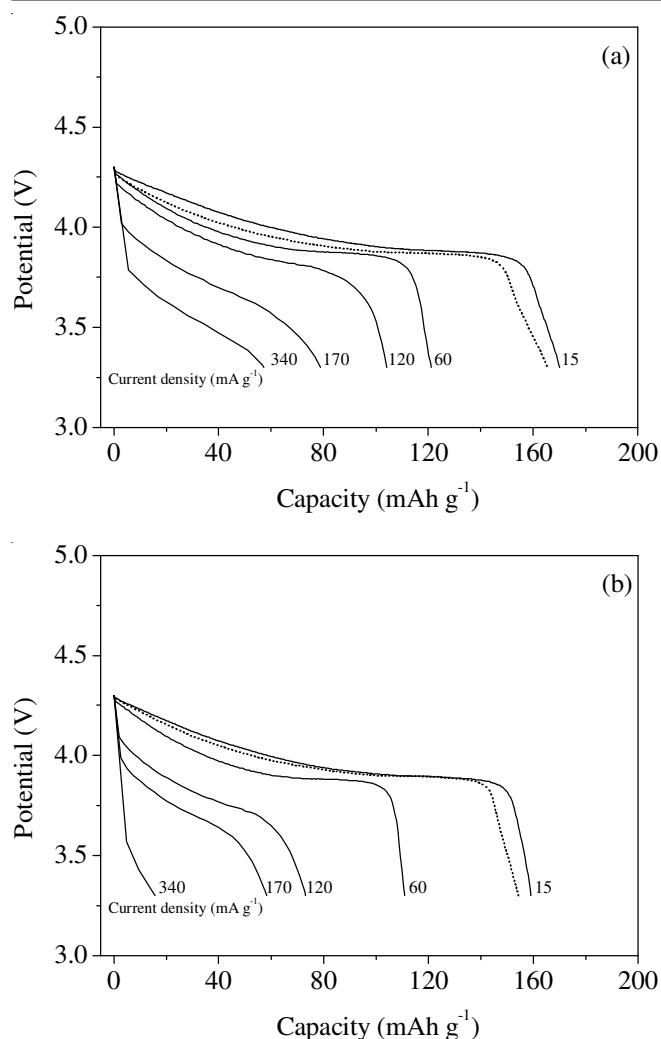
Fig. 6. Discharge curves of LiCoO₂ cathode in the third cycle under different current densities utilizing 15 wt. % polyaniline (a) and acetylene black (b) as conductive additives
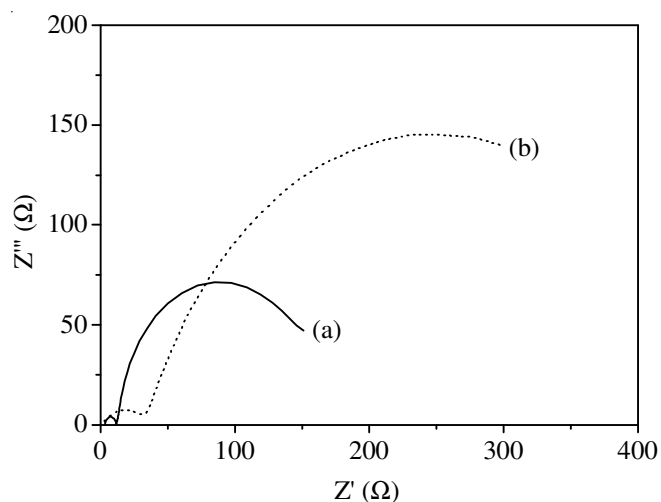

Fig. 7. Electrochemical impedance spectra of LiCoO₂ cathode in the 20th cycle using 15 wt. % polyaniline (a) and acetylene black (b) as conductive additives

polyaniline and acetylene black are used as conductive additives, the charge transfer resistance of LiCoO₂ cathode after 20 cycles is 123.6 O and 426.6 O, respectively. It is clear that the charge transfer resistance of LiCoO₂ cathode is much lower when polyaniline is used than that of acetylene black. Polyaniline is a kind of polymer material and its resilience can reduce the destruction to the conductive network caused by the expansion and contraction of LiCoO₂ in the charge and discharge process, so its conductive network is still integrity after 20 cycles.

Conclusion

Polyaniline synthesized by chemical polymerization possesses the typical features of conductive emeraldine salts. Its electric conductivity is 15.29 S cm⁻¹ which is more than that of acetylene black (7.77 S cm⁻¹). Polyaniline has some discharge capacity. Therefore, polyaniline can be used as not only conductive additive, but also the cathode materials. The relationships between the conductivity of LiCoO₂ cathode films and the content of conductive additive conform to the percolation theory. And the conductivity of cathode reaches its maximum value of 4.02×10^{-1} S cm⁻¹ when the content of polyaniline reaches 15 wt. %. When polyaniline is used as conductive additive, the electrochemical performances of LiCoO₂ cathode improved greatly. The discharge capacity of LiCoO₂ cathode is 95.9 mAh g⁻¹ at the current density of 170 mA g⁻¹. Because the resilience of polyaniline can reduce the expansion and contraction of LiCoO₂, conductive network of cathode stays in integrity after 20 cycles. When polyaniline is used, the charge transfer resistance of LiCoO₂ cathode in the 20th cycle is 123.6 Ω which is much lower than 426.6 Ω when acetylene black is used.

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