

Effects of C₆₀ film coating on the electrochemical performance of composite LiCoO₂ cathodes for lithium secondary batteries

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DOI: 10.5185/amlett.2018.6408

www.vbripress.com/aml

Abstract

In this work, LiCoO₂(LCO) composite electrodes were coated by fullerene C₆₀ thin film with different thickness of 60, 100 and 200 nm using a plasma thermal evaporation technique. The surface morphology of bare and coated samples was observed by scanning electron microscope (SEM). The electrochemical characteristics of the coated electrodes as cathode materials in Lithium Ion Batteries (LIB) were investigated by a galvanostatic charge-discharge tests at various C-rates between 3.0 and 4.5 V and compared with those of uncoated samples. An improvement of the performances of the coated electrodes in terms of higher initial coulombic efficiency, higher capacity retention and better rate capability was shown by the 60 nm thick C₆₀ coated LiCoO₂ electrodes. It can be said that the thin C₆₀ coating layer can minimize the dissolution of Co from the electrode to the electrolyte. As the thickness of coating layer was increased, the coated electrodes show a more severe capacity fade due to longer Li-ion diffusion path. Copyright © 2018 VBRI Press.

Keywords: LiCoO₂, fullerene, coating, cathodes, lithium battery

Introduction

Nowadays, lithium-ion batteries (LIBs) are known as the most leading energy storage devices for various applications in many electronic equipments such as laptop computers, cellular phones, camera and others. The application of LIBs are now extended for green transportation system such as hybrid electric vehicles [1]. This extended application require battery systems with enhanced electrochemical performances in terms of high energy and power density, excellent cycle profiles and more safety. Next to the anodes and the electrolytes, the cathode is one of the crucial components of LIBs since it affects the overall performance of the battery such as the specific capacity, charge-discharge profiles, cycle profiles, rate capability and thermal stability. LiCoO₂ (LCO) is the conventional cathode material which has been utilized in commercial LIBs [2]. The main advantages of LCO are the high specific capacity, good rate capability and high reversibility characteristics when it is cycled below cut-off voltage of 4.2 V (vs Li/Li⁺). Unfortunately, it has a limitation when it is cycled at voltages higher than 4.2 V. At the higher voltage, the rapid capacity fading is observed due to the dissolution of cobalt into the electrolyte. It is then followed by the structural changes of LCO and oxidative decomposition of the electrolyte [3].

Those typical problems can be solved by coating LCO with stable materials [4-8]. The coated LCO shows a much more improved electrochemical performances in terms of cycle stability, rate capability and thermal stability. However, the effect of the coating on the electrochemical performance of LCO is highly dependent on the coating material and its shape [4,5]. In this work, the electrochemical performance is evaluated for LCO coated with C₆₀ thin films by a plasma assisted thermal evaporation technique. Specifically, the main objective of this work is to investigate the effects of carbon film as the coating material and the coating thickness on cycle profile and rate capability. Our previous works related to the employment of C₆₀ coating on the surface of anode materials [9-12]. It is expected that the electrochemical performance of LiCoO₂ composite cathodes would be enhanced due to the presence of C₆₀ coating layer.

Experimental

Preparation of C₆₀ coated LiCoO₂

The LiCoO₂ composite cathodes were prepared by mixing the active material (LiCoO₂ powder – SEIMI Chemical Industrial Co.) with carbon black and poly-vinylidene fluoride (PVDF) binder in n-methyl pyrrolidone (NMP) solvent. The mixture was then coated on Al foil with

thickness of 20 μm . The C_{60} thin film was coated on the surface of LiCoO_2 cathodes using the plasma assisted evaporation technique. The evaporation chamber was operated at a base pressure of 1.5×10^{-5} Torr and a working pressure of 2.0×10^{-2} Torr at a plasma power of 150 W under an argon gas flow of 30 sccm. The substrate temperature was adjusted to a constant temperature of 150°C . The commercially available fullerene (C_{60}) powder was used as a raw coating material. The fullerene powder was evaporated and then it was deposited onto the LiCoO_2 cathodes. The deposition time of the fullerene film was varied to 10-30 minutes to control the coating film thickness.

SEM and EDS analysis

The surface morphology of the bare and C_{60} coated electrodes was observed by scanning electron microscope (SEM-Hitachi). The thickness of C_{60} coating layer is about 60, 100 and 200 nm for the deposition time of 10, 20 and 30 minutes, respectively. It may be noted that the estimation of the thickness of the deposited film is based on the thickness of the film deposited on a silicon wafer under similar process conditions. Electron dispersive spectroscopy (EDS) measurements were performed using a Hitachi scanning electron microscope.

Electrochemical characteristics

Electrochemical characteristics of the bare LiCoO_2 and C_{60} coated LiCoO_2 electrodes were investigated using half cells. Half cells were composed of the C_{60} coated LiCoO_2 as a working electrode, lithium metal as a counter and reference electrode and 1 M liquid electrolyte of LiPF_6 dissolved in the solvent mixture of ethylene carbonate-polyethylene carbonate-dimethyl carbonate (EC/PC/DMC). The cells were charged and discharged in the voltage range between 3 - 4.5 V with different C-rate (1, 1.5 and 2 C-rate) at room temperature by a Maccor battery tester. Cyclic voltammetry (CV) measurements were conducted at a scan rate of 0.05 mV/s between 3 and 4.5 V vs Li/Li^+ . Electrochemical impedance spectroscopy measurements were also conducted on cells using an impedance analyzer (Zahner IM6) with amplitude ratio of 5 mV and the frequency range from 10 mHz and 1MHz.

Estimation of the amount of cobalt dissolution in the electrolyte

To measure the dissolved amount of Co, sandwich-type half cells containing bare and C_{60} coated LiCoO_2 were charged to 4.5 V and then carefully disassembled in the dry room. The cathode materials were then peeled from the Al foil and were dissolved into the electrolyte at 50°C for 3 weeks. The amount of Co dissolution in electrolyte was estimated by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6100 DRC plus).

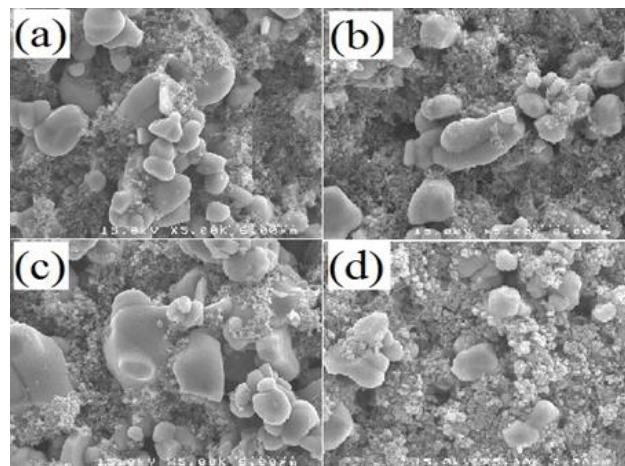


Fig. 1. SEM image of (a) bare LiCoO_2 electrode and (b) 60, (b) 100 and (c) 200 – nm- thick C_{60} coated LiCoO_2 electrode.

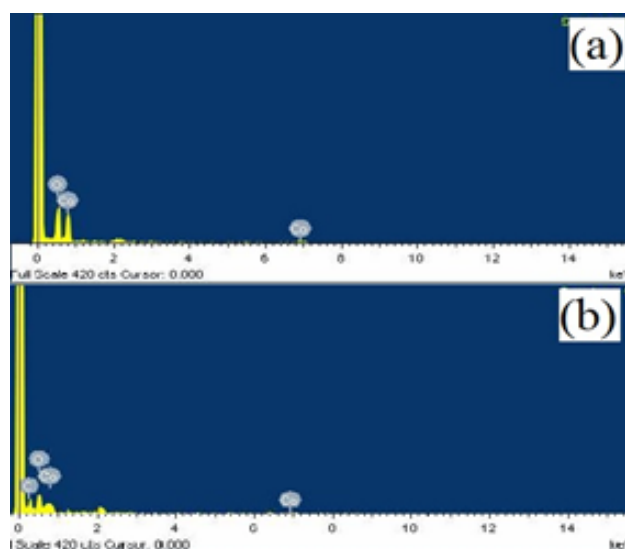


Fig. 2. EDS spectra of (a) bare and (b) C_{60} coated LiCoO_2

Results and discussion

Scanning electron micrographs of the bare and C_{60} coated LiCoO_2 electrodes are shown in **Fig. 1**. It can be seen that there are some fine particles on the surfaces of all samples and there is no obvious difference among them. EDS spectra of the bare and C_{60} coated LiCoO_2 electrodes are shown in **Fig. 2**, where the additional carbon peak are found in the case of coated samples. It implies that the coating layer of LiCoO_2 electrodes contains carbon.

Fig. 3 shows the first charge-discharge curves of the bare and C_{60} coated LiCoO_2 electrodes with different coating thickness at 1 C rate between 3.0 and 4.5 V. It can be seen that the initial coulombic efficiency for all the samples is higher than 90%, however the highest coulombic efficiency is obtained by the thinnest C_{60} coating layer of 60 nm. The coulombic efficiency is smaller when thicker C_{60} films (100 and 200 nm in thickness) are coated on the surface of LiCoO_2 cathodes.

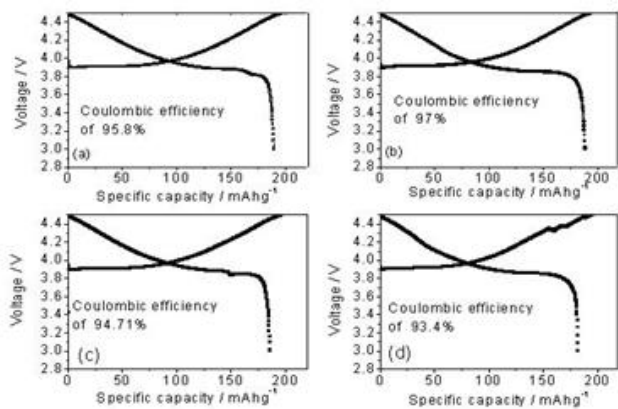


Fig. 3. Initial charge-discharge curves between 3.0 and 4.5 V at 1 C rate for (a) bare LiCoO₂ and LiCoO₂ electrodes coated by (b) 60, (c) 100 and (d) 200 nm thick of C₆₀ films.

The coulombic efficiency of bare electrodes is increased from 95.8% to 97% after the C₆₀ film coating of about 60 nm in thickness. Hence, we can say that the reversibility of LiCoO₂ cathodes may be improved by coating it with thin layer of C₆₀ film. The thin coating layer is responsible for protecting the cathode's surface against the side reaction with the electrolyte. The thicker coating layer may prohibit the transport of Li-ion at the electrode/electrolyte interface; therefore Li-ions can be trapped in the lattice of cathodes, producing a lower reversible capacity. The thicker coating layer causes the longer diffusion length of Li-ions from the electrodes surface to the electrolyte sides.

Fig. 4 shows the CV curves of the bare and C₆₀ coated LiCoO₂ electrodes at a scan rate of 0.05 mV/s which were measured during the first five cycles. It can be observed that the two CV profiles are quite different. In the case of bare electrodes, the oxidation peak is broad and located at 4.08 V, while reduction peak at 3.88 V so its potential difference is about 0.2 V. For C₆₀ coated samples, the oxidation peak is sharper and located at 3.97 V, while reduction peak at 3.87 V, hence the difference should be about 0.1 V. It implies that the reversibility of the coated electrodes is better than that of bare ones since their potential difference is smaller [12, 13].

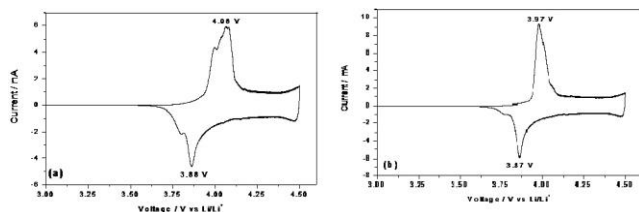


Fig. 4. Cyclic voltammograms of (a) bare and (b) C₆₀ coated LiCoO₂.

Fig. 5 shows the rate capability tests at 1, 1.5 and 2 C-rates between 3.0 and 4.5 V for bare LiCoO₂ and C₆₀ coated LiCoO₂ electrodes in the first ten cycles. In the case of 1 C-rate, all the samples show the decreasing trend with the 60 nm C₆₀ coated sample performs a slightly better capacity retention.

On the other hands, the bare samples suffer more rapid capacity fade from the first cycle since their surfaces are directly exposed to the electrolyte. The same observations are found for the 100 and 200 nm C₆₀ coated electrodes with a slightly higher capacity than that of bare sample. It can be related to the protection role of coating layer against the side reaction with the electrolyte from the initial cycling process. The rapid capacity fade is also observed from the 11th to 20th cycle at 1.5 C with the most severe fading is found for the bare and 200 nm C₆₀ coated electrodes. The thicker coating layer may cause an additional distance for diffusion of Li-ions from or into the electrodes. It seems that the 60 and 100 nm thick C₆₀ coating layer is quite effective to suppress the side reactions with the electrolyte at high C-rate.

In order to confirm the improved rate capability of the C₆₀ coated LiCoO₂ electrodes, electrochemical impedance spectra (EIS) analysis was then carried out. **Fig. 6 (a) and (b)** shows the Nyquist plots of bare and C₆₀ coated LiCoO₂ electrodes after 5 and 10 cycles in the range of 3.0 – 4.5 V, respectively. It can be observed that the all spectra consist of two main semicircles at high-medium frequency region, followed by a straight line at low frequency region. The semicircle observed in the high frequency region is related to the resistance due to the Li-ion transfer through the surface film (R_f), while the semicircles in the middle frequency region represents the charge transfer resistance [14, 15]. Both of the surface and charge transfer resistance of coated electrodes are significantly smaller than those of bare samples. This observation indicate that the C₆₀ coating layer improves the Li-ion transfer at the electrode/electrolyte interface and prevents the direct contact with the electrolyte, hence the side reactions can be more suppressed during the cycle tests. This leads to the more improved rate capability of C₆₀ coated LiCoO₂ electrodes.

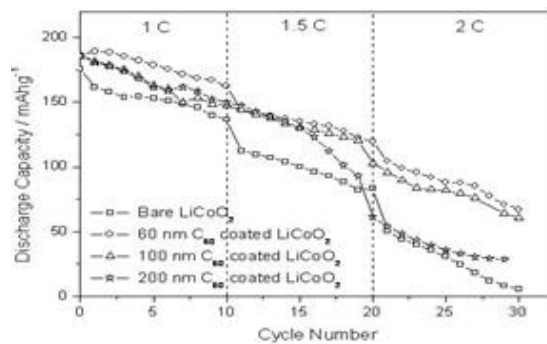


Fig. 5. Rate capability tests at 1, 1.5 and 2 C-rates between 3.0 and 4.5 V for bare LiCoO₂ and C₆₀ coated LiCoO₂ electrodes.

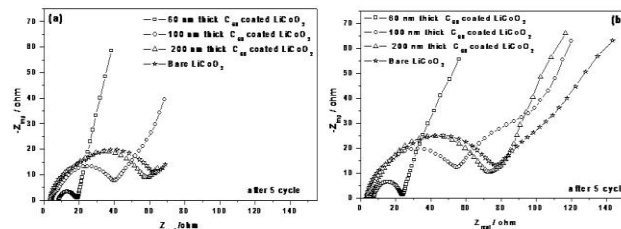


Fig. 6. Nyquist impedance spectra of bare and coated LiCoO₂ after (a) 5 and (b) 10 cycles.

In order to elucidate the role of C_{60} coating layer, the immersion experiments of cathode materials into the liquid electrolyte were then conducted. Fig. 7 shows the amount of Co dissolution into the electrolyte for the bare and coated samples.

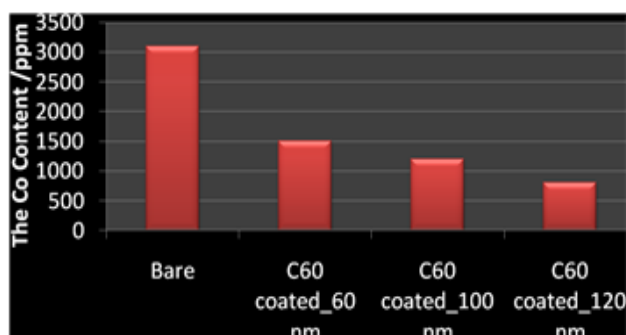


Fig. 7. The amount of Co dissolution into electrolyte for bare and coated samples.

The Co content was measured by ICP-MS after dissolving the cathodes into electrolyte for 3 weeks. It can be seen that the content of Co in bare samples dissolving in electrolyte is 3100 ppm. On the other hands, the content of Co in all coated samples dissolving in electrolyte is below 1500 ppm. The above results show that the C_{60} coating is successfully preventing the dissolution of Co from cathodes into electrolyte because it can minimize the direct contact with the electrolyte.

Based on the above experimental results, we can say that our carbon coated LCO electrodes showed some remarkable improvements in terms of the electrochemical characteristics such as higher initial coulombic efficiency and smaller charge transfer resistance in comparison with those of uncoated LCO electrodes. The coulombic efficiency can be increased to 97% in comparison with the uncoated LCO electrodes. Furthermore, the rate capability of coated electrodes was much more improved due to the passivation role of fullerene coating layer. It is believed that the coating layer could prevent the dissolution of Co into the electrolyte, so the cycling properties could be enhanced.

Conclusion

In this work, the C_{60} film coating on $LiCoO_2$ electrodes has been conducted by plasma assisted thermal evaporation technique. The carbon films were coated by varying their thickness (60, 100 and 200 nm). The thinnest coating layer can contribute the improved electrochemical characteristics of LCO electrodes. The improvement of electrochemical characteristics using the surface film coating has been found in terms of better reversibility characteristics at the first cycle and better rate capability tests in the voltage range of 3.0 - 4.5 V. It is attributed to the role of C_{60} coating layer which can suppress the cobalt dissolution from the $LiCoO_2$ electrodes into the electrolytes.

Acknowledgements

This work was supported by the National Research Foundation of Korea grant funded by the Korean Government (MEST).

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