Improved Cycling Stability of Lithium Electrodes in Rechargeable Lithium Batteries

Ik Su Kang, Yoon-Sung Lee, and Dong-Won Kim[*,z]

Department of Chemical Engineering, Hanyang University, Seungdong-gu, Seoul 133-791, Korea

Poly(3,4-ethylenedioxythiophene)-*co*-poly(ethylene glycol) copolymer was coated onto lithium metal as a protective layer. The thin conductive polymer with strong adhesion to the lithium electrode suppressed the corrosion of the lithium metal and stabilized the interface of the lithium electrode in prolonged contact with the organic electrolyte. The conductive polymer coating on the lithium metal caused the capacity retention of the Li/LiCoO$_2$ cell to increase from 9.3% to 87.3% after 200 cycles compared to the cell with the pristine lithium electrode. The improvement in cycling stability is attributed to the conductive polymer coating suppressing lithium dendrite growth and the deleterious reaction between the lithium electrode and the electrolyte solution during cycling.
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Rechargeable lithium batteries using lithium metal as a negative electrode are attractive candidates for high energy density power sources in portable electronic devices, electric vehicles and energy storage systems because lithium metal offers a high specific capacity ($\sim$3,862 mAh g^{-1}) and possesses a low electrochemical potential (-3.04 V versus the standard hydrogen electrode).[1,2] However, the development of rechargeable lithium metal batteries has been hindered for several decades by the high reactivity of lithium metal to liquid electrolytes and the occurrence of dendrite growth during charge and discharge cycles.[3–7] The formation and growth of lithium dendrites result in safety and cycle life problems. Additionally, continuous generation of the new solid electrolyte interphase (SEI) layer on lithium metal, which occurs from the exposure of lithium dendrites to the electrolyte, causes uncontrolled reductive decomposition of the organic electrolyte and gradual loss in capacity and cycling efficiency with repeated cycling. Therefore, protection of lithium metal and the formation of a stable SEI layer on the lithium electrode are very important for developing lithium metal batteries with good capacity retention and enhanced safety. In this respect, there have been significant efforts in surface modification of lithium metal to improve the interfacial properties of a lithium electrode. Protective layers formed on lithium metal by polymer coatings, gaseous additives such as CO$_2$, N$_2$O, or SO$_2$, inorganic additives such as AlCl$_3$ or SnI$_2$, silane-based coatings, carbon coatings, lithium nitride and reactive organic molecules enhance the electrochemical properties of a lithium electrode.[7–18] The electrochemical properties of the protective layer formed on lithium metal are influenced by various physicochemical factors such as reactivity with lithium, physical adhesion to a lithium metal and its electrical resistance.[19–23] Conductive polymer coatings for cathode active materials in lithium-ion batteries have been quite successful.[24,25] Recently, Cui group reported that a surface coating of silicon nanowire electrodes with poly(3,4-ethylenedioxythiophene) (PEDOT) was very effective for improving their cycling stability.[26] PEDOT has a high electrical conductivity and good electrochemical stability.[27–29] Another advantage of PEDOT is the insertion of ions from the electrolyte, which is a prerequisite for a fast lithium exchange. However, PEDOT is not an ionic conductive polymer but an electronic conductive polymer. It is thus interesting to investigate a PEDOT-based ion-conductive copolymer as a protective coating layer on lithium metal. Among the PEDOT-based ion-conductive copolymers, poly(3,4-ethylenedioxythiophene)-*co*-poly(ethylene glycol) (PEDOT-*co*-PEG) is a promising candidate for protective surface coating. In the copolymer, PEG is a highly ion-conductive polymer that transports lithium ions. However, the use of PEG homopolymer as a surface coating layer is not proper, since PEG is easily dissolved in the electrolyte solution. The PEDOT-*co*-PEG copolymer hardly dissolves in organic electrolyte and exhibits higher ionic conductivity. Additionally, the PEDOT-*co*-PEG copolymer possesses strong adhesive properties to a

lithium surface, which makes it effective for mechanically suppressing Li-dendrite growth.

In this work, a prospective approach for protecting a lithium surface is presented by coating with a conductive PEDOT-*co*-PEG layer, which allows for lithium ion diffusion and restricts the access of the reactive solvents to the lithium surface. The protective polymer layer played a positive role in reducing the reductive decomposition of the electrolyte and suppressing the dendrite growth of lithium during cycling. To this end, the conductive polymer coating on the lithium electrode notably improves the cycling stability of the lithium metal batteries.

Experimental

Cell assembly.— The PEDOT-*co*-PEG solution (1 wt% dispersion in nitromethane) was purchased from Sigma Aldrich and used as received. The surface of the lithium metal (Honjo Metal Co. Ltd., 100 μm) was coated with PEDOT-*co*-PEG by directly spin-coating the polymer solution in a dry box filled with argon gas. After 12 h, the polymer-coated lithium electrode was rinsed with dimethyl carbonate (DMC) and dried at 25°C for 24 h under vacuum. The positive electrode was prepared by coating the N-methyl pyrrolidone (NMP)-based slurry containing 85 wt% LiCoO$_2$, 7.5 wt% poly (vinylidene-fluoride)(PVdF) and 7.5 wt% super-P carbon onto aluminum foil. The electrode was roll pressed to enhance particulate contact and adhesion to the foil. The geometrical area of the positive electrode was 1.54 cm^2 and its active mass loading corresponded to a capacity of approximately 1.0 mAh cm^{-2}. The negative electrode consisted of a surface-modified lithium metal that was pressed on a copper current collector. The CR2032-type coin cell composed of a lithium negative electrode, a polypropylene separator (Celgard 3501) and a LiCoO$_2$ positive electrode was assembled with an electrolyte solution. The liquid electrolyte was 1 M LiClO$_4$ in ethylene carbonate (EC)/DMC (1:1 by volume, battery grade, Soulbrain Co., Ltd.). All cells were assembled in a dry box filled with argon gas.

Measurements.— Morphologies of the lithium electrodes were examined using a field emission scanning electron microscope (FE-SEM, JEOL KSM-6300). In order to investigate the interfacial behavior of pristine and modified lithium electrodes in prolonged contact with an organic electrolyte, AC impedance measurements were performed with a symmetrical Li/electrolyte/Li cell using a Zahner Electrik IM6 impedance analyzer over a frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV. The cycling performance of the Li/LiCoO$_2$ cells was evaluated over a voltage range of 3.0–4.2 V at different current densities using battery testing equipment (WBCS 3000, Wonatech). After the charge-discharge cycling, the lithium electrode was carefully separated from the cell and washed with highly purified DMC to remove residual electrolyte. The electrode was then dried under vacuum at room temperature for 12 h. The lithium electrode was hermetically sealed inside an aluminum plastic bag for safe transfer

*Electrochemical Society Active Member.
zE-mail: dongwonkim@hanyang.ac.kr

to SEM analysis without contamination. In order to get reliable and reproducible results, the cycling tests were performed for at least ten cells, and their average behavior was reported.

Results and Discussion

Figure 1a and 1b show the FE-SEM images of the surface of a lithium electrode before and after surface coating by the PEDOT-*co*-PEG copolymer. As shown in the figure, the pristine lithium electrode had a smooth surface. When the PEDOT-*co*-PEG copolymer was directly coated to the lithium surface, the polymer fully covered the surface of the lithium electrode. The thin polymer layer strongly adhered to the lithium metal surface and the thickness was approximately 380 nm. The polymer layer was expected to mechanically suppress the dendrite growth of lithium during cycling: from the solubility test, this layer was not dissolved in the electrolyte solution (1 M LiClO$_4$ in EC/DMC). The ionic conductivity of the PEDOT-*co*-PEG film soaked with the liquid electrolyte (1 M LiClO$_4$ in EC/DMC) was 3.5×10^{-3} S cm^{-1}, indicating fast ion transport through the thin surface layer.

AC impedance measurements of Li/organic electrolyte/Li cells were performed to investigate the interfacial stability of the lithium electrodes in prolonged contact with the organic electrolyte at 25°C.
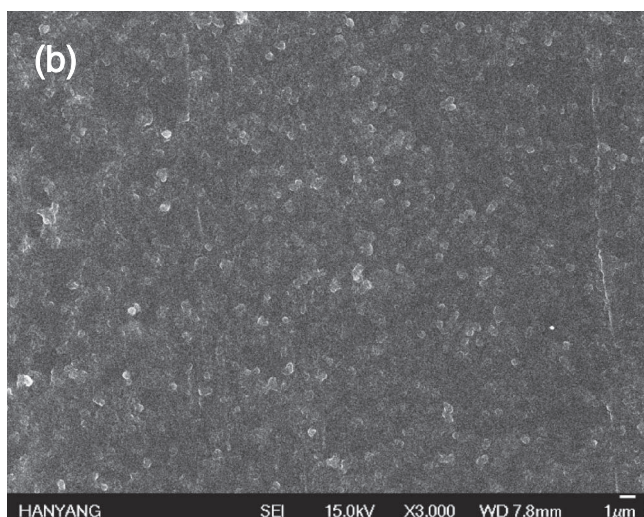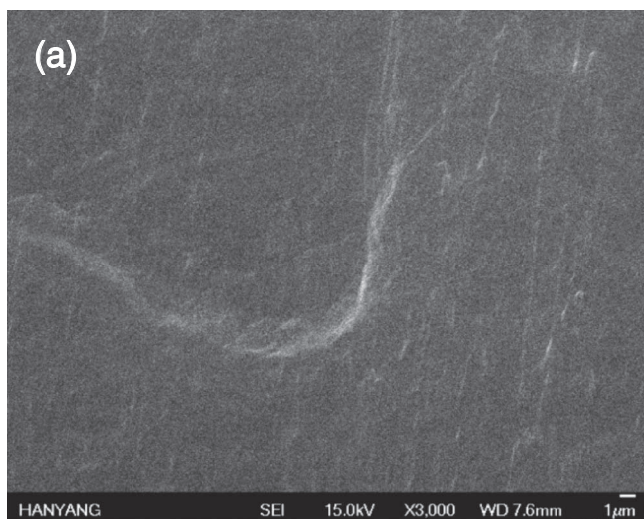

Figure 1. SEM images of the surfaces of the (a) pristine lithium electrode and (b) surface-modified lithium electrode with PEDOT-*co*-PEG copolymer.
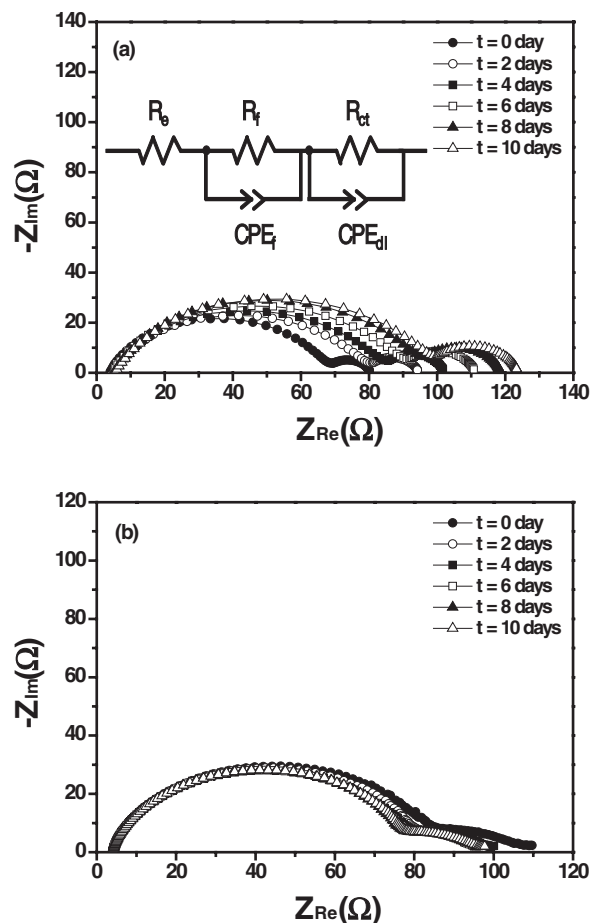

Figure 2. AC impedance spectra of a Li/electrolyte/Li cells with (a) pristine and (b) surface-modified Li electrodes as a function of storage time at 25°C.

Figure 2a and 2b present the time evolution of the AC impedance spectra of the cells with the pristine Li electrode and surface-modified Li electrode, respectively. In Figure 2b, both Li electrodes in the symmetrical cell were coated with PEDOT-*co*-PEG copolymer. The spectra are composed of two partially overlapping semicircles in high and low frequency regions. The first semicircle at high frequency is associated with the SEI layer that grows on the lithium electrode, and the low frequency semicircle is related to the charge transfer process between the electrodes and electrolyte.[30–32] These spectra could be analyzed using the equivalent circuit given in the inset of the figure. In this circuit, R$_e$ is the electrolyte resistance, which corresponds to the high frequency intercept at the real axis. R$_f$ and R$_{ct}$ are the resistance of the SEI film and the charge transfer resistance, respectively. CPE$_i$ (constant phase element) denotes the capacitance of each component to reflect the depressed semicircular shape. In the cell assembled with the pristine Li electrode, the initial interfacial resistances of the cell (R$_f$ and R$_{ct}$) are less than those of the cell using a surface-modified Li electrode. However, the R$_f$ value continuously increases with time, which can be attributed to the gradual growth of a resistive surface layer due to the reaction between the lithium electrode and the organic electrolyte.[33–35] A slight increase in R$_e$ implies a pronounced reaction between lithium and the electrolyte solution, which consumes the electrolyte in the cell. Growth of the resistive layer on the lithium electrode also restricts the charge transfer reaction, which results in an increase of R$_{ct}$. In the cell assembled with the surface-modified Li electrode, both R$_f$ and R$_{ct}$ initially decreased and eventually stabilized, and R$_e$ is nearly constant, irrespective of time. The initial decrease in interfacial resistances can be ascribed to the activation of the surface layer by a repetitive charge transfer reaction and transport of lithium
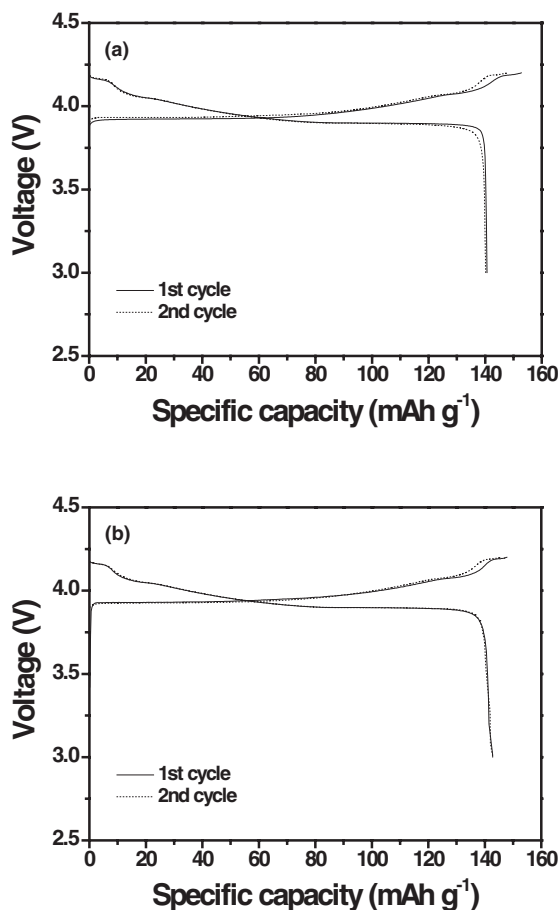
Figure 3. The two initial cycles of Li/LiCoO$_2$ cells assembled with (a) pristine and (b) surface-modified Li electrodes (0.1C, cutoff voltage: 3.0–4.2 V).

Figure 4. (a) Charge and discharge curves of the Li/LiCoO$_2$ cell assembled with a surface-modified Li electrode, and (b) discharge capacities of the Li/LiCoO$_2$ cells assembled with different lithium electrodes (0.5C, cutoff voltage: 3.0–4.2 V).

ions. The constant value of R$_f$ after some period indicates suppression of deleterious reactions between the surface-modified lithium electrode and the electrolyte solution, because the protective polymer layer can effectively restrict access of reactive solvents to the lithium surface. As a result, the interfacial stability of the lithium electrode is improved by the formation of a protective layer with PEDOT-*co*-PEG on lithium metal.

The Li/LiCoO$_2$ cells prepared with pristine and surface-modified Li electrodes were initially subjected to two preconditioning cycles over 3.0–4.2 V at low current density (0.10 mA cm^{-2}), and the resulting charge-discharge curves are shown in Figure 3. For the first cycle, the cell with the surface-modified Li electrode exhibited higher discharge capacity (142.8 mAh g^{-1}) and coulombic efficiency (96.6%) than the cell with the pristine Li electrode (140.7 mAh g^{-1}, 92.1%). The irreversible capacity at the first cycle is associated with irreversible reactions of organic solvents at the electrodes.[36,37] Higher initial charge capacity of the cell with pristine Li electrode (152.7 mAh g^{-1}) arises from the irreversible reductive decomposition of the electrolyte at negative electrode during first charging process. Thus, the greater coulombic efficiency in the cell with the surface-modified Li electrode suggests that the protective polymer layer can decrease the reductive decomposition of the organic electrolyte at the lithium electrode. For the second cycle, the coulombic efficiency of the Li/LiCoO$_2$ cell with a surface-modified Li electrode (98.0%) is still greater than that of the cell with the pristine Li electrode (94.9%), indicating that the surface-modified Li electrode has a more stable SEI layer allowing more reversible charge and discharge behavior.

The cycling performance of the Li/LiCoO$_2$ cells was evaluated at 0.5C rate for both charge (constant-current and constant-voltage mode) and discharge (constant-current mode) in the same poten-
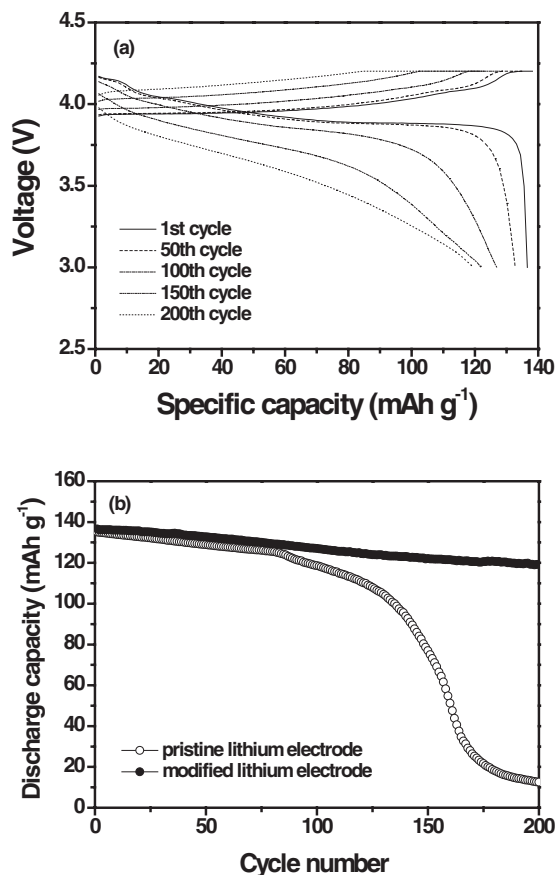
tial range. Figure 4a shows the voltage profiles for the 1st, 50th, 100th, 150th and 200th cycles of the Li/LiCoO$_2$ cell with a surface-modified Li electrode. The cell delivers an initial discharge capacity of 136.6 mAh g^{-1} based on the active LiCoO$_2$ material in the positive electrode. Although the overpotential increased and the reversible capacity decreased with cycling, the cell did not show any failure up to at least 200 cycles. Figure 4b compares the discharge capacities of the cells with pristine and modified Li electrodes as a function of cycle number. Clearly, the cell with the modified Li electrode exhibited much better capacity retention than that of the pristine Li cell. The cell with the modified Li electrode maintained 87.3% of its initial discharge capacity after 200 cycles, which corresponds to an average capacity decay of 0.06% per cycle. In contrast, the discharge capacity decays faster after the 100th cycle and an overall capacity of 9.3% was retained after 200 cycles for the cell with the pristine Li electrode. The primary failure mechanisms of rechargeable batteries with lithium metal electrodes are dendrite formation and exhaust of the electrolyte solution, as previously reported.[10,38,39] The formation of Li dendrites allows for a fresh Li metal surface to be exposed to the electrolyte, and thus continuously generates a new SEI layer with cycling, which consumes the electrolyte solution, eventually leaving the cell dry. Moreover, lithium dendrites can be isolated from the lithium electrode during repeated cycling and the isolated lithium can react with the organic electrolyte because it is chemically reactive,[40] which severely degrades the cycling performance. Thus, good capacity retention in the cell with a surface-modified lithium electrode can be ascribed to the presence of a thin conductive polymer layer covering the lithium electrode, which reduces the deleterious reactions of the electrolyte with lithium electrode and suppresses growth of the
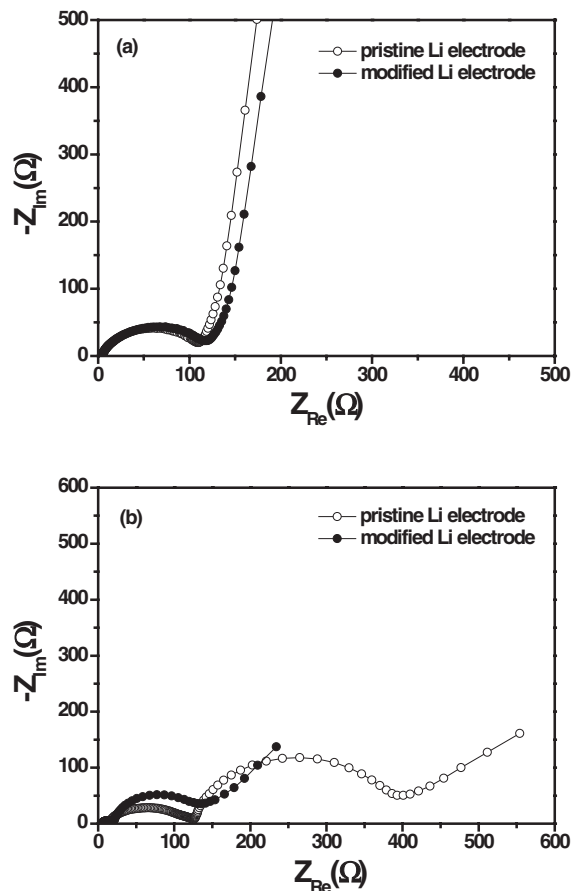
Figure 5. AC impedance spectra (a) before and (b) after 200 cycles in the Li/LiCoO$_2$ cells assembled with different lithium electrodes.

Figure 6. SEM images of (a) pristine and (b) surface-modified Li electrodes after 200 cycles.

lithium dendrite during cycling. Based on these results, the protective polymer layer may play an important role in the stable SEI layer on lithium electrodes.

In order to understand the effect of surface modification on the cell cycling performance, the AC impedance of the cell was measured before and after 200 cycles and the resultant AC impedance spectra are shown in Figure 5. Before cycling, the almost identical ac impedance spectra, except for small difference in interfacial resistance, indicate the coating of PEDOT-*co*-PEG onto lithium metal has little effect on the impedance behavior of the cell before cycling. After charge and discharge cycling, the cell with the surface-modified Li electrode revealed a much smaller interfacial resistance than the cell with the pristine Li electrode, which implies that the cell with the modified Li electrode had a more stable SEI layer that facilitated more efficient lithium ion transfer at the interfaces during cycling. As a result, the increase of cell impedance is remarkably suppressed in the cell with the surface-modified Li electrode, which results in good capacity retention during cycling. The electrolyte resistance corresponding to the high frequency intercept at the real axis was much greater in the cell with pristine Li electrode. This result can be ascribed to consumption of the electrolyte due to reactions between the Li deposits and the electrolyte solution.

SEM analysis of the lithium electrodes was performed after charge-discharge cycles to investigate the cause of the improved capacity retention in the Li/LiCoO$_2$ cell with a surface-modified lithium electrode. As shown in Figure 6, the SEM images of the surfaces for pristine and modified Li electrodes show conspicuous differences. The pristine Li electrode shows dendritic features with particulate. In contrast, the surface-modified Li electrode exhibits rather smooth and flat morphologies, which spread uniformly over the entire Li surface. Specifically, the dendritic morphology is not observed in the
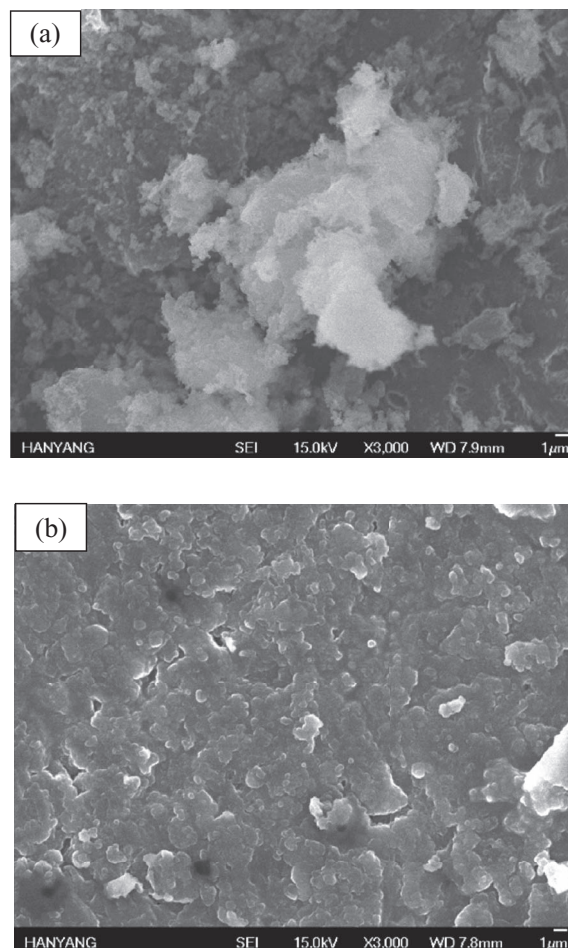
lithium electrode with the protective layer. These results suggest that the conductive polymer coating on the lithium electrode could act to maintain the mechanical integrity for effectively suppressing dendrite growth during cycling. Accordingly, the stable cycling performance and low interfacial resistances in the cell with the surface-modified Li electrode originate from the diminished Li-dendrite formation.

Figure 7 compares the discharge capacities of the Li/LiCoO$_2$ cells assembled with different Li electrodes, with the C-rate increasing from 0.1 to 2.0C every five cycles. The discharge capacities of the cell
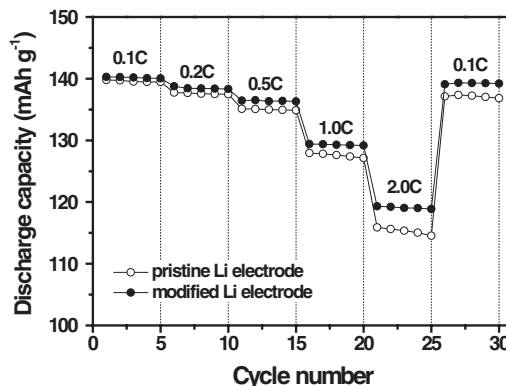

Figure 7. Discharge capacities of Li/LiCoO$_2$ cells at different current rates. The C rate was increased from 0.1 to 2.0C after every five cycles.

with the modified Li electrode are greater than those of the pristine Li electrode cell at all C-rates tested, and the difference in the discharge capacities between the two cells increased with increasing C-rate. Notably, the cycling stability of the cell with the pristine Li electrode decreases with increasing C rate, which may be due to the high current rates causing dendrite growth and enhancing the surface reactions of the solution species.[41] Favorable interfacial characteristics of the conductive polymer layer in the cell with the modified Li electrode led to the improved capacity retention, even at high current rates through cycling.

Conclusions

A conductive PEDOT-*co*-PEG copolymer was coated on a lithium electrode as a protective SEI layer. The thin polymer layer formed on the lithium metal stabilized the interface of the lithium electrode in prolonged contact with the organic electrolyte. The conductive polymer coating on the lithium metal led to a remarkable improvement in the cycling performance of the Li/LiCoO$_2$ cell. Stable cycling characteristics of the cell with a surface-modified lithium electrode can be ascribed to the protective layer that has several beneficial effects: stabilization of the SEI, and suppression of the electrolyte decomposition and dendritic growth during cycling.

Acknowledgments

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