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Cycling characteristics of lithium metal batteries assembled with a surface modified lithium electrode

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HIGHLIGHTS

- ► The surface modified lithium electrode is prepared by coating a protective polymer layer.
- ► The protective layer stabilizes the interface of lithium in contact with electrolyte.
- ► The cell with surface modified Li electrode exhibits good cycling performance.

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ABSTRACT

The surface modified lithium electrode is prepared by coating an ionic conductive poly(vinylene carbonate-co-acrylonitrile) layer as a solid electrolyte interphase on lithium metal. The thin protective polymer layer with strong adhesion to the lithium electrode suppresses the corrosion of lithium metal and stabilizes the interface of lithium electrode in prolonged contact with organic electrolyte. Cycling performance of the Li/$LiCoO_2$ cells can be improved by using the surface modified lithium electrode. SEM analysis of lithium electrodes after repeated cycling reveals that the use of a surface modified lithium electrode effectively suppresses dendrite growth during cycling, which results in stable cycling characteristics compared to that of the cell with an un-modified lithium electrode.

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1. Introduction

Rechargeable lithium batteries using lithium metal as an anode are attractive candidates for high energy density power sources in portable electronic devices, electric vehicles and energy storage systems, because the lithium metal offers the highest specific capacity (~3862 mAh g^{-1}) for a negative electrode material [1]. However, the development of rechargeable lithium metal batteries has been hindered by the high reactivity of lithium metal toward liquid electrolytes and the occurrence of dendrite growth during charge and discharge cycles [2–6]. Dendrite formation is undesirable for lithium batteries due to the safety and cycle life concerns. In addition, the non-uniform current distribution on the lithium metal electrode, which arises from the heterogeneous composition of solid electrolyte interphase (SEI) layer formed on lithium by the reductive decomposition of organic electrolyte, results in a low cycling efficiency and gradual capacity loss with repeated cycling. Therefore, the protection of lithium metal and the control of the lithium electrode/electrolyte interface are very important for developing the lithium metal batteries with good capacity retention and enhanced safety. In this respect, there have been significant efforts placed in surface modification of the lithium metal to improve the interfacial properties of a lithium electrode. It has been reported that the protective layer formed on lithium metal by polymer coating, gaseous additives such as CO_2, N_2O, SO_2, inorganic additives such as $AlCl_3$, SnI_2, silane-based coating, carbon coating, lithium nitride and reactive organic molecules could enhance the electrochemical properties of lithium electrode [7–20]. Most of protective coatings by *in-situ reaction* between lithium and other chemical compounds failed to protect the lithium metal effectively due to their porous morphologies [16]. Other methods based on

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ex-situ coating, such as sputtering and polymerization, are not favorable due to their high fabrication cost. Ota et al. reported that the cycling performance of lithium metal batteries could be improved by adding a small amount of vinylene carbonate (VC) into the electrolyte [21]. The VC-derived SEI film formed on lithium metal, which consisted of polymeric species such as poly(vinylene carbonate) (PVC), the oligomer of VC and the ring-opening polymer of VC, suppressed the deleterious reaction between the lithium electrode and the electrolyte solution. Thus, creating an artificial PVC-based SEI layer to protect the reactive lithium electrode would be an effective way to minimize deleterious reactions with organic electrolyte and suppress the occurrence of dendrite growth during cycling.

In the present work, we report a new approach for protecting the lithium surface by coating with a thin poly(vinylene carbonate-co-acrylonitrile) (P(VC-co-AN)) layer, which allows lithium cation diffusion and restricts the access of reactive solvents to the lithium surface. It is thus expected that the protective polymer layer plays a positive role as SEI in the lithium metal batteries. In this paper, we investigate the electrochemical properties of surface modified lithium electrodes and evaluate the cycling performance of lithium metal batteries assembled with surface modified lithium electrodes.

2. Experimental

2.1. Polymer synthesis and characterization

P(VC-co-AN) was synthesized via solution radical polymerization with dimethylsulfoxide (DMSO) as a solvent at 60 °C in a glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel and a mechanical stirrer [22], as illustrated in the synthetic scheme of Fig. 1. The molar ratio of VC to AN in the reaction feed was 63:37, and azobisisobutyronitrile (AIBN) was used as a free-radical initiator in the radical polymerization. The copolymerization was continued for 24 h with vigorous agitation. After polymerization, the resulting solution was added drop by drop to excess ethanol. The polymer was isolated by filtration and washed successively with ethanol to remove any impurities such as residual monomers and initiator. The product was then dried in a vacuum oven at 80 °C for 24 h. The chemical structure of P(VC-co-AN) copolymer was determined by ^{1}H NMR using a VARIAN (Mercury 300) NMR spectrometer with DMSO-d_6 solvent.

2.2. Electrode preparation and cell assembly

To prepare the polymer solution to form the protective layer on lithium metal, P(VC-co-AN) copolymer was dissolved in DMSO at a concentration of 15 wt.%. The surface modified lithium electrode was then prepared by spin-coating the resulting solution onto the lithium metal (thickness: 100 μm). The cathode was prepared by coating the N-methyl pyrrolidone (NMP)-based slurry containing $LiCoO_2$, poly (vinylidienefluoride) (PVdF) and super-P carbon (85:7.5:7.5 by weight) onto aluminum foil. The electrode was roll pressed to enhance particulate contact and adhesion to foil. The anode consisted of a surface modified lithium metal that was pressed onto a copper current collector. The CR2032-type coin cell composed of a lithium anode, a polypropylene separator (Celgard 3501) and $LiCoO_2$ cathode was assembled with electrolyte solution. The liquid electrolyte used was 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume, battery grade, Soulbrain Co., Ltd.). All cells were assembled in a dry box filled with argon gas.

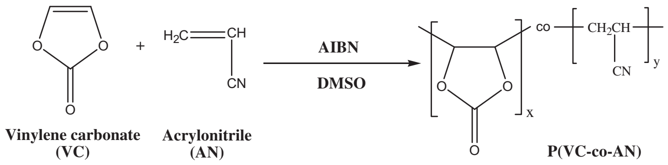

Fig. 1. Reaction scheme for synthesis of P(VC-co-AN) copolymer.

2.3. Measurements

Morphologies of surface modified lithium electrodes were examined using a field emission scanning electron microscope (FE-SEM, JEOL KSM-6300). In order to investigate the interfacial behavior of non-modified and modified lithium electrodes in prolonged contact with 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–100 kHz with an amplitude of 10 mV. Cycling performance of Li/$LiCoO_2$ cells was evaluated over a voltage range of 3.0–4.2 V at a current density of 0.4 mA cm^{-2} (0.5 C rate) with battery testing equipment. After the charge–discharge cycling, the lithium electrode was removed from the coin cell and washed with highly purified DMC. The surface morphology of cycled lithium electrodes was observed using FE-SEM.

3. Results and discussion

Molar composition of P(VC-co-AN) copolymer was determined from ^{1}H NMR spectrum, as shown in Fig. 2. In the ^{1}H NMR spectrum of P(VC-co-AN) copolymer, PVC has a broad peak of the proton H-1 around 5.35 ppm [23]. On the other hand, the peaks of methylene proton (H-2) and methine proton (H-3) in PAN are observed at 2.06 and 3.14 ppm, respectively. The molar composition of each co-monomer unit could thus be estimated by the total intensity of the corresponding monomer unit. The molar ratio of VC and AN was determined to be 67:33. Lower AN molar composition (0.33) in the P(VC-co-AN) copolymer compared to that in reaction feed (0.37) may be caused by the comparatively low reactivity of AN for copolymerization [24]. The P(VC-co-AN) copolymer was not soluble in the organic electrolyte used in this study, which was the reason we synthesized P(VC-co-AN) copolymer instead of PVC homopolymer. PVC homopolymer was confirmed to be soluble in the organic electrolyte. Note that a soaking of the membrane based on PAN homopolymer in the organic electrolyte resulted in gelation

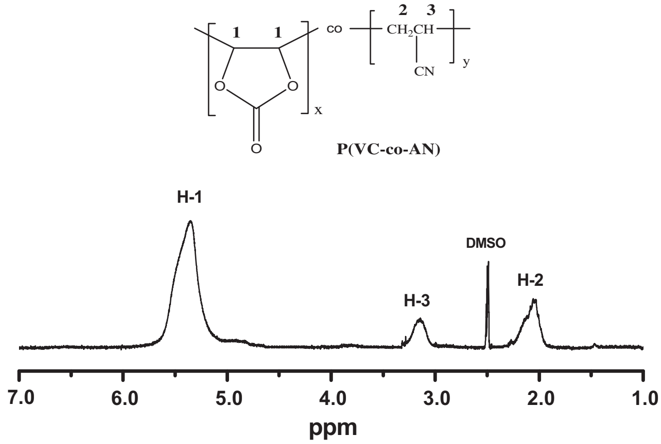

Fig. 2. ^{1}H NMR spectrum of P(VC-co-AN) copolymer in DMSO-d_6.

rather than dissolution, which contributed to the mechanical stability of the film [25,26].

Lithium metal is highly reactive with O_2, N_2 and H_2O in the atmosphere. In order to examine the reactivity of lithium electrodes considered in this study, both un-modified lithium metal and modified lithium metal samples were left in atmospheric conditions for 20 min. As seen in Fig. 3, the un-modified lithium metal corroded quickly to a dull silvery gray and then black tarnish. It can be ascribed to the chemical compounds formed on the surface of lithium, such as lithium hydroxide (LiOH), lithium nitride (Li_3N) and lithium carbonate (Li_2CO_3). On the contrary, the surface modified lithium metal changed little with time. This result suggests that the coating layer composed of P(VC-co-AN) effectively protects the lithium metal from O_2, N_2 and H_2O in the atmosphere. Moreover, the spin coating process of P(VC-co-AN) onto the lithium metal is very simple and cost effective as compared to other coating methods.

Fig. 4(a) shows the FE-SEM image of the surface of a lithium electrode with the protective layer. As shown in the figure, the lithium electrode had a very homogeneous and smooth surface. Since the protective layer is directly formed on the lithium surface by spin coating, the uniform P(VC-co-AN) polymer layer was very strongly adhered to the lithium metal surface. Fig. 4(b) shows the cross-sectional image of the surface modified lithium electrode. The dark black layer on the top of the electrode is the P(VC-co-AN) polymer layer. The thickness of the protective polymer layer was measured to be approximately 150 nm.

We attempted to investigate the interfacial behavior of a surface modified lithium electrode in prolonged contact with organic electrolyte. Fig. 5(a) and (b) shows the time evolution of the AC impedance spectra of Li/organic electrolyte/Li cells with different lithium electrodes under open-circuit potential conditions. The spectra are composed of two partially overlapped semicircles in medium and low frequency regions. The first arc is associated with SEI layer that grows on the lithium electrode, and the low frequency arc is related to charge transfer process between the SEI layer and the lithium electrode [27–29]. These spectra can be analyzed by using the equivalent circuit given in the inset of Fig. 5(a). In this circuit, R_e is the electrolyte resistance and 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. Fig. 5(c) presents the resistance of the SEI film (R_f) and the charge transfer resistance (R_{ct}) as a function of time. In the cell assembled with modified Li electrodes, both R_f and R_{ct} are almost constant, irrespective of time. The constant value of R_f suggests no growth of the resistive surface film on the lithium electrode, indicating suppression of a deleterious reaction between the lithium electrode and the electrolyte solution. This result suggests that the protective polymer layer effectively restricts the access of reactive solvents to the lithium surface. With regard to the un-modified lithium electrode, initial interfacial resistances of the cell (R_f and R_{ct}) are lower than those of the cell using a surface modified lithium electrode. However, the value of R_f continuously increases with time, which can be attributed to the gradual growth of a resistive surface layer due to the reaction between lithium electrode and organic electrolyte. An increase in R_{ct} as well as R_f suggests that the resistive surface film formed at lithium electrode hampers charge transport at the electrode and electrolyte interface. As a result, both R_f and R_{ct} in the cell with an un-modified lithium electrode are higher than those in the cell with a surface modified lithium electrode after 10 days. From these results, it is apparent that the interfacial stability of the lithium electrode is enhanced by the

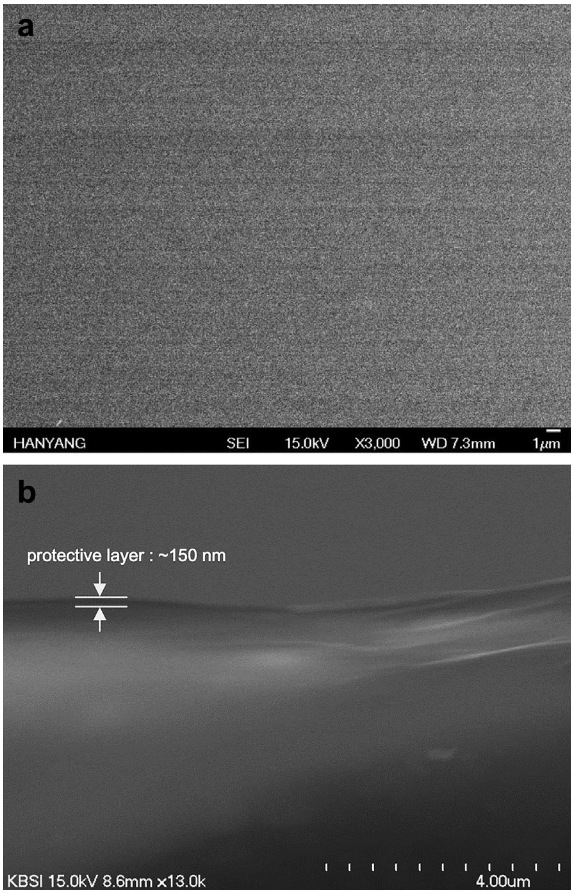

Fig. 4. SEM image of (a) the surface and (b) cross-section of the surface modified lithium electrode.

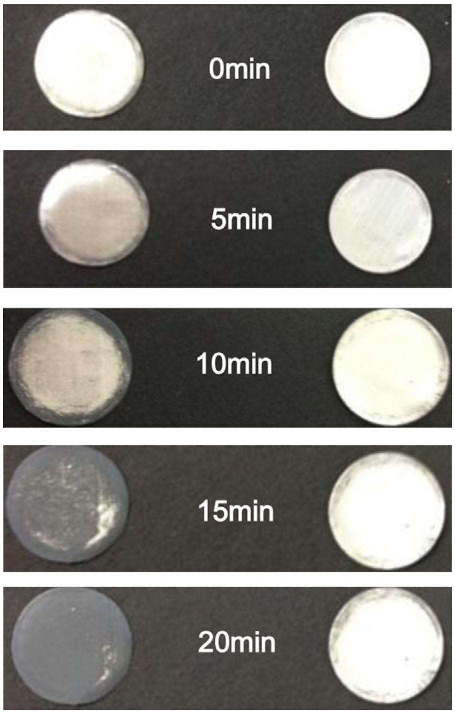

Fig. 3. Photographic images showing the corrosion of lithium metals exposed to the atmosphere as a function of exposure time. The left image is an un-modified lithium metal, and the right image is a surface-modified lithium metal.

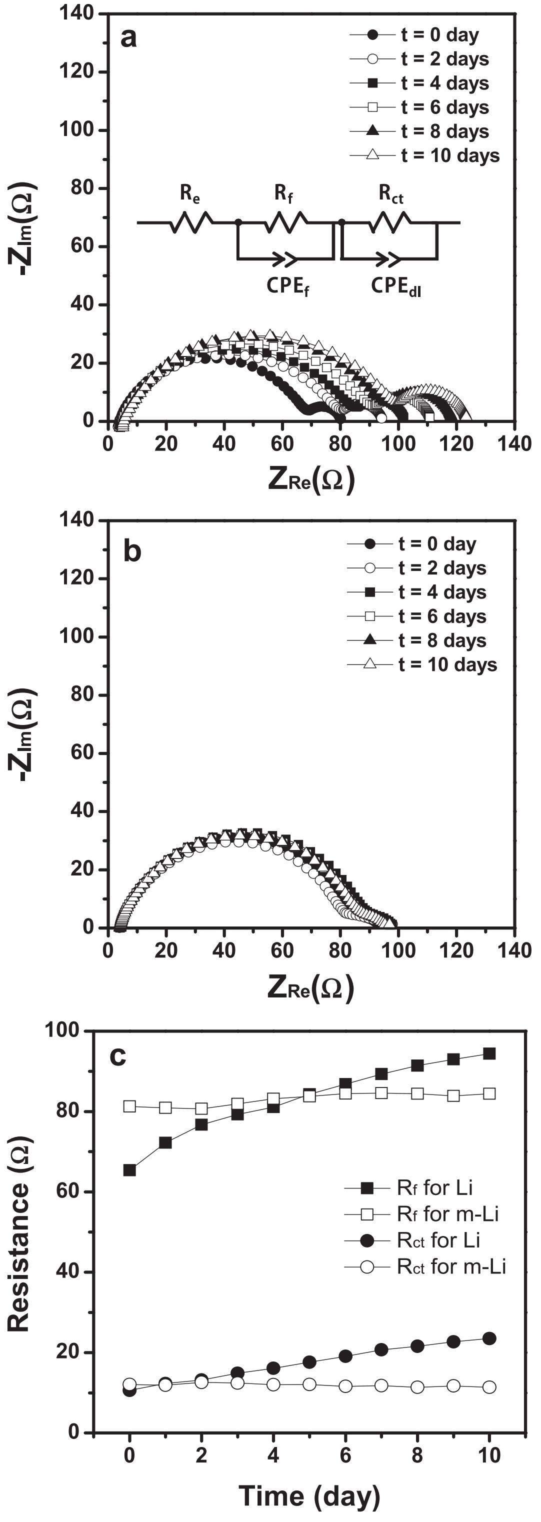

Fig. 5. AC impedance spectra of a Li/electrolyte/Li cell with an un-modified electrode (a) and a surface modified lithium electrode (b), as a function of storage time at 25 °C, and (c) the variation in R_f and R_{ct} of the Li/electrolyte/Li cells with un-modified (closed symbol) and modified lithium electrode (open symbol).

introduction of a protective layer consisting of P(VC-co-AN) polymer on lithium metal.

Cycling performances of Li/LiCoO$_2$ cells prepared with un-modified and modified lithium electrodes were evaluated. The assembled cells were initially subjected to the first preconditioning cycle over 3.0–4.2 V at a constant current of 0.08 mA cm^{-2} (0.1 C rate). The first preconditioning charge–discharge curves of Li/LiCoO$_2$ cells with different lithium electrodes are shown in Fig. 6. As shown, the initial charge capacity of the cell with an un-modified lithium electrode is higher than that of the cell with a surface modified lithium electrode. This result can be explained by irreversible electrochemical reduction of organic solvents at the surface of lithium electrode during the first charging process, since the reduction of organic electrolyte is liable to irreversibly occur at lithium electrode during the first charging process [30,31]. The reduction of organic solvents consumes a portion of the capacity which corresponds to irreversible capacity loss. On the other hand, when the protective layer is formed on the lithium electrode, the formation of a resistive layer due to the deleterious reaction with organic electrolyte can be suppressed during the first charging process. Moreover, the lithium ions may more easily transport through the thin P(VC-co-AN) layer formed on the surface modified lithium electrode. Thus, the initial discharge capacity of the Li/LiCoO$_2$ cell with a surface-modified lithium electrode is higher than that of the cell with an un-modified lithium electrode. Accordingly, the cell with a surface modified lithium electrode has a higher coulombic efficiency than the cell with an un-modified lithium electrode.

After two cycles at 0.1 C rate, the cells were cycled over a voltage range of 3.0–4.2 V at a current density of 0.4 mA cm^{-2}. Fig. 7 presents the discharge capacities of the cells with un-modified and modified lithium electrodes, respectively, as a function of cycle number. In this figure, the specific capacity was estimated based on LiCoO$_2$ active material in the cathode. The cell with an un-modified lithium electrode has a first discharge capacity of 132.9 mAh g^{-1}, and the discharge capacity of the cell declines to 101.4 mAh g^{-1} after 100 cycles. Coulombic efficiency initially increased but decreased again after the 11th cycle. On the other hand, the coulombic efficiency of the cell with a modified lithium electrode steadily increased and stabilized with cycle number and was greater than 99% after the initial few cycles. The cell with a modified lithium electrode has a discharge capacity of 125.2 mAh g^{-1} at the 100th cycle, which corresponds to a 90.7% initial discharge capacity. Good capacity retention in the cell with surface modified lithium electrode can be ascribed to the presence of a thin ionic conductive polymer layer covering the lithium electrode, which reduces the reductive decomposition of electrolyte on lithium electrode and suppress growth of lithium dendrite during cycling. Based on these results, we believe that the

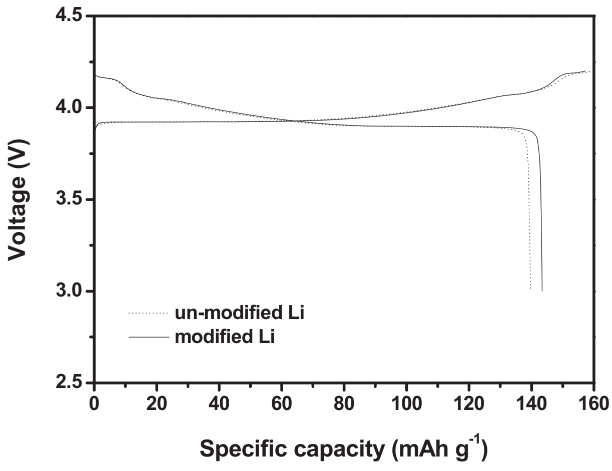

Fig. 6. First preconditioning cycles of Li/LiCoO$_2$ cells assembled with un-modified and modified lithium electrodes (0.1 C, cut-off voltage: 3.0–4.2 V).

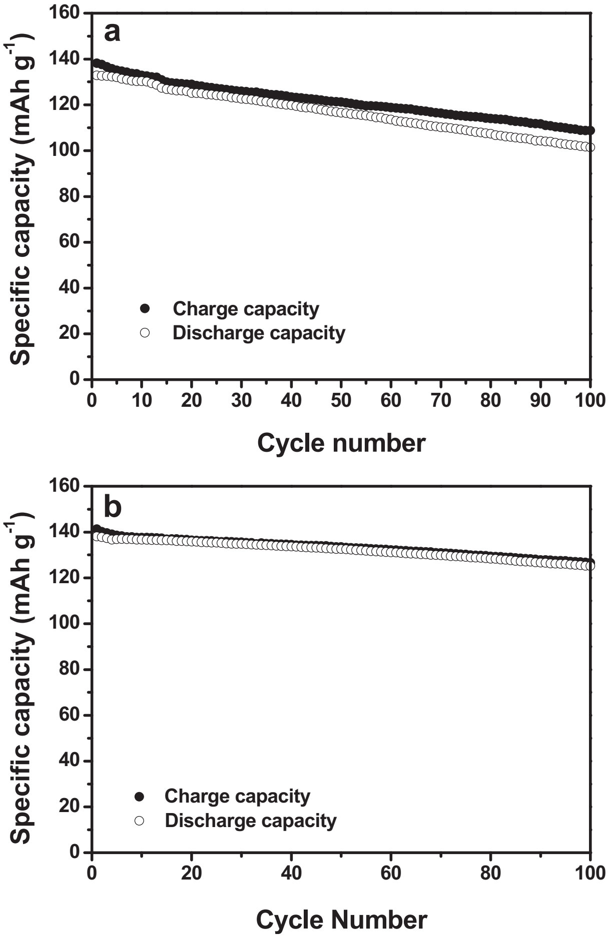

Fig. 7. Charge and discharge capacities of the Li/LiCoO$_2$ cells assembled with different lithium electrodes. (a) Un-modified lithium electrode and (b) modified lithium electrode (0.5 C, cut-off voltage: 3.0–4.2 V).

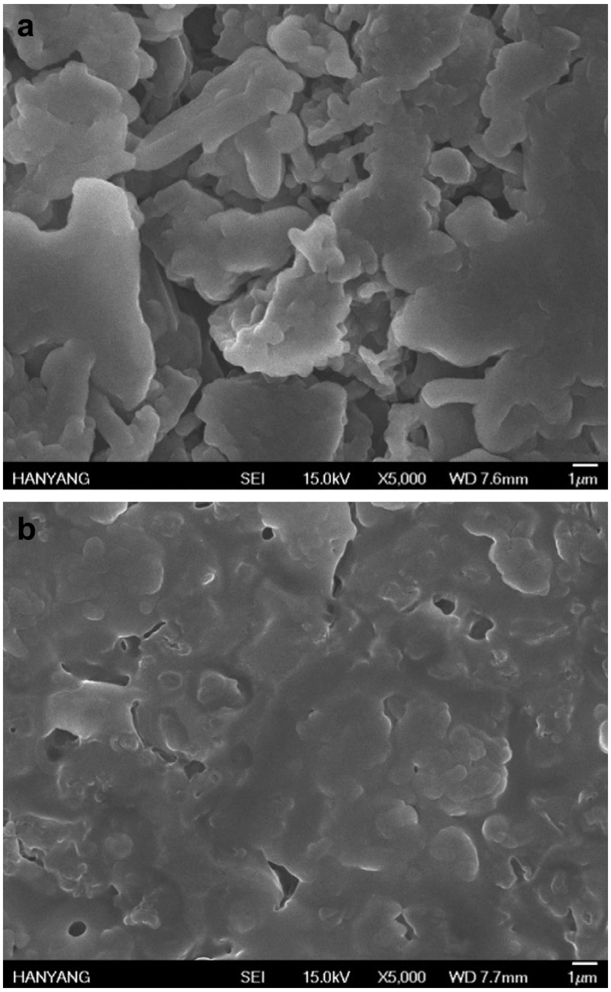

Fig. 8. SEM images of lithium electrodes after 100 cycles. (a) Un-modified lithium electrode and (b) modified lithium electrode.

protective polymer layer plays an important role as SEI on lithium electrodes.

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, since the cycling behavior of the cells is closely related to the morphology of the lithium anode. Fig. 8 shows the SEM images of the surfaces for un-modified and modified lithium electrodes after 100 cycles. Some dendritic and particulate morphologies were observed on the surface of the un-modified lithium electrode. It has been reported that the formation and growth of lithium dendrites lead to a decrease of cycling efficiency [32–35]. As discussed previously in Fig. 7(a), the cycling efficiency was decreased with cycling in the cell assembled with an un-modified lithium electrode. The lithium dendrite may be isolated from the lithium electrode during the discharge process, and the isolated lithium can react with the organic electrolyte because it is chemically reactive [35]. As a result, the dendritic morphology leads to a decrease of cycling efficiency and discharge capacity with cycling. In contrast, the dendritic morphology was hardly observed in the lithium electrode with the protective layer. In this electrode, a rather flat morphology could be observed. These results suggest that the use of the surface modified lithium electrode may effectively suppress the dendrite growth during cycling. Accordingly, the cell assembled with a surface modified lithium electrode exhibited stable cycling characteristics compared to that of the cell with an un-modified lithium electrode.

4. Conclusions

P(VC-co-AN) was successfully synthesized and employed as a protective SEI layer on a lithium electrode. The thin and uniform protective polymer layer formed on lithium metal suppressed the corrosion of lithium and stabilized the interface of lithium electrode in prolonged contact with organic electrolyte. The Li/LiCoO$_2$ cell assembled with the surface modified lithium electrode exhibited high discharge capacity and good capacity retention. Good cycling performance with a modified lithium electrode could be ascribed to the protective SEI layer that suppresses both the electrolyte decomposition on the lithium anode and the growth of lithium dendrites during cycling. It is thus concluded that the surface modification of lithium electrodes with P(VC-co-AN) is very useful for improving cycling performance of lithium metal batteries for practical application.

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