

Fullerene coated silicon electrodes prepared by a plasma-assisted evaporation technique for the anodes of lithium secondary batteries

Arenst Andreas Arie and Joong Kee Lee*

Advanced Energy Materials Processing Laboratory, Battery Research Center, Korea Institute of Science and Technology, P.O.BOX 131, Cheongryang, Seoul 130-650, Korea

With the aim of enhancing the silicon anode performance in lithium secondary batteries, we have studied the effect of a fullerene thin film as a coating material. The fullerene films were prepared by a plasma assisted evaporation technique from fullerene powder on a Cu foil. As a result, excellent electrochemical performance of fullerene-coated silicon electrodes in terms of stable cycle performance and high specific capacity were observed. The enhanced performances are attributed to the formation of a polymeric phase of the fullerene film as confirmed by Raman spectroscopy, FTIR spectroscopy and XPS analysis. The polymeric layer could act as passive layer to provide mechanical stability against the volume expansion during prolonged cycling tests.

Key word: Thin film, Coating, Lithium battery, Polymeric phase.

Introduction

In the last few decades, lithium ion secondary batteries have been admitted as advanced storage systems to meet the demand in many applications since they offer relatively high specific capacity in comparison with conventional battery systems [1]. On the other hand, the lithium ion battery technology still relies on a graphite anode which has a limited capacity (372 mAh/g) for future applications such as hybrid electric vehicles and miniaturized devices [2]. Therefore, much effort has been made to develop new anode materials that can give a higher capacity than a graphite-based anode [3].

Silicon has been identified as a promising high energy density intercalation material since it can give a maximum capacity of 4200 mAhg⁻¹ from its intercalated compound with lithium [4]. However, it has been known that a silicon-based anode suffers for a poor electrochemical performance due to the volume expansion phenomena during alloying and de-alloying reactions between silicon and lithium [5]. Many efforts have been attempted by researchers to improve the electrochemical performance of silicon anodes including the application of a carbonaceous material as a coating material [6].

The main source of carbon material being used as a precursor in these experiments is fullerene. The fullerenes, discovered in 1985, are a family of carbon allotropes and they are similar in structure to graphite [7]. Fullerenes are cage-like all-carbon molecules which can form polymeric materials when they are excited by high intensity photons,

electron irradiation or plasma operation. This polymeric material has a charge transfer property [8]. In this study, we introduced carbon coatings origins from a fullerene using a plasma assisted evaporation technique to improve the electrochemical properties especially the specific capacity of a silicon anode for a lithium secondary battery.

Experimental

Preparation of thin films

At first, silicon thin films were deposited using radio frequency-plasma enhanced chemical vapor deposition (rf-pecvd) of a gas mixture of silane and argon gas at 200 W onto a 20 µm thick 2 × 2 cm² copper foil. The deposition process was done under a base pressure of 1.5 × 10⁻⁵ Torr (1.99 × 10³ µPa) and a working pressure of 8.0 × 10⁻² Torr (1.06 × 10⁷ µPa). This pressure was controlled by the argon flow rate of 30 sccm. The silane gas was used as the gas precursor with a constant flow of 10 sccm while the substrate temperature was set at 150 °C. The thickness of the Si thin film was about 300 nm. A plasma-assisted thermal evaporation technique was then carried out to coat the silicon anode with a carbon film origins from the fullerene powder. The evaporation chamber was operated at a base pressure of 1.5 × 10⁻⁵ Torr (1.99 × 10³ µPa) and a working pressure of 1.0 × 10⁻² Torr (1.33 × 10⁶ µPa) at a plasma power of 200 W. The fullerene powder was evaporated from a Knudsen cell and then it was deposited on to the silicon thin film. The argon flow rate and substrate temperature were also held at the same values as for the previous deposition conditions. The deposition time of the fullerene film was adjusted to 20 minutes. The thickness of fullerene film was estimated as 100 nm.

*Corresponding author:
Tel : +82-2-958-5252
Fax: +82-2-958-5229
E-mail: leejk@kist.re.kr

Cell assembly

For electrochemical measurements, half cells were then prepared in a dry room (maximum moisture level of 5%). The half-cells were fabricated by sandwiching a polyethylene (PE) separator between the fullerene-coated Si thin electrode (as the working electrode) and Li metal (as the counter electrode) after soaking it in the liquid electrolyte. The half-cell (2 cm × 2 cm) was then sealed in an aluminized polyethylene bag. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1 : 1 : 1 by volume).

Characterizations

The surface morphology and chemical property of the films was observed by scanning electron microscopy (SEM, HITACHI), Raman spectroscopy (Nicolet Almega XR Dispersive Raman Spectrometer, Thermo Electron Corporation, USA with the 633 nm line of an Ar laser), Fourier transform infra red (FTIR) spectroscopy and X ray photo electron spectroscopy (XPS, VG Scientific ESCALAB 200R) respectively. Electrochemical characteristics were investigated by galvanostatic charge/discharge tests (Maccor series 4000, cut off voltage of 0.001 V-2 V vs Li/Li⁺ and current density of 100 μA/cm²) and electrochemical impedance spectroscopy (EIS, Zahner IM 6 with frequency range of 0.01 Hz-1 MHz and amplitude of 5 mV).

Results and Discussion

Fig. 1 shows FTIR spectra of the deposited fullerene films with and without plasma excitation (thermally evaporated film). In the case of films deposited without plasma excitation, four sharp peaks of the fullerene molecule at 527, 576, 1183 and 1428 cm⁻¹ can be characterized. However, the FTIR spectrum of films deposited with plasma excitation shows a different pattern with many new absorption peaks centered at 1100 cm⁻¹, 1375 cm⁻¹ and 1548 cm⁻¹, corresponding with the vibrations of C-C, C=C and C=O. This result implies that by performing a plasma operation during the deposition process, the fullerene

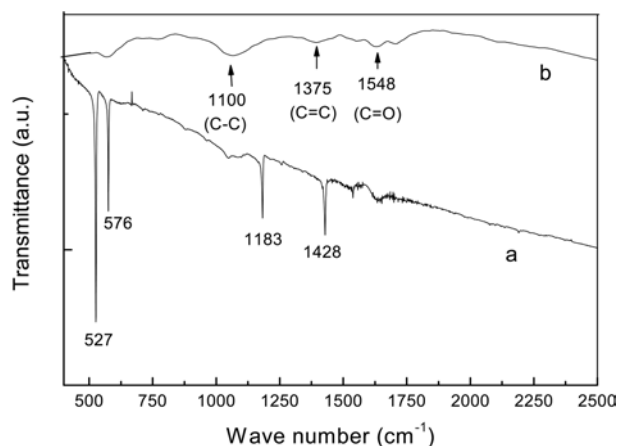


Fig. 1. FTIR spectra of fullerene film (a) without and (b) with plasma excitation during the deposition process.

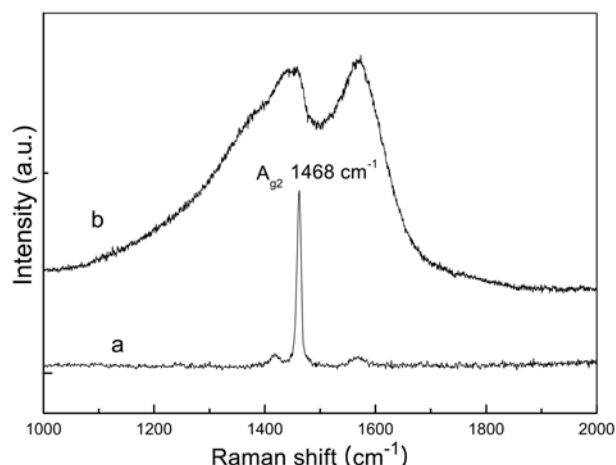


Fig. 2. Raman spectra of fullerene film (a) without and (b) with plasma excitation during the deposition process.

molecules have been transformed into another form of carbon structure. It is possible that a polymeric structure of fullerene has been formed since the deposition process is carried out under plasma excitation.

Fig. 2 displays the Raman spectra of the deposited fullerene thin films with and without plasma excitation. In the spectrum of the deposited film without plasma excitation, one strong peak (A_{g2}) at a wave-number of 1468 cm⁻¹ is clearly observed, corresponding to the vibration mode of fullerene molecules [9]. However, the spectrum of the plasma-deposited fullerene film demonstrates a different pattern since; the shape of the spectrum is very similar to that of amorphous carbon, which means that the film is transformed into an amorphous state. We can also see that the strong peak at 1468 cm⁻¹ has been broadened, indicating that the fullerene molecules are destroyed because of the formation of a fullerene polymer [9-11].

The XPS C1s peaks of both fullerene films with and without plasma excitation (thermal evaporated) are presented in Fig. 3. For the evaporated films, the binding energy is

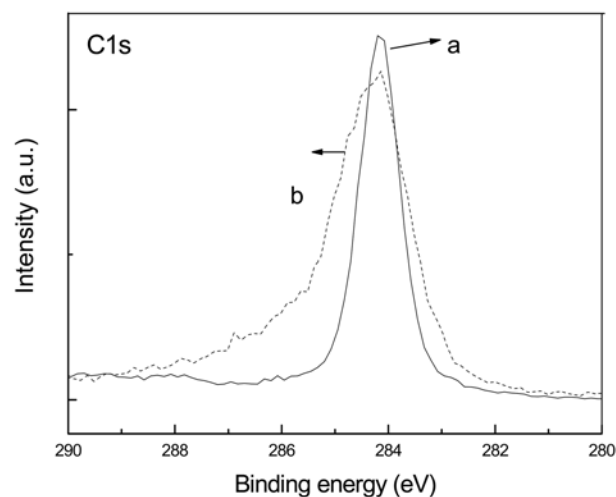


Fig. 3. C 1 s XPS spectra of fullerene film (a) without and (b) with plasma excitation during the deposition process.

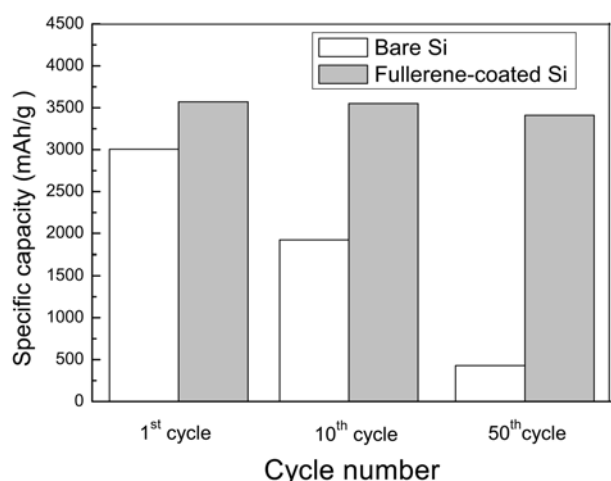


Fig. 4. Bar chart comparisons of the specific capacity for a bare silicon electrode and a fullerene-coated silicon electrode.

about 284.2 eV with a full width at half maximum (FWHM) of 0.96 eV. As seen in Fig 3, the broader FWHM and asymmetric shape are demonstrated by the plasma-deposited films compared with the evaporated films. This much broader peak implies that there is more than one type of bonding for carbon in the plasma-deposited fullerene films. Thus, the XPS results certainly confirm the formation of a polymeric phase of fullerene.

Fig. 4 gives the bar chart comparison of the specific capacity for bare silicon electrode and fullerene-coated silicon electrode during the cyclic tests. The high specific capacity of the fullerene-coated silicon electrode can be maintained at about 3500 mAhg^{-1} in the end of the 30th cycle. While for the bare Si electrode, the rapid capacity fade was observed even in the initial cycle and finally, at the end of 30th cycle, its capacity was 490 mAhg^{-1} . This was due to the large volume expansion phenomena occurred during the cyclic tests. It would be followed by the loss of electrical contact between active material (Si) and current collector (Cu) so resulted in the low specific capacity. By contrast, the high specific capacity of the fullerene-coated silicon electrode was closely related to the formation of polymeric carbon layer, as identified by Raman spectroscopy. The presence of polymeric carbon layer should be the main factor determining the stability of anode surface against the volume expansion problem.

Fig. 5 shows the Nyquist impedance spectra of a bare Si thin film and a fullerene-coated silicon electrode after the first cycle. It can be seen that the bare silicon electrodes displayed the larger diameter of semicircle in the middle frequency range in comparison with that of fullerene-coated silicon electrodes. It means that the bare silicon electrodes demonstrated larger impedance for charge transfer of Li-ions. This was caused by continuous formation of the solid electrolyte interphase (SEI) layer [12]. The direct contact with the electrolyte could be the main factor responsible for the formation of such kind of layer. However, this phenomena is not observed in the case of

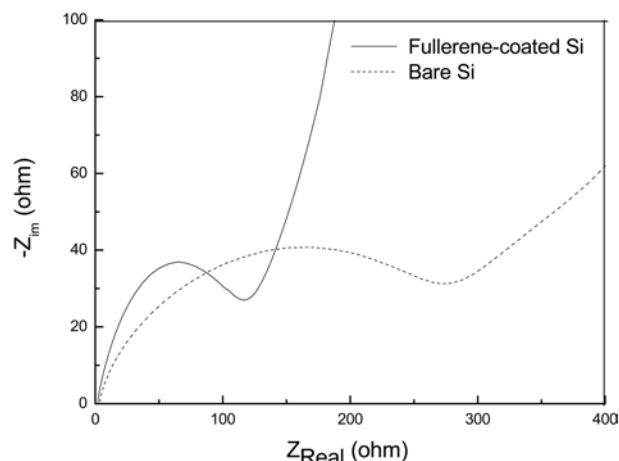


Fig. 5. Electrochemical impedance spectra (EIS) of a bare silicon electrode and a fullerene-coated silicon electrode over a frequency range of 0.01 Hz-1 MHz.

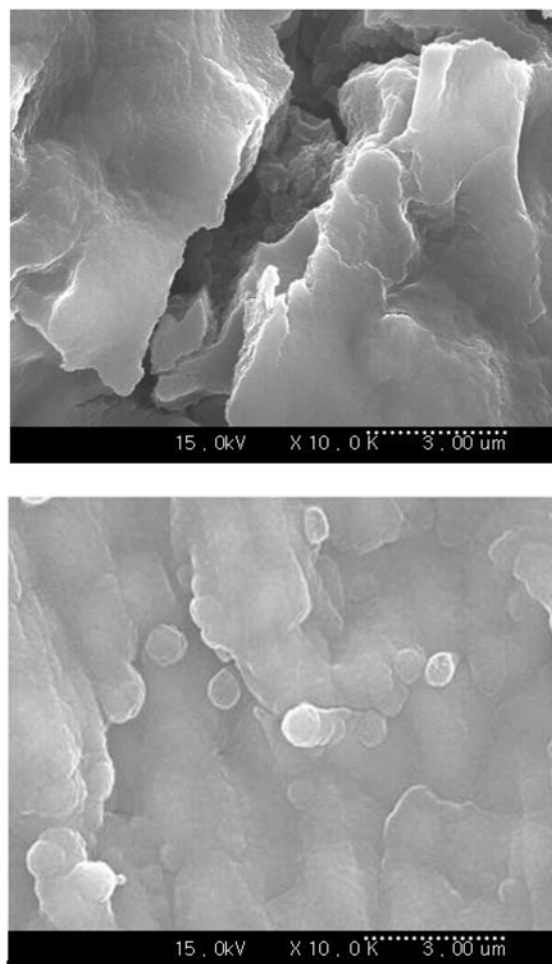


Fig. 6. SEM images of (a) silicon electrode and (b) fullerene-coated silicon electrode after cyclic tests (after 30th cycle).

fullerene-coated silicon film anodes, as observed in Fig. 5, its impedance is much smaller since it could protect the silicon surface against the side reaction with the electrolyte.

Fig. 6 compares the SEM images of a bare Si thin film and a fullerene-coated silicon thin film after 30 cycles

of cyclic tests. From Fig. 6, it can be seen that there are large cracks on the surface of bare Si film and eventually these cracks cause the rapid capacity fading as shown in Fig. 4 due to the lost of electrical contact. In the case of fullerene-coated silicon, there were no surface cracks on its surface. It seems that the polymeric layer could prevent the propagation of the cracks in the initial cycling. Therefore, the effect of surface cracking due to the volume change could be reduced. As a result, the fullerene-coated silicon thin film anodes gave much better cycling stability and high specific capacity compared with the bare Si thin film anodes as can be observed in Fig. 4.

Conclusions

In this study, carbon thin films have been deposited onto the surface of silicon anodes by a plasma assisted evaporation technique using a fullerene as a carbon precursor. It was observed from SEM images that the cracking on the surface of a silicon thin film could be avoided by the presence of a fullerene film coating. Raman spectroscopy, FTIR spectroscopy and XPS results showed that the carbon layer formed was in the polymeric form of fullerene. This has lead to better electrochemical properties of the fullerene-coated silicon thin film since much higher specific capacity, stable cyclic performance and lower interfacial impedance can be achieved. It seems that the polymeric fullerene layer gives a mechanical stability against the volume expansion of the electrode during charge-discharge tests. Further research is still in progress to control the structure of the polymeric fullerene layer as well as to further improve the electrochemical performance.

Acknowledgement

This research was supported by a grant(code #: 2009K000448) from 'Center for Nanostructured Materials Technology' under '21st Century Frontier R&D Programs' of the Ministry of Education, Science and Technology, Korea. The silicon electrodes are kindly prepared by Seok Min Moon.

References

1. J.M. Tarascon and M. Armand, *Nature* 414 (2001) 359.
2. O. Bitsche and G. Gutmann, *J. Power Sources* 127 (2004) 8-15.
3. Y. Nishi, *J. Power Sources* 100 (2001) 101-106.
4. M.N. Obrovac and L. Christensen, *Electrochem. Solid-State Lett.* 7 (2004), p. A93.
5. R.A. Huggins, *Solid State Ionics* 113-115 (1998) 57-67.
6. M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov and Z. Ogumi, *J. Electrochem. Soc.* 149[12] (2002) A158-A1603.
7. P.C. Eklund and A.M. Rao, "Fullerene Polymers and Fullerene Polymer Composites" (Springer, Berlin-Heidelberg, 2000), p.1-3.
8. F. Giacalone and N. Martin, *Chem. Rev.* 106 (2006) 5136-5190.
9. A.M. Rao, P.C. Eklund, J-L. Hodeau and L. Marques, M. Nunez Regueiro, *Phys. Rev B*, 55 (1997) 4766.
10. V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V. Agafonov, H. Allouchi, R. Ceolin, A.V. Dzyabchenko and V.M. Senyavin, H. Szwarc, *Phys. Rev B*, 58[14] (1998) 786.
11. P.C. Eklund, P. Zhou, K.A. Wang, M.S. Dresselhaus and G. Dresselhaus, *J. Phys. Chem. Solids*, 53 (1992) 1391.
12. T.D. Hatchard, J.R. Dahn *J. Electrochem. Soc.* 151[6] (2004) A838-A842.