Short communication

# Effects of carbon coating on the electrochemical properties of sulfur cathode for lithium/sulfur cell

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## ARTICLE INFO

## ABSTRACT

Carbon-coated sulfur cathodes were prepared by sputtering method and electrochemical properties of lithium/sulfur cells were investigated. As a result of charge/discharge test, sulfur cathode having carbon layer of 180 Å showed the highest capacity of 1178 mA h$g^{-1}$ at first discharge. Moreover, discharge capacity showed about 500 mA h$g^{-1}$ until 50th cycle, which is two times larger than that of no-coated sulfur cathode. This capacity increase could be considered due to the decrease of polysulfides dissolution and the enhancement of electrical contact by surface carbon layer. The changes of sulfur cathode during discharge process were investigated by SEM observation, XRD and DSC measurements. From these results, a discharge reaction mechanism of lithium/carbon-coated sulfur cell was suggested.

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## 1. Introduction

The rapid advancement of electronic technology and the widespread use of mobile devices have been continuously demanding a next generation battery. Lithium/sulfur battery is very attractive because of its high theoretical specific capacity of 1675 mA h$g^{-1}$-sulfur, assuming a complete reaction to $Li_2S$. Besides, elemental sulfur is very cheap, abundant and nontoxic material [1,2]. Despite of those advantages, lithium/sulfur battery is difficult to commercialize due to low sulfur utilization and poor cycle life property. Those problems are caused by soluble polysulfides ($S_n^{2-}$, $n \geq 4$), which generate during charge/discharge process. Because polysulfides dissolution into the liquid electrolytes cause the active material loss and the viscosity increase of liquid electrolyte as well as the morphology change of sulfur cathode [2–5]. Additionally, 100% sulfur cathode cannot be made due to very low electrical conductivity of sulfur ($5 \times 10^{-30}$ S cm$^{-1}$ at 25 °C) [6,7]. It must contain electronically conductive materials such as carbon and metallic powders [4,8,9].

To solve the problems, Gorkovenko [10] added micro-sized vanadium oxide, silicates and transition chalcogenides into sulfur cathode in order to prevent the polysulfides dissolution. Although metal oxides are effective for polysulfides adsorption due to their large specific area, those materials are not desirable as additive for lithium/sulfur cells due to their insulating property. Also, the sulfur utilization [11] was increased by addition of multi-walled carbon nanotubes (MWNTs) and cycle life property [12] was improved by addition of carbon nanofibers into sulfur cathode. Because those linear carbon materials give an effective electron conduction path and their network-like structure forms a structural stability of sulfur cathode during charge/discharge process. However, carbon nanotubes and nanofibers are very expensive and the manufacturing process is complex. Recently, many interesting cathode materials, such as $LiMPO_4$ (M = Fe, Mn, Ni, Co), $LiFeBO_3$ or $Li_2MSiO_4$ (M = Fe, Mn, Ni), have been treated by carbon coating to enhance electrical conductivity [13]. A surface modification has been used in anode materials for lithium ion batteries to reduce the large irreversible capacity [14,15].

In this study, in order to enhance electrical conductivity, carbon was coated on a surface of sulfur cathode by using carbon coater and effects of carbon coating on the electrochemical properties were investigated.

## 2. Experimental

Raw materials for fabrication of sulfur cathode were kept in a vacuum oven (80–120 °C) to remove residual water. To decrease

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**Fig. 1.** Schematic diagram of cell components including electrodes.

**Table 1**
The thickness of carbon coating layer

| | The thickness at the number of carbon coating times (Å) | | | |
|---|---|---|---|---|
| | 1st | 2nd | 3rd | Average |
| 4 s | 180 | 175 | 185 | 180 |
| 12 s | 220 | 250 | 230 | 231 |
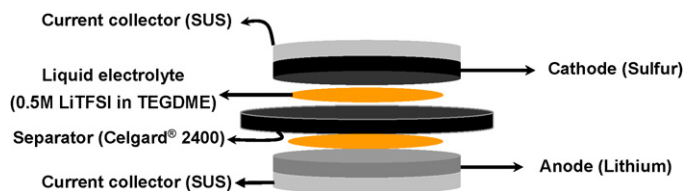


**Fig. 3.** Cyclic voltammograms of lithium/sulfur cells with 0.01 mV s$^{-1}$ scan rate: (a) no-coated, (b) coated for 4 s and (c) coated for 12 s.

size of sulfur powder, commercially produced sulfur powder (−325 mesh, Aldrich) was sieved to get size of below 25 μm. After sieving, it was mechanically milled by planetary milling machine. Then, sulfur having particle size of below 10 μm was obtained.

Fabrication procedure of sulfur cathode is as follows. Pretreated sulfur powder, acetylene black (<1μm, Alfa) and PVDF (Mw = 534,000, Aldrich) were added into zirconia container with NMP (99%, Aldrich) solvent at the weight ratio of 60:20:20. The suspension was mechanically mixed with zirconia ball by planetary ball milling for 3 h. After homogeneous mixing, the slurry was coated on an aluminium current collector. Finally, it was dried at 80 °C for 12 h until the solvent was completely evaporated.

To investigate effects of carbon coating, carbon was coated on a surface of sulfur cathode by using carbon coater (CARBON COATER 208, CRESSINGTON) in a vacuum of 10$^{-3}$ Torr for 4 and 12 s, respectively. The thickness of carbon coating layer was measured by using Tencor P-11 surface profiler (KLA-Tencor Corp.).

Liquid electrolyte to evaluate electrochemical properties of lithium/sulfur cells was prepared by dissolving 0.5 M LiTFSI (LiN(CF$_3$SO$_2$)$_2$, Aldrich) salt into TEGDME (99%, Aldrich) organic solvent. Fabrication of liquid electrolyte was carried out in an argon-filled glove box and water content was kept below 20 ppm by adding 4 Å molecular sieve.

The morphology change of sulfur cathode before and after charge/discharge test was observed with scanning electron microscope (JSM-5600, JEOL Co.). Test cell was assembled in a stainless-steel case (Swagelok®) by stacking a lithium foil, polypropylene separator (Celgard® 2400) containing liquid electrolyte and sulfur cathode in turn. Schematic diagram of cell components including electrodes is presented in Fig. 1. All processes of assembling were carried out in an argon-filled glove box. Redox profiles of lithium/sulfur cells were investigated by using cyclic voltammetry method in the voltage range of 1.5–3.2 V (vs. Li$^+$/Li) at 0.01 mV s$^{-1}$ scan rate. The interfacial resistance of cell was evaluated by using electrochemical impedance spectroscopy (CMS100, Gamry Instruments Inc.) in the frequency range of 0.1 to 10$^5$ Hz with 0.1 mV amplitude. The cut-off voltage and current density for charge/discharge tests were 3.2/1.5 V (vs. Li) and 100 mA g$^{-1}$, respectively. Cell tests were carried out with galvanostatic method by using WBCS3000 battery cycler. To analyze change of reaction product during discharge, X-ray diffraction (RINT2500 V, Rigaku Co.) and differential scanning calorimeter (TA2040, TA Instruments) measurements were performed.
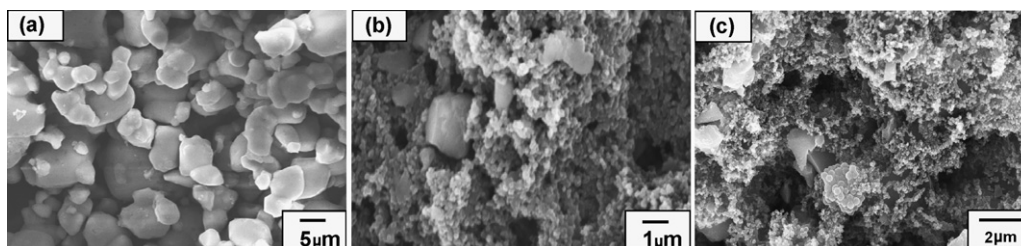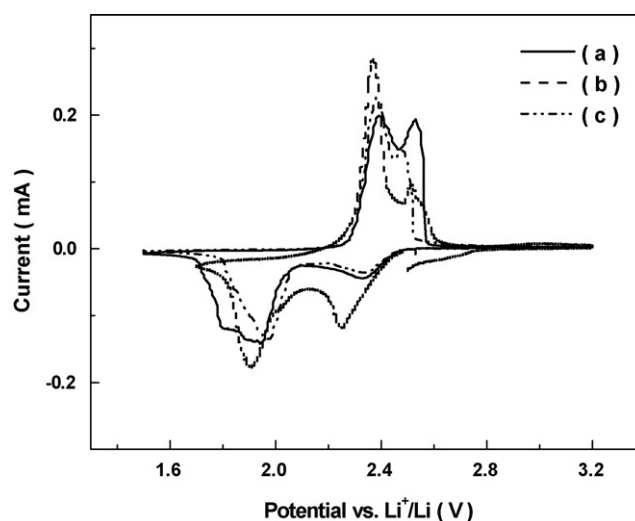
## 3. Results and discussion

Fig. 2 shows SEM morphologies of sulfur powder and sulfur cathodes. In a present study, commercial sulfur powder having size of below 45 μm was pre-treated by sieving and mechanical milling to decrease particle size of sulfur. After size decreasing, sulfur particles showed size of below 10 μm as shown in Fig. 2(a). With decreasing sulfur particle size, sulfur utilization would be increased due to the decrease of cathode resistance and the increase of specific surface area [16], because sulfur is an insulator. As shown in Fig. 2(b and c), carbon particles are well dispersed in the sulfur cathodes. In case of the carbon-coated sulfur cathode, surface roughness was increased and sulfur particles were well covered with carbon particles compared to the no-coated sulfur cathode. These differences of surface morphologies could be considered due to carbon coating layer. Table 1 shows the thickness of carbon coating layer at the number of coating times.

Fig. 3 shows cyclic voltammograms of lithium/sulfur cells tested with 0.01 mV s$^{-1}$ scan rate. Sulfur cathode without carbon coating shows three cathodic peaks at 1.8, 1.9 and 2.3 V as well as two anodic peak at 2.4 and 2.5 V, respectively. The detailed mechanisms for oxidation and reduction of sulfur, polysulfides and lithium sulfide during charge/discharge were already reported. [17,18]. First
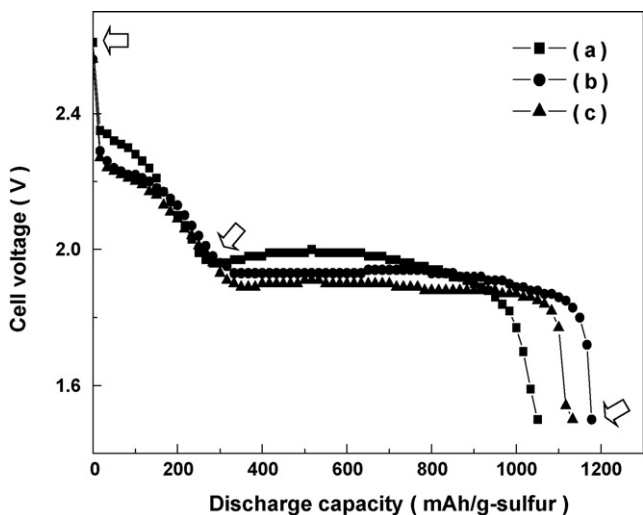


**Fig. 2.** SEM morphologies of sulfur powder (a), no-coated (b) and carbon-coated sulfur cathode (c).

**Fig. 4.** Discharge voltage profiles of lithium/sulfur cells tested at $100\,mA\,g^{-1}$: (a) no-coated, (b) coated for 4 s and (c) coated for 12 s.



**Fig. 5.** Cycle life properties of lithium/sulfur cells tested at $100\,mA\,g^{-1}$: (a) no-coated, (b) coated for 4 s and (c) coated for 12 s.

cathodic peak is well known as the formation of short polysulfides ($S_6{}^{2-}$ and $S_4{}^{2-}$) by cyclooctasulfur ($S_8$) reduction. In addition, other cathodic peaks correspond to the formation of insoluble lithium sulfide ($Li_2S_2$ or $Li_2S$) by short polysulfides reduction. In case of carbon-coated sulfur cathodes, anodic peak appearing at 2.37 V was slightly shifted to lower potential. These potential shifts means that $Li_2S$ (or $Li_2S_2$) accumulated on the surface of carbon was easily oxidized, because much more electron conduction paths were provided to the insulating discharge products by surface carbon coating.

Fig. 4 shows first discharge voltage profiles of lithium/sulfur cells. All of lithium/sulfur cells showed two discharge reaction plateaus. Discharge voltage values of upper and lower plateau coincide with the CV results as shown in Fig. 3. Theoretically, standard potentials of upper and lower plateau are $E^0 = 2.33$ V and $E^0 = 2.18$ V. Usually, some degrees of discharge voltage drop are taking place. This voltage drop is well known as IR loss, which is mainly generated by internal resistance of the cell. Here, internal resistance is
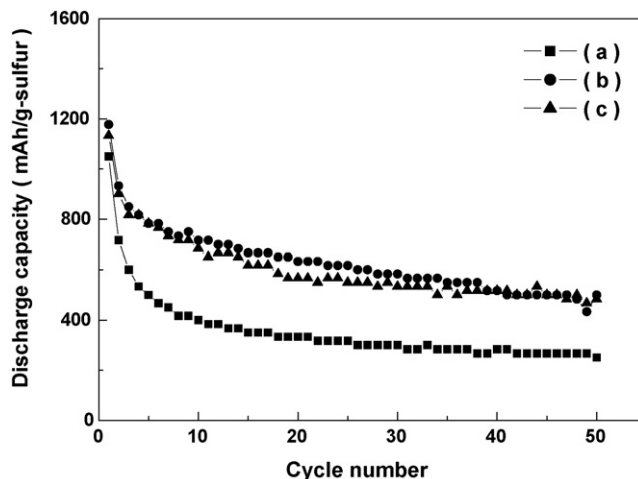
a sum of ionic resistance of the electrolyte, electronic resistance of electrode-current collector and interfacial resistance of electrode-electrolyte, etc. In case of the carbon-coated cathodes, more voltage drop was occurred. This could be explained by relatively low electrolyte wetability of carbon layer existing on the cathode surface. According to previous report, wetability of carbon materials is poor due to their large advancing contact angle [19]. However, in spite of IR loss, carbon-coated sulfur cathodes showed a high discharge capacity of 1178 (coated for 4 s) and 1113 mA h$g^{-1}$ (coated for 12 s), respectively. These high discharge capacities could be considered due to increase of sulfur utilization by enhancement of electrical contact.

Cycle life properties of lithium/sulfur cells are given in Fig. 5. In case of the no-coated sulfur cathode, first discharge capacity showed 63% of theoretical capacity. At subsequent cycles, discharge capacity was rapidly decreased to 400 mA h$g^{-1}$ until 10th cycle. On the other hand, capacity fading of carbon-coated sulfur cathodes was relatively slow and discharge capacity showed 716 mA h$g^{-1}$ in the case of the carbon-coated for 4 s at 10th cycle. Cycle life
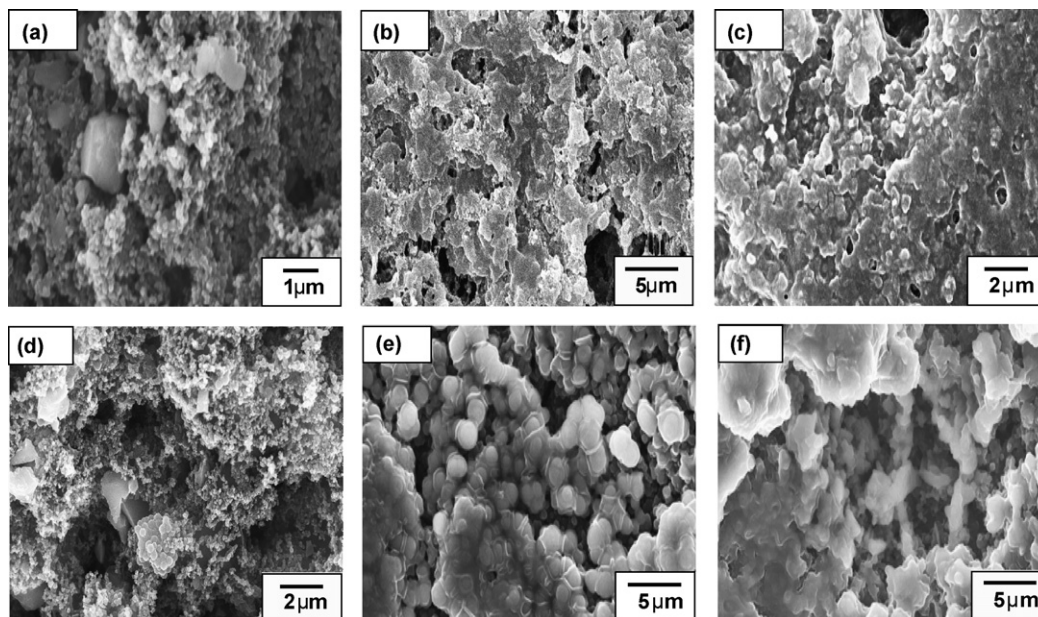


**Fig. 6.** SEM morphologies of sulfur cathodes during discharge process: (a) before discharge, (b) after upper plateau reaction ends and (c) after lower plateau reaction ends.

behaviors were similar to both no-coated and carbon-coated sulfur cathodes. However, discharge capacity of carbon-coated sulfur cathodes showed about 500 mA h g$^{-1}$ at 50th cycle, which is two times larger than that of no-coated sulfur cathode. As seen in Figs. 4 and 5, first discharge capacity shows above 1000 mA h g$^{-1}$. According to the previous study, Choi et al. [16] reported that sulfur utilization can be increased by a reduction of particle size and a use of carbon black having larger surface area, which provides more electrochemical reaction sites. From the results of cycle tests, capacity increase could be considered that electrical contact between sulfur and carbon was improved by carbon coating on the surface of sulfur cathode. Moreover, it could be assumed that surface carbon layer was acted as ceramic additive adsorbing lithium polysulfides. To investigate the change of sulfur cathode during discharge process, SEM observation, XRD and DSC measurements were performed at the indicated point by arrow in the Fig. 4.

After first discharge, sulfur cathodes were dried in an argon-filled glove box under low vacuum. Also, residual liquid electrolyte was completely removed before analysis. Morphology changes of sulfur cathodes during discharge process are shown in Fig. 6. At the end of the upper discharge region, most of the sulfur was disappeared in the no-coated sulfur cathode as can be seen in Fig. 6(b). This surface might be composed of acetylene black and polymer binder. Because solid discharge products (e.g. Li$_2$S$_2$ or Li$_2$S) could not be formed above lower discharge region [5]. After a full discharge, the surface of no-coated sulfur cathode was changed to dense by deposition of lithium sulfide [3,11]. However, surface morphology of carbon-coated sulfur cathode was remarkably different. At the end of the upper discharge region, particles having spherical shape were appeared. According to the suggested model by Rye et al. [2], these spherical particles might be constituted by internal sulfur and outer lithium polysulfides (e.g. Li$_2$S$_n$, $n \geq 4$). This suggestion was agreed with the XRD analysis and DSC measurement as shown in Figs. 7 and 8. Also, lithium polysulfides adsorbing effects of inorganic additives [10,11,20] were already reported. It was suggested that inorganic additives such Mg$_{0.6}$Ni$_{0.4}$O, Al$_2$O$_3$ and MWNTs gives a beneficial effect on the improving cycle life property of lithium/sulfur cell because of their large specific area. In a present study, one of the reasons for capacity increase could be explained due to the lithium polysulfides adsorption by surface carbon layer. As the results of SEM observation during discharge process, above-mentioned evidence could be found by surface morphology changes of sulfur cathode.

Fig. 7 shows the changes of XRD patterns of sulfur cathode (coated for 4 s) during discharge process. After the fabrication of sulfur cathode, the crystal structure of sulfur is orthorhombic corresponding to cyclooctasulfur molecule (S$_8$). At the end of the first reaction region, peak intensity related to sulfur is decreased. Diffraction peaks corresponding to the lithium sul-
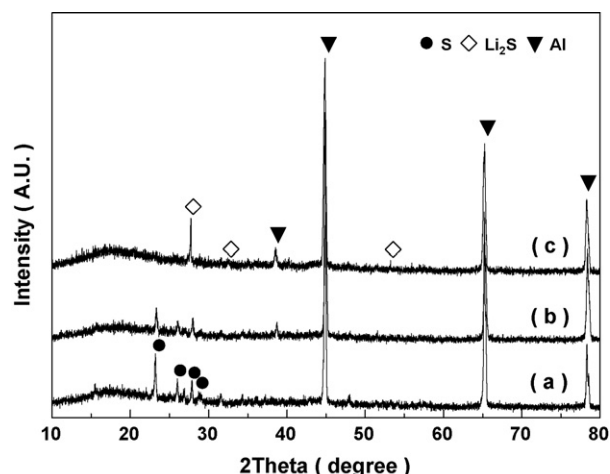


Fig. 7. XRD patterns of carbon-coated sulfur cathode during discharge process: (a) before discharge, (b) after upper plateau reaction ends and (c) after lower plateau reaction ends.
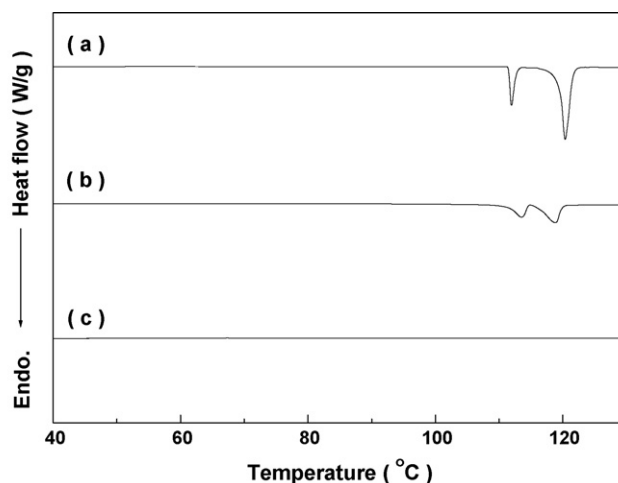


Fig. 8. The change of DSC curves of carbon-coated sulfur cathode during discharge process: (a) before discharge, (b) after upper plateau reaction ends and (c) after lower plateau reaction ends.

fide (Li$_2$S) appears after complete discharge process as shown in Fig. 7(c). These results coincide with the DSC curves as shown in Fig. 8. In the DSC results, two sharp endothermic peaks appears at 112 °C (rhombic melting point) and 120 °C (monoclinic melting point) [1]. The intensity of endothermic peaks decreases at the end of first reaction region. Finally, endothermic peaks are completely
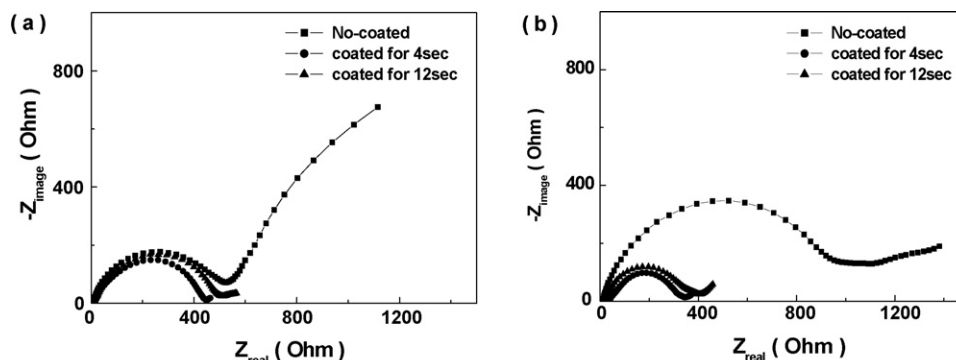


Fig. 9. Changes of interfacial resistance of lithium/sulfur cells: (a) before discharge and (b) after 50 cycles.

disappeared after full discharge. From the results of SEM observation, XRD analysis and DSC measurements, a discharge reaction mechanism of lithium/carbon-coated sulfur cell could be suggested as follows.

First reaction region : $nS + 2Li^+ + 2e^- \rightarrow Li_2S_{(n-1)} + S (4 \leq n \leq 8)$

$$(1)$$

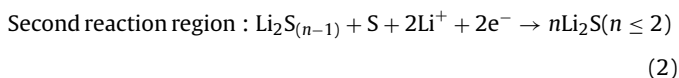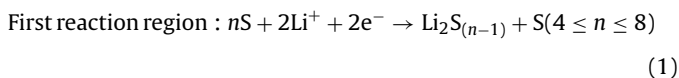Second reaction region : $Li_2S_{(n-1)} + S + 2Li^+ + 2e^- \rightarrow nLi_2S (n \leq 2)$

$$(2)$$

Fig. 9 shows typical Nyquist plots of lithium/sulfur cells after 50 cycles. Before charge/discharge tests, all of sulfur cathodes show similar size of the semi-circle at high frequencies corresponds to the faradic charge-transfer behavior. Particularly, no-coated sulfur cathode represents the straight line at low frequencies corresponds to the linear diffusion process, which is called a Warburg diffusion. Moreover, the angle of the Warburg diffusion is very close to 45°. This could be thought that electrode surface is relatively flat [21]. However, after 50 cycles, the angle of the Warburg diffusion decreases due to the slow ion diffusion into the sulfur cathode by concentration increase of lithium polysulfides at the cathode-electrolyte interface. Then, charge-transfer resistance largely increases to 969 Ω due to poor electrical contact originated by severe morphology change of sulfur cathode. On the contrary, interfacial resistance of lithium/sulfur cells were somewhat decreased in the presence of carbon layer. From the results of interfacial resistance measurements, capacity increase of carbon-coated sulfur cathode could be explained by three reasons representing below:

(i) Increase of sulfur utilization by smaller particle size,
(ii) enhancement of electrical contact and
(iii) decrease of active material loss due to lithium polysulfides adsorption by coated carbon.

## 4. Conclusions

Carbon-coated sulfur cathodes were prepared by sputtering method and effects on the electrochemical properties of lithium/sulfur cells were investigated. The average thickness of carbon coating layer was 180 Å (coated for 4 s) and 231 Å (coated for 12 s). After first discharge, carbon-coated sulfur cathodes showed a high discharge capacity of 1178 (coated for 4 s) and 1113 mA hg$^{-1}$ (coated for 12 s), respectively. Capacity fading of carbon-coated sulfur cathodes was relatively slow compare to no-coated sulfur cathode and it showed discharge capacity about 500 mA hg$^{-1}$ at 50th cycle. Capacity increase could be explained that electrical contact between sulfur and carbon was improved by carbon coating. Additionally, it could be considered due to the polysulfides (e.g. $S_8^{2-}$, $S_6^{2-}$ and $S_4^{2-}$) adsorption by surface carbon layer. From the results of SEM observation, XRD and DSC measurements after discharge, cyclooctasulfur molecule ($S_8$) was completely changed to lithium sulfide ($Li_2S$). After 50 cycles, interfacial resistance of no-coated sulfur cathode was largely increased to 969 Ω due to poor electrical contact originated by severe morphology change of sulfur cathode. Therefore, it could be concluded that carbon coating gives beneficial effects on the improvement of discharge capacity and cycle performance by enhancement of electrical contact and adsorption of lithium polysulfides.

## Acknowledgement

## References

[1] R.P. Tischer, The Sulfur Electrode, Academic Press, 1983.
[2] H.S. Ryu, H.J. Ahn, K.W. Kim, J.H. Ahn, J.Y. Lee, J. Power Sources 153 (2006) 360–364.
[3] S.E. Cheon, J.H. Cho, K.S. Ko, C.W. Kwon, D.R. Chang, H.T. Kim, S.W. Kim, J. Electrochem. Soc. 149 (2002) A1437–A1441.
[4] B.H. Jeon, J.H. Yeon, K.M. Kim, I.J. Chung, J. Power Sources 109 (2002) 89–97.
[5] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, J. Electrochem. Soc. 150 (2003) A796–A799.
[6] J.A. Dean, Lange's Handbook of Chemistry, third ed., McGraw-Hill, New York, 1985, pp. 3–5.
[7] E. Peled, Y. Sternberg, A. Gorenshtein, Y. Lavi, J. Electrochem. Soc. 136 (1989) 1621.
[8] M.Y. Chu, US Patent US05,814,420 (1998).
[9] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, J. Power Sources 89 (2000) 219.
[10] Gorkovenko, US Patent 6,210,831 B1 (2001).
[11] S.C. Han, M.S. Song, H. Lee, H.S. Kim, H.J. Ahn, J.Y. Lee, J. Electrochem. Soc. 150 (2003) A889–A893.
[12] Y.J. Choi, K.W. Kim, H.J. Ahn, J.H. Ahn, J. Alloys Compd. 449 (2008) 313–316.
[13] J. Moskon, R. Dominko, R. Cerc-Korosec, M. Gaberscek, J. Jamnik, J. Power Sources 174 (2007) 683–688.
[14] J.H. Lee, H.Y. Lee, S.M. Oh, S.J. Lee, K.Y. Lee, S.M. Lee, J. Power Sources 166 (2007) 250–254.
[15] W. Xing, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 1195.
[16] Y.S. Choi, S. Kim, S.S. Choi, J.S. Han, J.D. Kim, S.E. Jeon, B.H. Jung, Electrochim. Acta 50 (2004) 833–835.
[17] H. Yamin, J. Pensiner, A. Gorenshtain, M. Elam, E. Peled, J. Power Sources 14 (1985) 129.
[18] J. Shim, K.A. Striebel, E.J. Cairns, J. Electrochem. Soc. 149 (2002) A1321–A1325.
[19] Y. Xie, P.M.A. Sherwood, Appl. Spectrosc. 45 (1991) 1158–1165.
[20] M.S. Song, S.C. Han, H.S. Kim, J.H. Kim, K.T. Kim, Y.M. Kang, H.J. Ahn, S.X. Dou, J.Y. Lee, J. Electrochem. Soc. 151 (2004) A791–a795.
[21] C.M.A. Brett, A.M.O. Brett, Electrochemistry, Oxford Science Publication, 1993, 224 pp.