Int. J. Electrochem. Sci., 10 **(2015)** 7574 - 7581

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Influence of the Electrode Materials on the Electrochemical Performance of Room Temperature Li-SO_2 Rechargeable Battery

Seong Soon Park, Yongju Jung[*]

Department of Chemical Engineering, Korea University of Technology and Education
(KOREATECH), Cheonan 330-780, Korea
[*]E-mail: yjung@koreatech.ac.kr

Received: 16 June 2015 / *Accepted:* 8 July 2015 / *Published:* 28 July 2015

The influence of the electrode material on the electrochemical properties of Li/SO_2 rechargeable batteries containing a $LiAlCl_4$-based inorganic electrolyte solution was investigated using various carbon black materials such as Ketjenblack EC-600JD (KB-600), Ketjenblack EC-300J (KB-300), Printex XE-2, and acetylene black. The electrochemical reaction of sulfur dioxide (SO_2) in an inorganic electrolyte was found to be strongly dependent on the type of carbon black material. The test cells with KB-600, KB-300 and Printex XE-2 exhibited much larger discharge capacities of more than 1650 mAh/g in the first cycle with respect to the carbon weight in the cathode compared to that (~560 mAh/g) of the test cell with acetylene black. In particular, the cell with KB-600 showed extremely high capacities of 1280 mAh/g at a C-rate of 5.0 C and considerable capacity retention (87%) after 50 cycles.

Keywords: Li-SO_2, $LiAlCl_4{\cdot}3SO_2$, Carbon black, Rechargeable batteries

1. INTRODUCTION

Lithium/sulfur dioxide (Li/SO_2) batteries, which have a high energy density of up to 260 Wh/kg and a wide operating temperature range (–60°C to +70°C) are one of the most advanced lithium primary batteries[1-2]. The Li/SO_2 batteries consist of a carbon positive electrode, a lithium metal negative electrode and a nonaqueous electrolyte containing sulfur dioxide (SO_2) in an organic solvent, typically acetonitrile. The electrode reaction of SO_2, the active cathode material, proceeds on the surface of the carbon electrode. The overall reaction of the cell is explained in the following way:

$$2Li + 2SO_2 \rightarrow Li_2S_2O_4$$

The internal cell pressure of a fresh cell can reach up to 3~4 atm at 20°C because of the high vapor pressure of SO_2. During discharge, the internal cell pressure decreases gradually as the SO_2 is consumed. In general, discharge process is terminated when the lithium metal, the limiting electrode, is fully consumed. Li/SO_2 primary batteries are now manufactured in a range of cylindrical cells and are used mainly in military applications. The charging of Li/SO_2 primary batteries is not recommended due to safety issues. Li/SO_2 batteries based on a totally inorganic electrolyte have also been developed as a high-energy-density lithium secondary battery, but they have not been commercialized[3-6]. Many inorganic salts, such as $LiAlCl_4$ and $LiGaCl_4$, form stable solvates with SO_2, leading to a highly conductive liquid inorganic electrolyte[7-11]. The proposed overall reaction mechanism of Li/SO_2 rechargeable batteries containing $LiAlCl_4{\cdot}3SO_2$ electrolytes is as follows[3]:

$$3Li + LiAlCl_4{\cdot}3SO_2 \rightarrow LiAlCl(SO_2)_3 + 3LiCl$$

It is generally accepted that upon discharge, $3SO_2$ molecules in the $LiAlCl_4{\cdot}3SO_2$ electrolytes are reduced to $3SO_2^-$ ions, of which the attack on $AlCl_4^-$ ions results in the formation of $AlCl(SO_2)_3^-$ with the ejection of chloride ions, leading to the formation of LiCl[3]. The insoluble lithium chloride precipitates on the surface of the carbon electrodes as it is formed. The carbon electrode material can contribute directly to the electrode reaction of SO_2 because it occurs on the carbon electrode surface. To date, however, the influence of the electrode materials on the electrode reaction of SO_2 in the $LiAlCl_4{\cdot}3SO_2$ electrolyte has not been explored extensively. In this study, the electrochemical properties of $Li/LiAlCl_4{\cdot}3SO_2/SO_2$ rechargeable batteries were investigated using a variety of carbon black materials.

2. EXPERIMENTAL SECTION

The carbon cathodes consisted of carbon black (90 wt%) and polytetrafluoroethylene (PTFE) binder (10 wt%). A mixture of carbon black and PTFE was coated and pressed on an expanded nickel metal current collector to maintain the integrity of the cathode. A range of carbon black materials, including Ketjenblack EC-600JD (Lion Co., Japan), Ketjenblack EC-300J (Lion Co., Japan), Printex XE-2 (Degussa Co., Germany), and acetylene black (Denka, Japan), were used as an electrode material. In this paper, Ketjenblack EC-600JD and Ketjenblack EC-300J are denoted as KB-600 and KB-300, respectively. The nitrogen sorption tests were performed using a Micromeritics TriStar 3000 to determine the surface area, pore volume and pore size distribution of the carbon black materials used. The surface area was determined in the range of relative pressure (P/P_0) = 0.01–0.10 using the Brunauer–Emmett–Teller (BET) method. The total pore volume (V_t) was measured at a relative pressure (P/P_0) of 0.95 using the Barrett-Joyner-Halenda (BJH) method. The mesopore volume (V_{meso}) was estimated by subtracting the volume of nitrogen adsorbed at P/P_0 = 0.10 from the total pore volume (V_t). The average loading of the carbon black material was ~2.2 mg/cm^2. The carbon cathodes were dried at 100°C under vacuum for 12 h to remove water. Lithium metal foil was used as the counter electrode to assemble the coin type cells. The inorganic electrolyte solution of $LiAlCl_4{\cdot}3SO_2$ was prepared by reacting gaseous sulfur dioxide (Alpha Gas, Korea) with a mixture of LiCl (Alfa Aesar) and $AlCl_3$ (Alfa Aesar) in a glass vessel without exposure to air. Excess SO_2 in the electrolyte was degassed through a bubbler. The resulting electrolyte contained 3.02 SO_2 molecules per a $LiA1C1_4$ formula unit, as measured by weight. The volume of the inorganic electrolyte solution used to fabricate of the coin type cells was 0.2 mL.

Galvanostatic charge/discharge tests were performed in a voltage range of 2.20 to 3.95 V versus Li/Li^+ at 25°C. The prepared $Li/LiAlCl_4{\cdot}3SO_2/SO_2$ cells were discharged and charged at a rate of 0.1 C for the first two cycles. Subsequently, the rate property of the cells was evaluated at discharge rates ranging from 0.2 C to 5.0 C with a fixed charge rate of 0.2 C. In addition, cycle tests were carried out for additional 50 cycles at the following constant C rates: 0.5 C for discharge and 0.2 C for charge. In this study, the third cycle was considered the first cycle of the cycle tests and 1.0 C rate is defined as a current of 1500 mA per gram of carbon black material. Note that the initial two cycles are regarded as a formation step for the normal operation of prepared cells and capacities are expressed with respect to the mass of carbon black.

3. RESULTS AND DISCUSSION

Figure 1 shows the nitrogen adsorption/desorption isotherms of the carbon black samples. The KB-600 and Printex XE-2 exhibited hysteresis curves over a broader range of P/P_0 (0.5–0.9), which is a general characteristic of a mesoporous material. This feature may be associated with the aggregation of primary carbon black particles. On the other hand, the KB-300 and acetylene black showed typical type II isotherms which are generally observed in nonporous materials[12]. KB-600, KB-300 and Printex XE-2 showed substantially larger surface areas (>760 m^2/g) compared to that of acetylene black (54 m^2/g).

In this study, it was postulated that the electrode reaction of SO_2 would be quite sensitive to the type and area of the carbon black materials used because the charge transfer reaction occurs at the interface of the carbon electrode and electrolyte. To confirm this, the cathodes of the Li-SO_2 cells were constructed using the four types of carbon black: KB-600, KB-300, Printex XE-2, and acetylene black. Figure 2 presents the charge/discharge curves for the first two cycles of the Li-SO_2 cells with different carbon black materials. A significant hysteresis between the charge and discharge curves was observed regardless of the type of carbon black materials, which is consistent with that observed in the previous work of Dey et al. [3]. It seems that the hysteresis is mainly caused by the solid LiCl particles with high lattice energy, which are formed during discharge. In the first cycle, the test cells with KB-600, KB-300 or Printex XE-2 exhibited much larger discharge capacities (more than 1650 mAh/g with respect to the carbon weight in the cathode) compared to those (1000 ~ 1400 mAh/g) reported elsewhere [3,13]. In contrast, acetylene black showed much lower capacity (~560 mAh/g) than the other carbon blacks materials. This appears to be closely related to the practical area of the carbon electrodes, considering that the electrode reaction of SO_2 in the electrolyte would be more favorable in the carbon electrodes with a large surface area. Interestingly, the cells containing KB-600, KB-300 or Printex XE-2 experienced a considerable increase in discharge capacity during the second cycle. This may be due to a change in contact area between the carbon black materials and electrolyte solutions. It is expected that a sufficient contact area was not achieved in the fresh cells, but the contact area increased gradually due to mass transfer of the electrolyte solution during the first cycle. Above all, the Li-SO_2 cells using KB-600, KB-300 or Printex XE-2 as an electrode material showed much higher reversible capacities, compared to Li-S cells, which are considered to be the most promising post lithium-ion batteries[14-16].

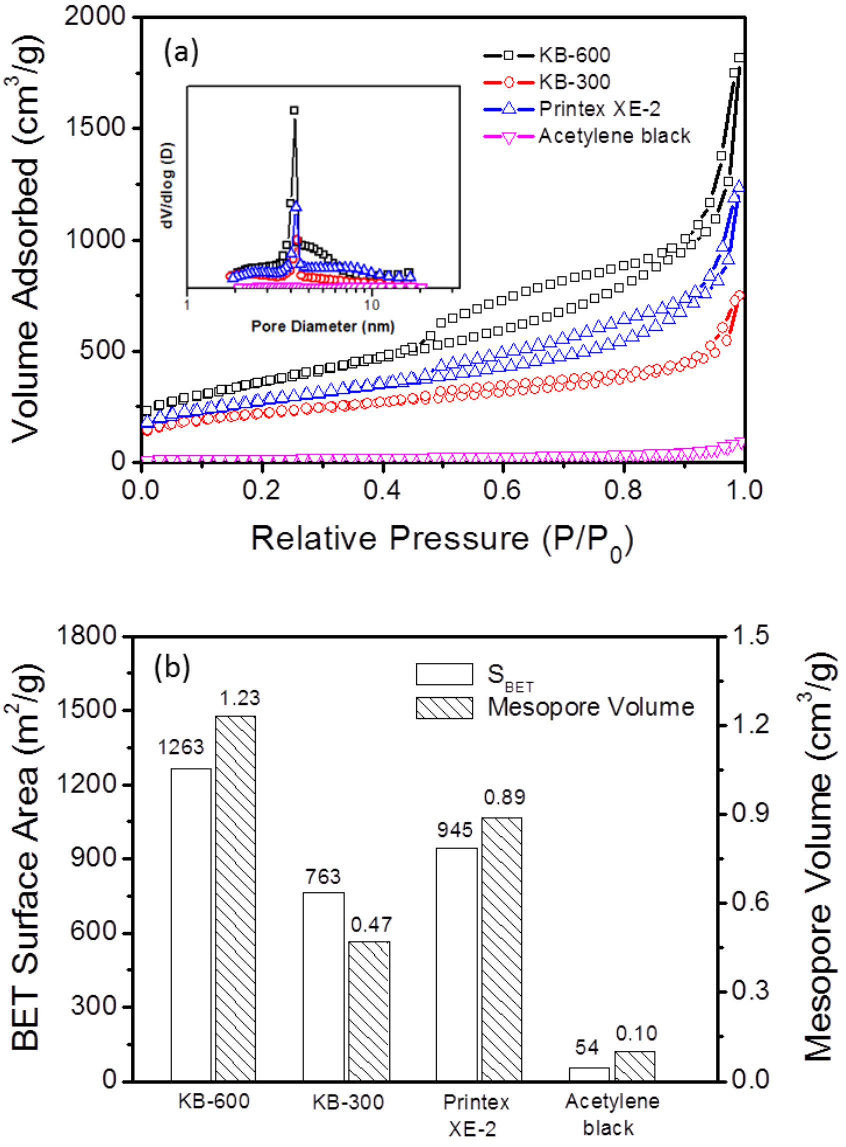

Figure 1. (a) Nitrogen adsorption and desorption isotherms of the carbon black samples: the inset shows their pore size distribution. (b) The BET surface area and mesopore volume of the carbon black samples.

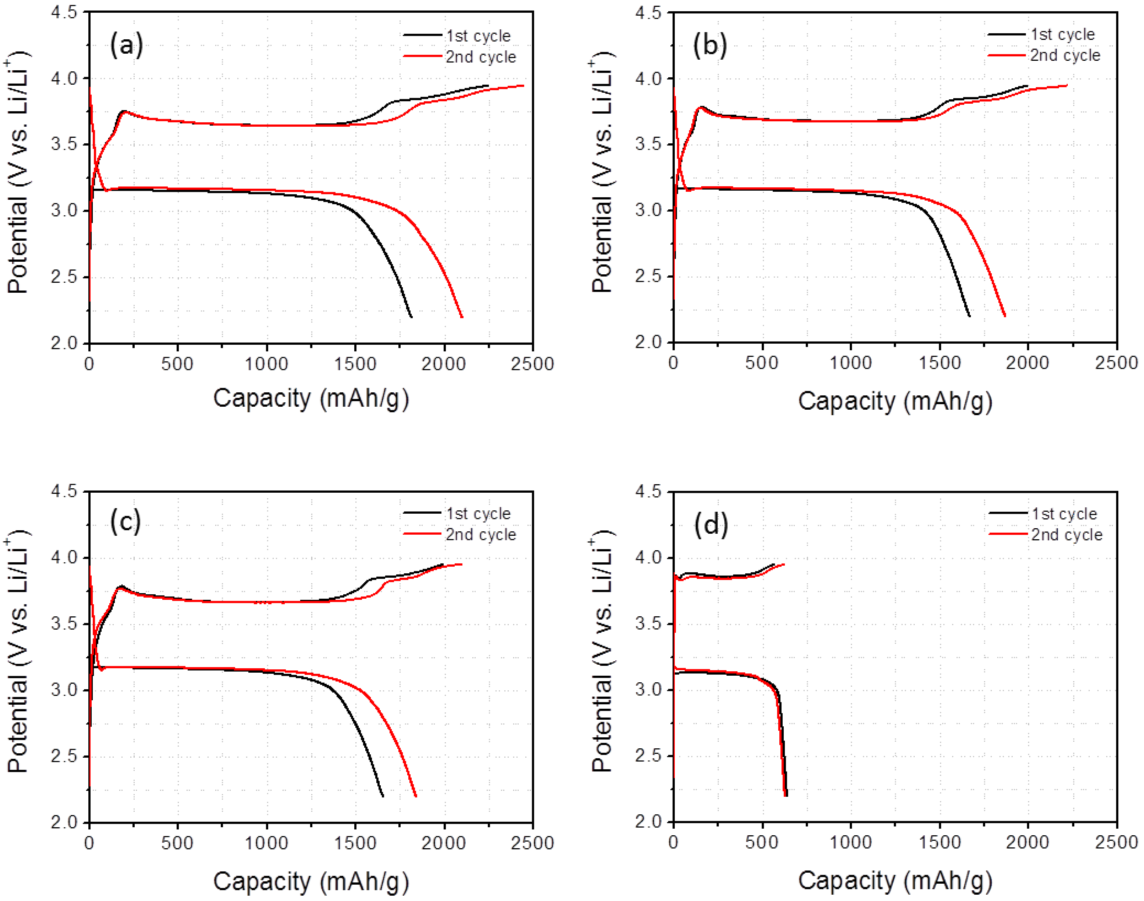

Figure 2. Charge/discharge curves for the first two cycles of Li/$LiAlCl_4 \cdot 3SO_2/SO_2$ batteries with different carbon black materials: (a) KB-600, (b) KB-300, (c) Printex XE-2, and (d) acetylene black.

Figure 3 presents the cycle performance of Li-SO_2 cells after the first two cycles. The test cell with KB-600 showed relatively higher capacity (~1600 mAh/g) with considerable capacity retention (87%) after 50 cycles. KB-300 and Printex XE-2 showed similar performance before 10 cycles, but a large difference in cycling stability was observed. Although KB-300 has a lower mesopore volume to store the electrolyte solution than Printex XE-2, KB-300 showed much higher capacity retention of 93% after 50 cycles, suggesting that the cycling stability may be strongly dependent on the chemical nature of the carbon black material used.

Figure 4 shows the rate capabilities of the Li-SO_2 cells with different carbon black materials. The discharge capacity was very sensitive to the type of carbon black materials. This relationship was clearer as the C-rate was increased. At 5.0 C, the test cells with KB-600, KB-300 or Printex XE-2 exhibited excellent capacity retention of more than 55% versus their discharge capacities at 0.2 C, whereas the test cell with acetylene black showed very low capacity retention of 37%. In particular, the cell with KB-600 showed an extremely high capacity of 1470 mAh/g and 1280 mAh/g at a C-rate of 2.0 C and 5.0 C, respectively. This feature may have been caused by the large surface area and high mesopore volume due to KB-600 aggregation.

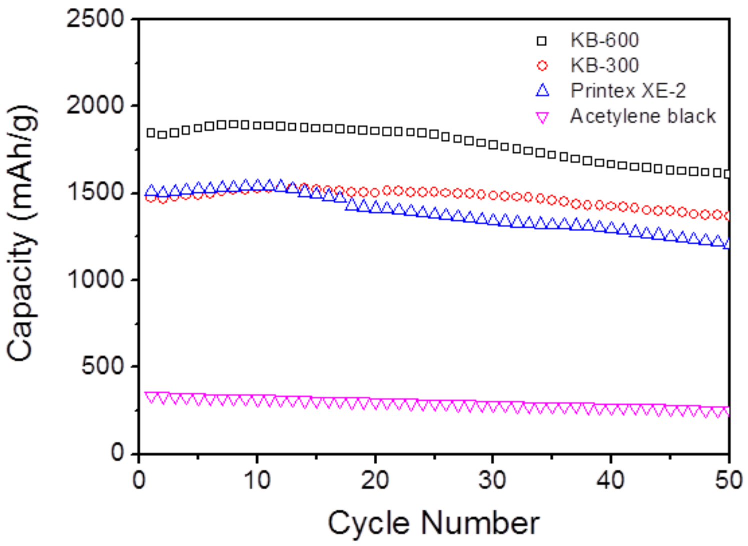

Figure 3. Cycle performance of Li/$LiAlCl_4 \cdot 3SO_2/SO_2$ rechargeable batteries.

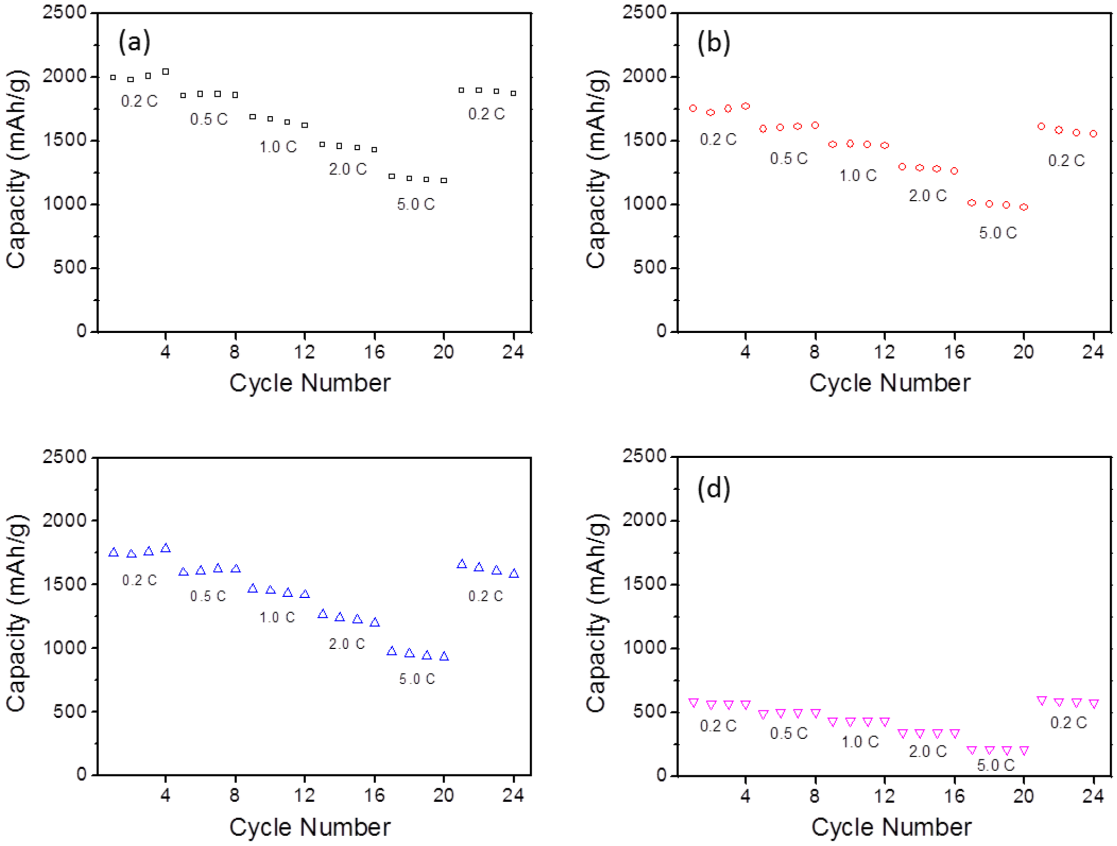

Figure 4. Rate properties of Li/$LiAlCl_4 \cdot 3SO_2/SO_2$ rechargeable batteries: (a) KB-600, (b) KB-300, (c) Printex XE-2, and (d) acetylene black.

On the other hand, it was expected that Printex XE-2 would show better rate performance than KB-300 in that the rate capability was directly proportional to the electrode surface area. Interestingly, Printex XE-2 with a relatively larger surface area showed a similar rate property to KB-300. This feature can be attributed to the lower dispersion properties of Printex XE-2, which leads to a slight decrease in the practical surface area available to the electrode reaction of SO_2 in an inorganic electrolyte solution.

4. CONCLUSION

This study examined the influence of the carbon black electrode material on the electrochemical performance of room temperature $Li/LiAlCl_4{\cdot}3SO_2/SO_2$ rechargeable batteries. The electrochemical reaction of SO_2 was affected significantly to the type of carbon black material used. The carbon black materials (KB-600, KB-300 and Printex XE-2) with a large surface area exhibited extremely high capacities of more than 1650 mAh/g in the first cycle, compared to acetylene black (~560 mAh/g). Surprisingly, the cell with KB-600 retained high capacities of 1280 mAh/g at a C-rate of 5.0 C and considerable capacity retention (87%) after 50 cycles. In particular, despite that KB-300 has relatively lower pore volume and surface area than Printex XE-2, KB-300 demonstrated high capacity and rate property comparable to Printex XE-2, maintaining excellent capacity retention of 93% after 50 cycles.

ACKNOWLEDGMENTS
This study was supported by the Energy Efficiency and Resources Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), the financial resources granted from the Ministry of Trade, Industry and Energy, Republic of Korea (No. 20132020000260), and the Education and Research Promotion Program of KOREATECH.

References

1. W. F. Meyers, B. Bell, J. W. Simmons, *U.S. Patent* 3,423,242 (1969).
2. D. Linden, B. Macdonald, *J. Power Sources* 5 (1980) 35.
3. A. N. Dey, H. C. Kuo, P. Piliero, M. Kallianidis, *J. Electrochem. Soc*. 135 (1988) 2116.
4. G. T. K. Fey, *J. Power Sources* 35 (1991) 153.
5. I. R. Hill, B. G. Anderson, M. Goledzinowski, R. J. Doré, *J. Electrochem. Soc*. 142 (1995) 3267.
6. M. Goledzinowski, R. J. Doré, I. R. Hill, *J. Power Sources* 54 (1995) 356.
7. D. L. Foster, H. C. Kuo, C. R. Schlaikjer, A. N. Dey, *J. Electrochem. Soc*. 135 (1988) 2682.
8. M. Aubay, E. Lojou, *J. Electrochem. Soc*. 141 (1994) 865.
9. R. J. Mammone, M. Binder, *J. Electrochem. Soc*. 133 (1986) 1312.
10. R. Hartl, M. Fleischmann, R. M. Gschwind, M. Winter, H. J. Gores, *Energies* 6 (2013) 4448.
11. R. Mews, E. Lork, P. G. Waston, B. Görtler, *Coord. Chem. Rev.* 197 (2000) 277.
12. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 57 (1985) 603.
13. S. Hossain, P. Harris, R. McDonald, F. Goebel, *Proceedings of the 34th International Power Sources Symposium*, IEEE, 185 (1990).
14. M. S. Park, B. O. Jeong, T. J. Kim, S. Kim, K. J. Kim, J. S. Yu, Y. Jung, Y. J. Kim, *Carbon* 68 (2014) 265.

15. A. Fedorkova, R. Orinakova, O. Ceck, M. Sedlarikova, *Int. J. Electrochem. Sci*. 8 (2013) 10308.
16. Z. Wen, D. Lu, S. Li, J. Sun, S. Ji, *Int. J. Electrochem. Sci.* 9 (2014) 1.