Electrochemical Performance of a Large Size All-Solid-State Lithium-Ion Battery

Satoshi Fujiki, Yuichi Aihara, Takanobu Yamada, Seitaro Ito, Koji Hoshiba, and Nobuya Machida*

Samsung Yokohama Research Institute, Minoh Semba Center Bldg. 13F, Semba Nishi 2-1-11, Minoh, Osaka, 562-0036, Japan
*Department of Chemistry, Faculty of Science and Engineering, Konan Univ., Okamoto 8-9-1, Higashinada-ku, Kobe, Hyogo, 658-8501, Japan

An all-solid-state lithium-ion battery (SSB) with non-flammable solid electrolytes is one of the candidates for next-generation high performance power source, because of its high safety. Recently, sulfide based electrolytes are of considerable practical interest because of its high ionic conductivity at room temperature range.[1,2] The cell performances have been also reported. However, there are still some serious issues to realize the practical batteries. Since the ionic and the electric conduction passes are given by the solid particles, the cell impedance is much higher than that of conventional lithium-ion batteries. Consequently, most of the SSBs need an external pressure during the charging and discharging.[3] Also, several papers have suggested the necessity of a thin buffer layer on the cathode surface to prevent the mutual diffusion of atoms between the metal oxide and sulfide electrolyte.[3,4] In order to create a SSB of practical size, we adopted Li_2O-ZrO_2 (LZO) thin layer coating on the cathode material for reducing the solid-solid interface resistance.

LZO coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode material was prepared by sol-gel method. The LZO coating solution was prepared from iso-propanol, lithium methoxide and zirconium(IV) tetrapropoxide ($Zr(OC_3H_7)_4$) in a molar ratio 200 : 2 : 1. The NCA was added into the LZO solution and ultrasonically agitated at 40 °C. The mixture was concentrated under pumping, and the residual was obtained as a precursor. The precursor was heated at 350 °C for 1 h under the air. Influence of the LZO coating was investigated by the electrochemical impedance (EIS) method and the charge/discharge cycle tests using a test cell (the metal cell in the right side at Figure 1). The test cell consisted of LZO coated NCA based cathode, graphite anode and amorphous $80Li_2S$-$20P_2S_5$ sulfide as the solid electrolyte.

Figure 2 shows the Nyquist plots of the test cells using a NCA cathode coated by 0.5 mol% of LZO after 1st charge until 4.0V, compared with the bare NCA adopted one at the same SOC. The results indicate that interfacial resistance was significantly reduced by the LZO coating. Significant improvements in the discharge capacity and capacity retention were found from the battery cycle test.

Large size SSBs were constructed using the same materials given above. The electrodes and solid-electrolyte layer were prepared by a printing method from the composite slurries containing polymer binders. The capacities of the practical size of SSBs were designed by a stack of single cells, and were 125mAh (the minimum in a single cell) to above 1Ah (stacked one). The stable charge-discharge cycle was obtained without an artificial external pressure at 25 °C. To verify the protection effect of LZO coating from the side reactions, a single cell (125mAh class) was tested at 60 °C to enhance the side reaction. Figure 3 shows the capacity retention of the practical size single cell. Even though the number of the cycle is still limited, the capacity is still retained above 80%.

In this work, we demonstrated the applicability of the sulfide based electrolyte for a practical size SSB. Although further development is still needed, SSBs hold a great promise as next generation energy storage.

1. F. Mizuno, A. Hayashi, K. Tadanaga, and M. Tatsumisago, *Advanced Materials*, **17**, 918 (2005).
2. N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, and A. Mitsui, *Nature Materials*, **10**, 682 (2011).
3. N. Machida, J. Kashiwagi, M. Naito, and T. Shigematsu, *Solid State Ionics*, **225**, 354 (2012).
4. N. Ohta, K. Takada, L.-Q. Zhang, R.-Z. Ma, M. Osada, and T. Sasaki, *Advanced Materials*, **18**, 2226 (2006).

Figure 1. A large-size SSB (left) and a test cell (right).

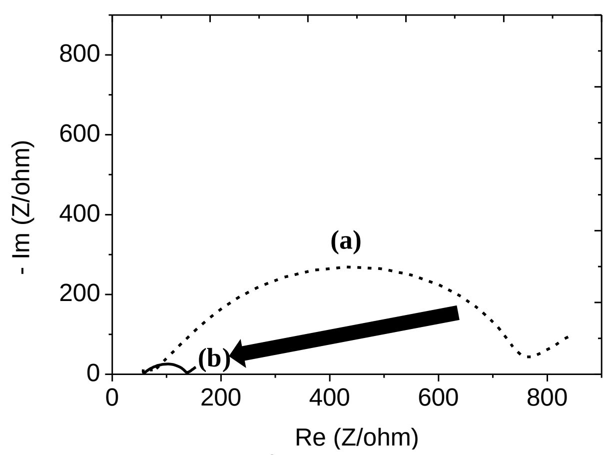

Figure 2. Nyquist plots of the test cells using (a) NCA and (b) LZO treated NCA for the cathode active materials at 25°C.

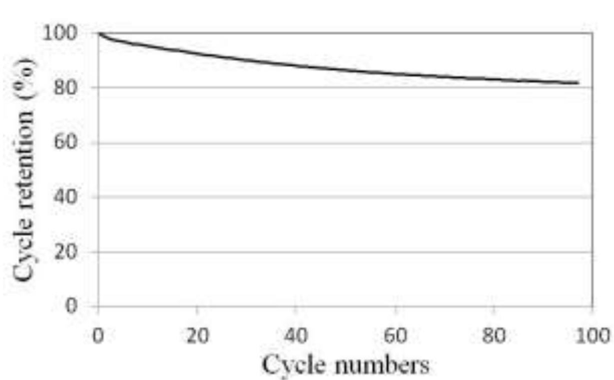

Figure 3. Cycle performance of 125mAh-class single cell at 60 °C.