

Study on Improving Cycle Durability of Anode-free All-solid-state Batteries (Second Report)

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All-solid-state batteries using lithium metal anodes are one of the leading candidates to surpass the performance of conventional lithium-ion batteries. However, the high reactivity of lithium metal with air and moisture, growth of Li dendrites, and low coulombic efficiency of lithium metal-based batteries make their practical application difficult. The first report demonstrated that high-performance, long-life anode-free all-solid-state batteries can be achieved by introducing an intermediate layer between the solid electrolyte layer and the anode current collector, and by forming a thin metal layer containing Ni and Ag on the anode current collector. This second report presents the effects of varying Ag content on output characteristics and cycle durability. Furthermore, by optimizing the silver content, the prototype pouch cell in this study achieved a low DC resistance of less than $10 \Omega \text{ cm}^{-2}$ at 45°C , a stable coulombic efficiency of over 99.96%, and a long cycle life (500 cycles) at a low confinement pressure of 1.5 MPa.

The standard cell (a) is an anode-free all-solid-state battery with cathode area of 20 mm^2 and capacity of approximately 15 mAh. For the cathode, a composite electrode was made using lithium nickel cobalt manganese oxide $\text{LiNi}_{0.7}\text{Co}_{0.1}\text{Mn}_{0.2}\text{O}_2$ (NCM712) as the active material and an argyrodite-type sulfide solid electrolyte, $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ ($x \sim 2$, LPSC), together with a binder. The solid electrolyte layer (separator layer) was a composite film consisting of LPSC solid electrolyte and a binder. An interlayer was placed between the solid electrolyte layer and anode current collector. Copper foil ($8 \mu\text{m}$ thick) was used as the anode current collector. The cathode and solid electrolyte layer and an interlayer were stacked in order and pressure molded to achieve a high density. The anode current collector was arranged on the interlayer side to form the electrode stack. The stack was placed inside an aluminum-laminate pouch and vacuum sealed to create the anode-free all-solid-state standard cell (a).

Cell (b): Same as Cell (a), but with a modified anode current collector consisting of a Ni layer and an appropriate amount of Ag layered on top of the copper foil.

Using Cell (b) as the reference, Cell (c) contained five times the amount of Ag, and Cell (d) contained ten times the amount of Ag.

Fig.1 shows the initial output characteristics at 25°C and 45°C . Cell (a) and Cell (b) exhibited equivalent output characteristics. Cell (c) showed a slight increase in resistance at 25°C , while Cell (d) showed a significant increase in resistance at both 25°C and 45°C .

Fig.2 shows the cycle discharge capacity retention rate at 45°C . Cell (b), with both Ni layer and an appropriate amount of Ag layer, showed significant enhancements in cycle durability compared to Cell (a). Cell (c), which contained five times the amount of Ag, exhibited lower cycle stability than Cell (b). Cell (d), which contained ten times the amount of Ag, showed a sharp decline in discharge capacity.

By using an interlayer between the solid electrolyte layer and the negative electrode current collector foil, and by forming a thin metal film layer containing Ni and an appropriate amount of Ag on the negative electrode current collector foil, excellent output characteristics and a significant increase in cycle durability were achieved.

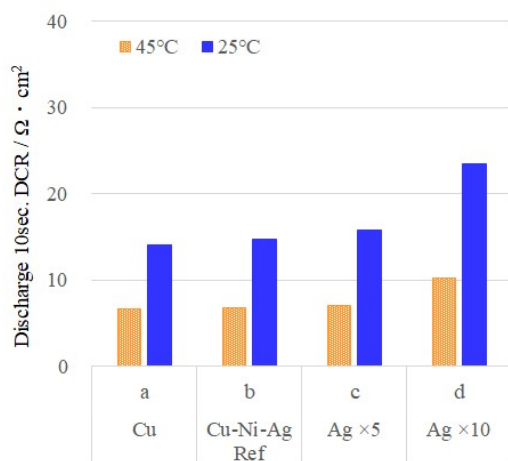


Fig. 1 Discharge 10sec. DCR
(Current density: 15 mA cm^{-2})

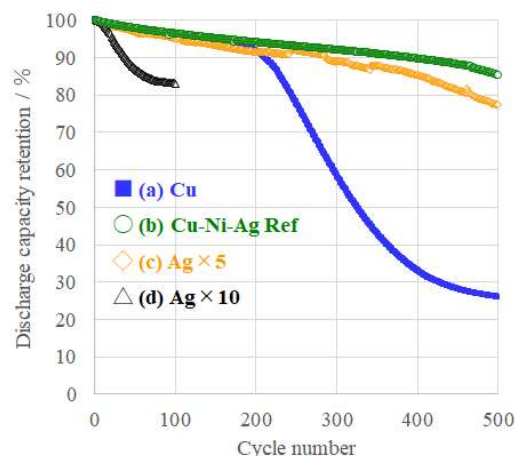


Fig. 2 Discharge capacity retention