Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

All-solid-state rechargeable aluminum-air battery with hydroxide ion-conducting Sb(V)-doped SnP_2O_7 electrolyte

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Experimental Section

The $Sn_{0.92}Sb_{0.08}P_2O_7$ electrolyte membrane was synthesized according to a previously reported procedure.[1] Briefly, SnO_2 and Sb_2O_5 were mixed with 85% H_3PO_4 and deionized water. The mixture was stirred at 300°C until it formed a high viscosity paste. The paste was calcined in an alumina pot at 650°C for 2.5 h and then ground into a powder with a mortar and pestle. A total of 0.04 g of polytetrafluoroethylene (PTFE) powder was added to 1.00 g of $Sn_{0.92}Sb_{0.08}P_2O_7$ powder, kneaded using a mortar and pestle, and finally cold-rolled to a thickness of 300 μm using a laboratory rolling mill.

A chip (1×1 cm^2) was cut from a pure aluminum plate (99.999%, Nilaco). The surface of this chip was polished with abrasive paper, followed by washing with deionized water in an ultrasonic bath for 5 min. A commercially available gas diffusion electrode (Electrochem. Inc., Pt loading: 1 mg cm^{-2}) was modified to establish a three-phase boundary structure in the electrode as follows. A total of 1.00 g of $Sn_{0.92}Sb_{0.08}P_2O_7$ powder was ground in 10.0 g of tetrahydrofuran using a planetary ball mill at 150 rpm for 10 h. After ultrasonic treatment for 20 min, the resultant ink was painted on the surface of the electrode using a high-pressure spray coating technique (Tamiya, 180D). The weight of the Pt/C catalyst in the electrode was adjusted to 1 mg by controlling the electrode area.

The aluminum electrode before and after the charge-discharge tests was characterized using XRD and SEM with an EDX detector. Diffraction patterns were collected using a Rigaku Miniflex II diffractometer operated at 45 kV and 20 mA with Cu Kα radiation (λ = 1.5432 Å). The SEM and EDX images were obtained using a Hitachi S-4800 microscope at accelerating voltages of 5 and 15 kV, respectively, with a beam current of 0.2 nA.

The electrolyte membrane was sandwiched between the aluminum and Pt/C electrodes, as shown in Fig. S2. The perimeter of the aluminum electrode was sealed with an organic adhesive to prevent the penetration of air into the gap between the electrolyte and the electrode. A Pt reference electrode was attached to the surface of the electrolyte at the Pt/C electrode side, which was exposed to atmospheric air. EIS was performed for the aluminum and Pt/C electrodes using a Solartron SI 1260 impedance analyzer and Solartron 1287 electrochemical interface. The frequency range for the measurements was 0.1–10^6 Hz and the AC amplitude was 10 mV. Four types of polarization curves were obtained: (1) anodic

polarization curve for the aluminum electrode; (2) cathodic polarization curve for the aluminum electrode; (3) cathodic polarization curve for the Pt/C electrode; and (4) anodic polarization curve for the Pt/C electrode. The charge-discharge performance was evaluated in the potential range from 0 to 3.5 V at current densities of 0.2, 0.4, 0.6, and 1.0 mA cm^{-2}. Air was supplied to the Pt/C electrode at a flow rate of 30 mL min^{-1}. The discharge and charge capacities were normalized according to the weight of the Pt/C catalyst.

References

1 a) T. Hibino, Y. B. Shen, M. Nishida and M. Nagao, *Angew. Chem. Int. Ed.*, 2012, **51**, 10786-10790; b) T. Hibino, K. Kobayashi, *J. Mater. Chem. A*, 2013, **1**, 6934-6941.

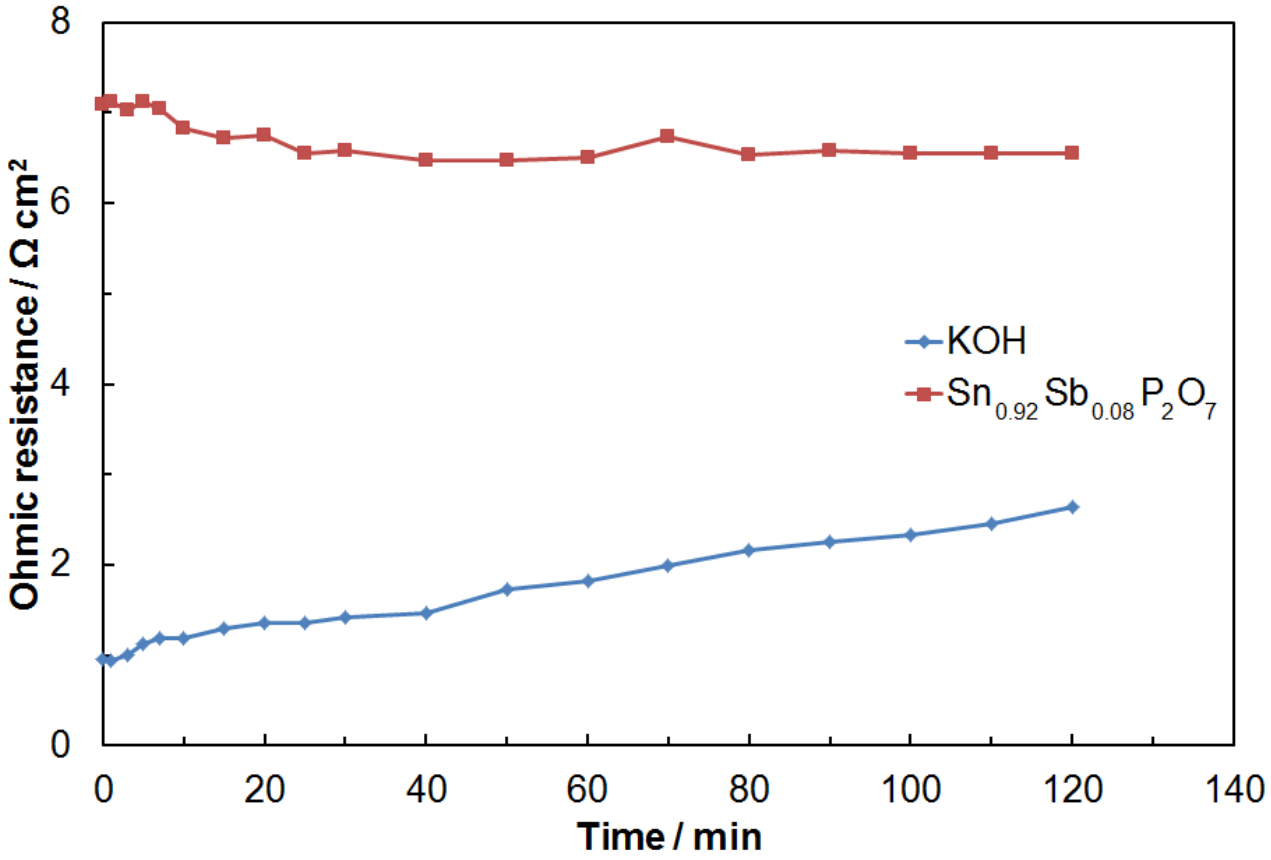

Fig. S1. Changes in ohmic resistance for a KOH solution and an $Sn_{0.92}Sb_{0.08}P_2O_7$ membrane in air including 1% CO.

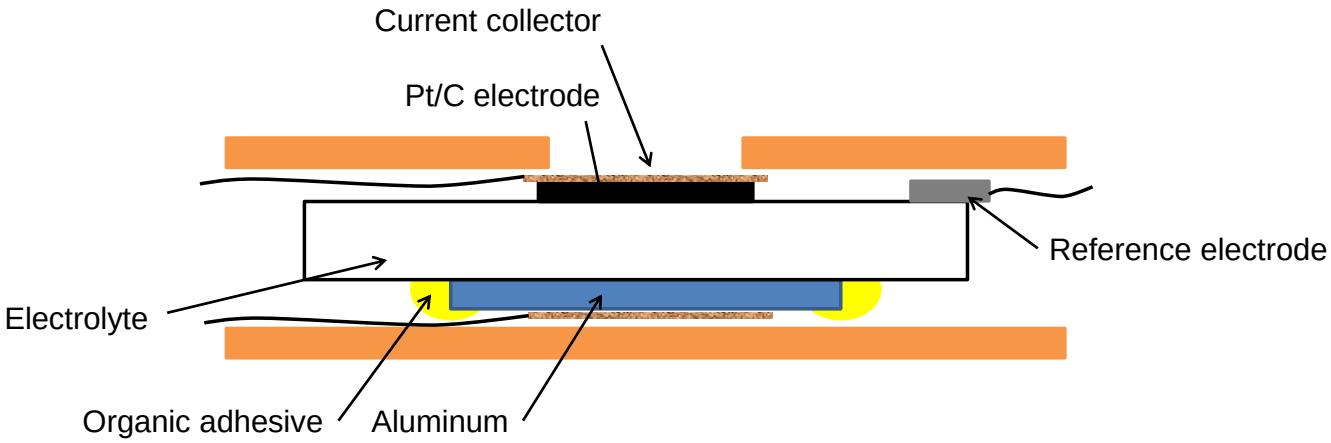

Fig. S2. Illustration of an aluminum-air secondary battery.

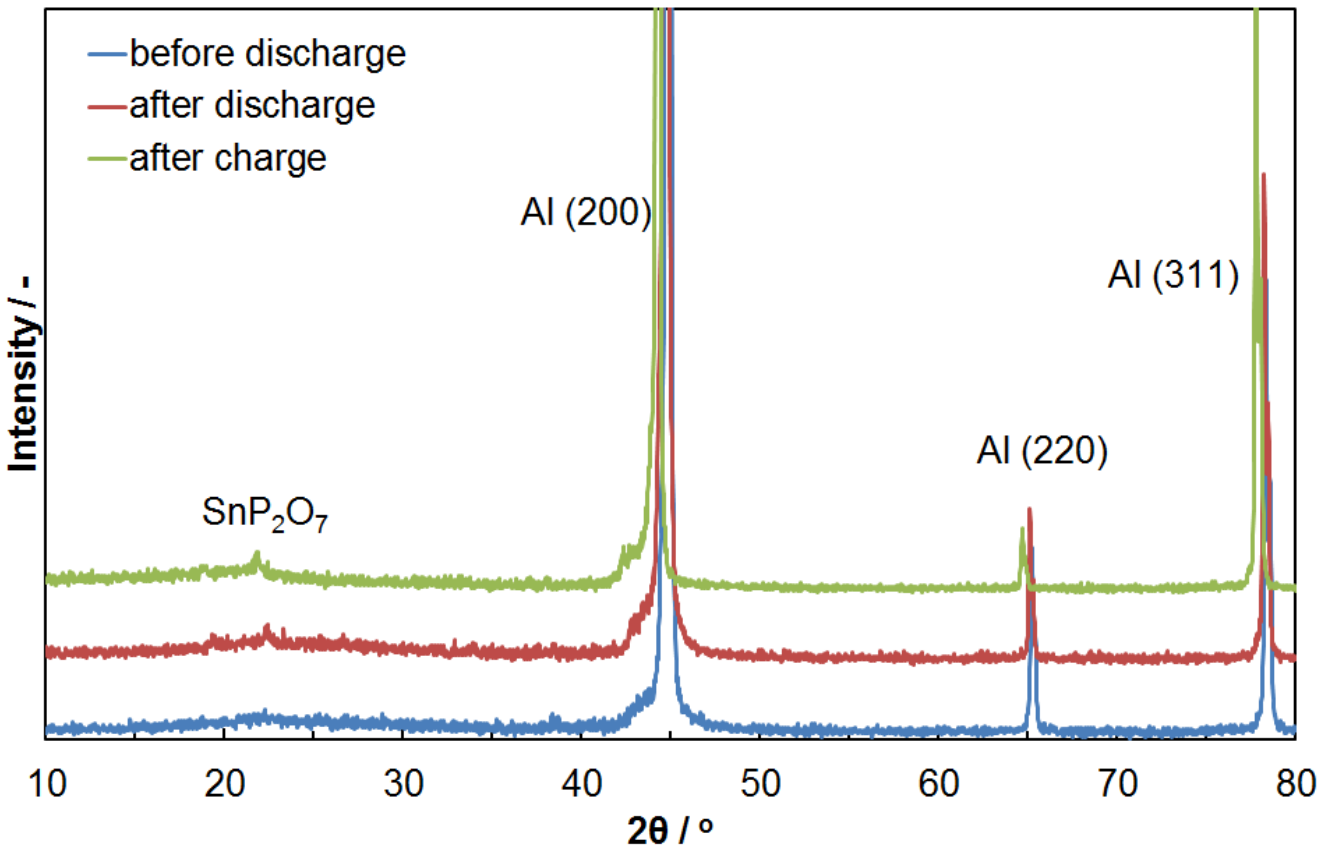

Fig. S3. XRD patterns for the aluminum electrode before and after discharge-charge tests.

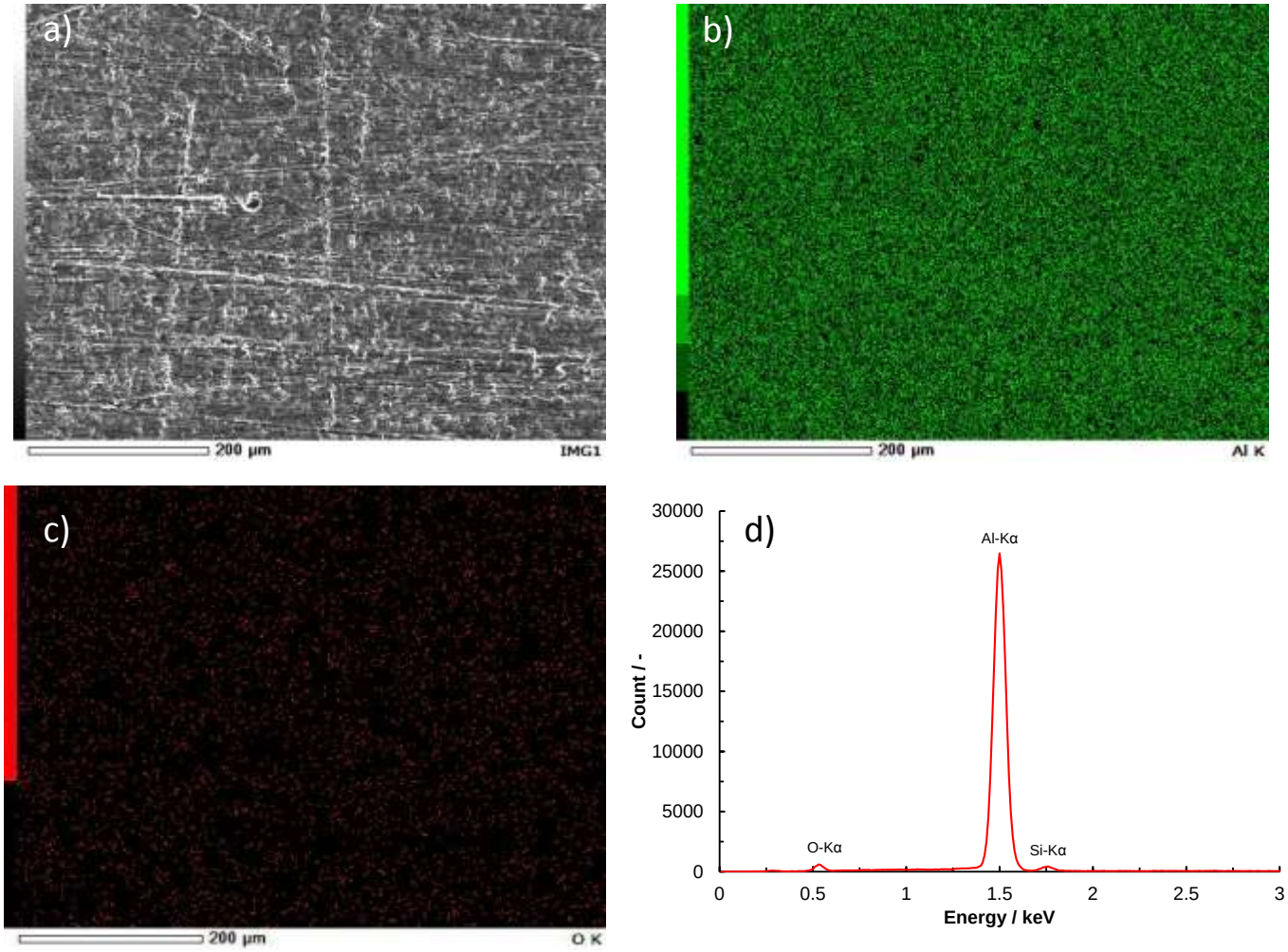

Fig. S4. (a) SEM and EDX elecmental maps of (b) Al and (c) O in the aluminum electrode before charge-discharge tests. (d) EDX spectrum.

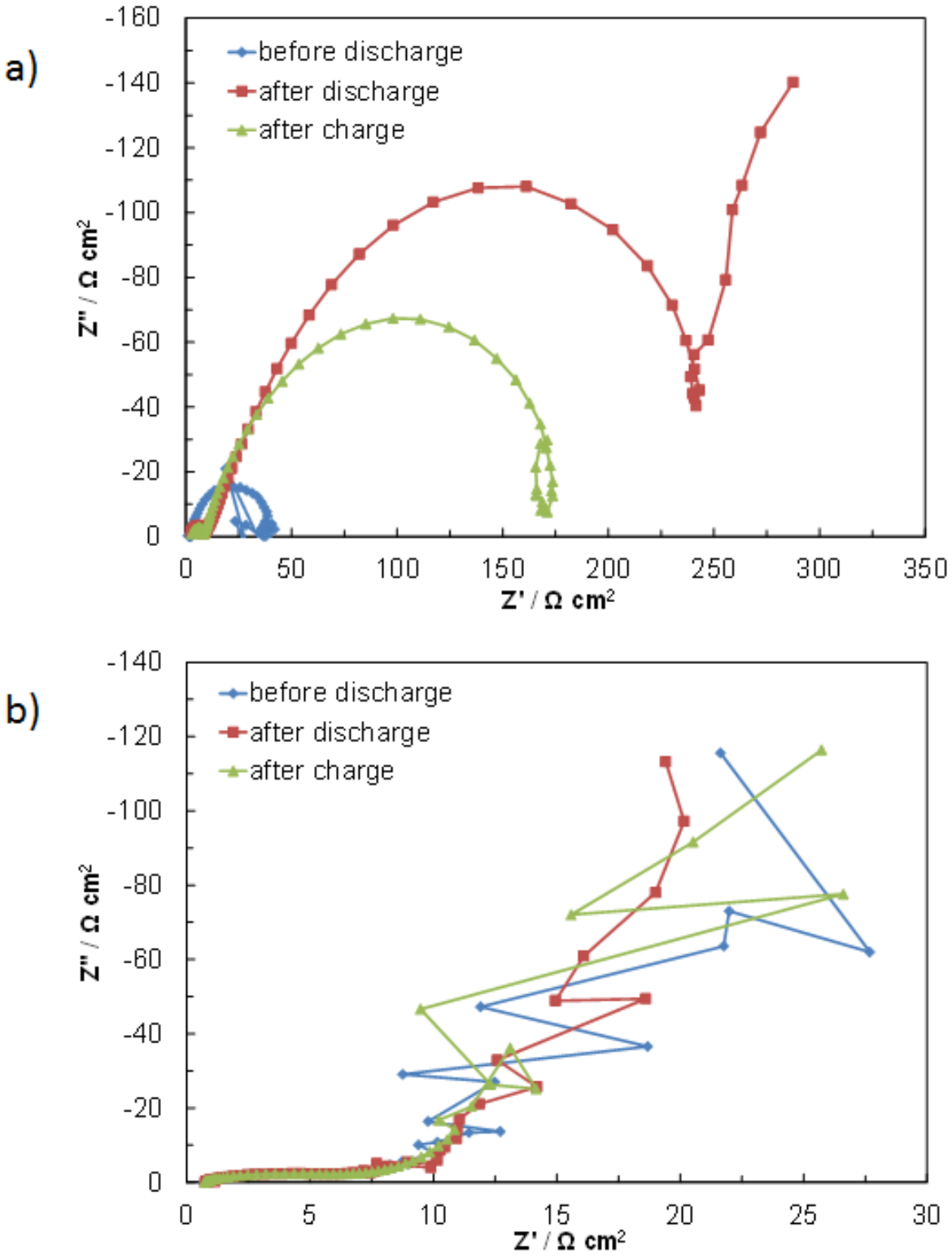

Fig. S5. Impedance spectra for the (a) aluminum and (b) Pt/C electrodes before and after discharge-charge tests.