Supporting information

A Rechargeable Si-air Solid State Oxygen Shuttle Battery Incorporating an Oxide Ion Conductor

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Experimental method

Approximately 10 ml of Ca-stabilized ZrO_2 (ZR-11, Nikkato, CSZ) contained in a tube was used as the electrolyte. Pt paste (TR-7902, Tanaka Kikinzoku Kogyo) was painted on the inside and outside of the CSZ tube to form the anode and cathode, respectively, followed by calcining at 1273 K for 30 min (surface area of the electrode: 13 cm^2). Si powder (Wako, 10, 20 or 50 mg), and/or SiO (Kishida, 20 mg) were inserted into a small alumina tube fixed inside the CSZ electrolyte tube and the CSZ tube was sealed with epoxy resin, except for a stainless gas inlet line to allow the introduction of Ar gas. After filling the tube with Ar, the gas lines were closed using stop valves and the cell was heated to 1073 K. Charge and discharge measurements were performed at 0.5 mA (ca. 0.04 mA cm^{-2}) in constant current mode, using the two probe method. Dry air was fed into the cathode side at a flow rate of 100 ml min^{-1}. Impedance analysis was performed under open circuit conditions with a frequency range of 0.1 – 100,000 Hz and 10 mV

ac amplitude using a Solartron 1260 /1287 impedance analyzer. Morphological and elemental analyses of the Si powder were performed using SEM-EDX (VE-7800, Keyence, EDAX type 7980).

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SEM images and EDX results of Si powder after first discharge and third charge

Figure S1 shows the SEM images of Si powder after being kept at 1073 K in Ar and after third charge. After third charge, it seems that porous structure was formed indicating that the observed increase in capacity with repeated redox cycles is assigned to either increased porosity or decreased particle size of the Si powder.

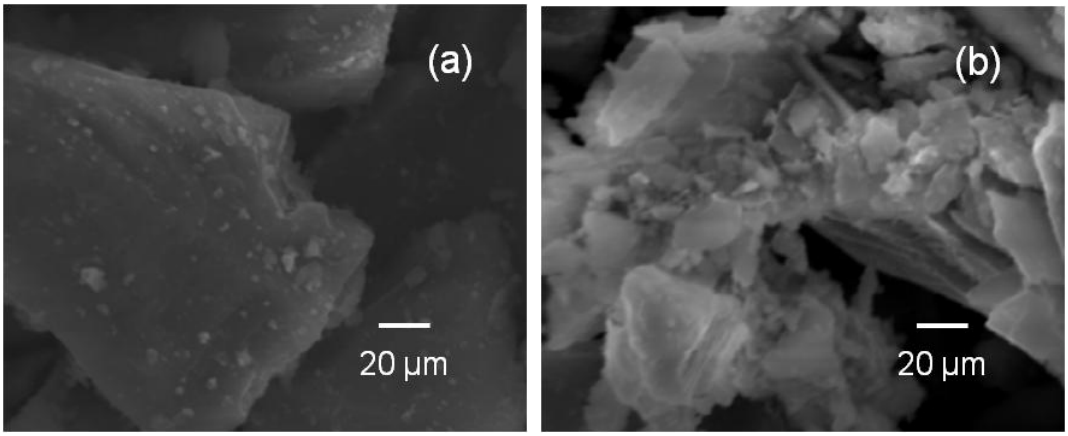

Fig.S1 SEM images of Si powder after first discharge and third charge

(a) Before charge-dischare (Keep in Ar for 10 h at 1073 K), (b) After third charge.

The state of the Si powder after first discharge and third charge were characterized by EDX analysis (Table S1). The estimated atomic ratio of silicon to oxygen were 1.01 and 1.50 (Si/O) after first discharge and third charge, respectively.

Table S1 EDX results of Si powder after first discharge and third charge.

Si powder	Atomic ratio of Si/O
After 1st discharge	1.01
After 3rddischarge	1.50

XRD pattern of Si powder after discharge

Figure S2 shows the XRD pattern of the Si powder following discharge, in which prominent peaks attributed to Si and SiO along with weak peaks due to SiO_2 are observed, indicating that the cell discharge products are SiO and SiO_2.

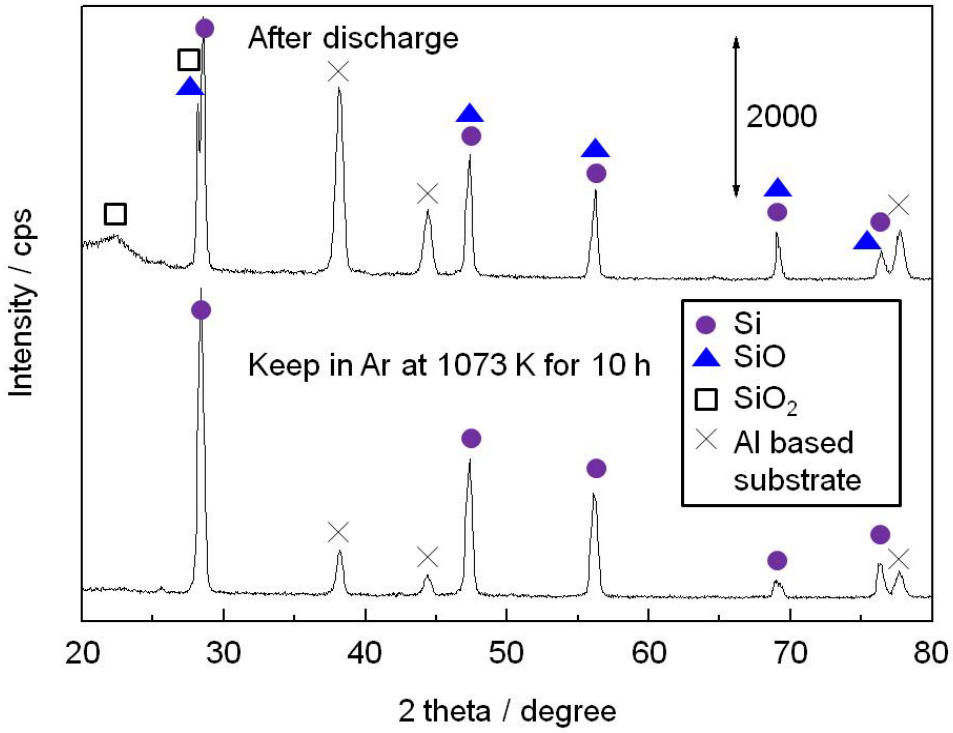

Fig.S2 XRD pattern of Si powder after discharge.

Charge-discharge measurement from reduction of SiO by oxygen pumping

To provide evidence showing the redox of Si/SiO, charge-discharge measurements starting from the reduction of SiO as the Si source were performed, with the results summarized in Figure S3. During these trials, the charge was cut off at the theoretical charge capacity required to reduce SiO to Si (1908 mAh/g-Si). After sufficient charge was applied to reduce SiO to Si, a discharge capacity of 599 mAh/g-Si was obtained, which is a reasonable value considering the discharge capacity measured when using Si, as shown in Figure 2 in main text. In addition, the observed discharge potential dur ing this test was almost the same as that observed in discharge tests in which Si was used as the starting material.

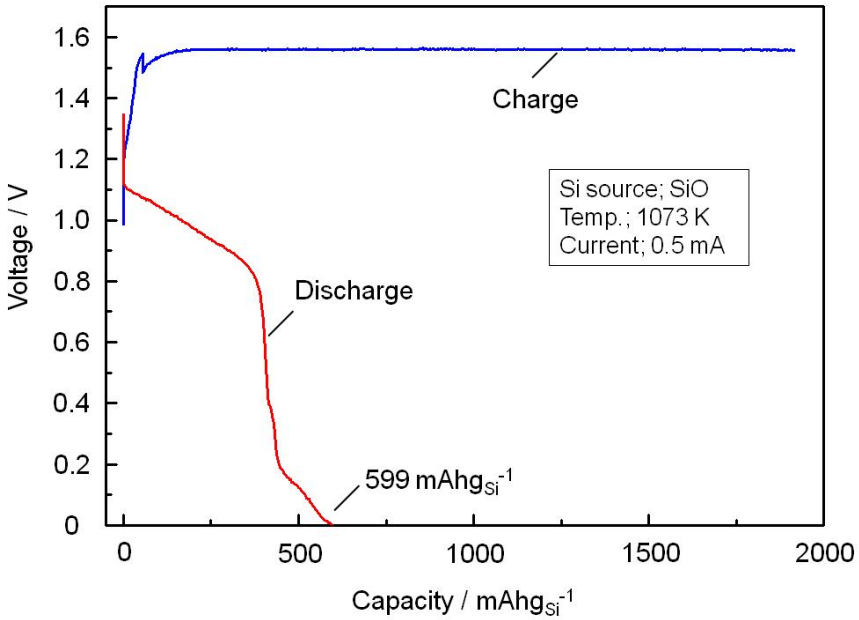

Fig. S3 Charge-discharge curve obtained using SiO as the Si source.