

Supporting Information

Very High Energy Density Silicide-Air Primary Battery[†]

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Experimental Section

Magnesium silicide thin film fabrication and measurement: Magnesium silicide thin films were synthesized in a horizontal tube furnace (Lindberg/Blue M, Thermo Scientific) with a 1-inch diameter quartz tube. An n-type silicon wafer with resistivity of 0.001-0.002 $\Omega\cdot\text{cm}$ (University Wafers) was placed on the top of an alumina boat filled with magnesium powder (99.8 %, Alfa Aesar). The alumina boat was then placed in the center of the furnace. Finally, the chamber was heated to 650 °C under argon flow for 1 hour followed by natural cooling to room temperature to obtain a silicon substrate with a layer of blue silicide thin film (~30 μm thick).

Magnesium silicide thin film electrochemical performance measurement: The battery device consisting of a silicide thin film with a film thickness around 30 μm on the silicon wafer (~1.5 cm \times 2 cm, 500 μm thick), an air diffusion electrode (Quantumsphere Co. Ltd) and a PDMS stamp with an open-through hole (~0.5 cm diameter) was sandwiched tightly by aluminum sheet and plastic plate with open windows at the center of the air electrode to allow air diffusion. An aqueous solution of 30 % potassium hydroxide (KOH) was then injected into the cell as the electrolyte.

Silicide pellet electrochemical performance measurement: 1.5 g of TiSi_2 (99.5 %), CoSi_2 (99%) and VSi_2 (99.5%) and ~0.7g of Mg_2Si (99.5%) powders (Alfa Aesar) were pressed to form pellets with ~0.5 inch in diameter and ~0.25 cm in height (29) and annealed under argon flow for 2 h at different temperatures (1,100 °C for TiSi_2

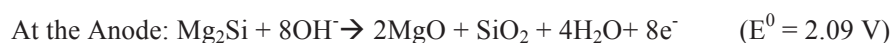
and VSi_2 , 900 °C for CoSi_2 , 700 °C for Mg_2Si). Discharge measurements were then carried out with the silicide pellet as anode, an air diffusion electrode as cathode and 30 % potassium hydroxide (KOH) as the electrolyte.

Silicide powder capacity measurement: For the capacity measurement, a gel was made by adding poly-acrylic acid (Carbopol 711, BF Goodrich) into KOH solution. The gel was then casted onto a nickel foil (0.025 mm thick, Alfa Aesar) with silicide powder. A full cell is constructed similarly except that the silicon wafer was substituted with the silicide pasted nickel foil with a separator (Celgard 3501) on the top.

Characterization: All the discharge curves were achieved using a Maccor 4304 battery test system. Linear sweep voltammograms and electrochemical impedance spectroscopy were performed with a 3-electrode configuration on VersaSTAT 4 from Princeton Applied Research. The as-synthesized magnesium silicide thin films were characterized by scanning electron microscopy (SEM JEOL 6700) and Energy-dispersive X-ray spectroscopy. X-ray Diffraction (XRD) pattern was carried out by a Bruker Smart 1000K Single Crystal X-ray Diffractometer.

The calculation of theoretical voltages for various metal silicides

Magnesium Silicide



Thermodynamic reaction to obtain anode half-cell:



$$\Delta G^{\circ}_f(\text{H}_2\text{O}, \text{l}) = -237.1 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{SiO}_2, \text{s}) = -856.3 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{Mg}_2\text{Si}, s) = -75.31 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{OH}^-, \text{aq}) = -157.2 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{MgO}, s) = -569.3 \text{ kJmol}^{-1}$$

$$\Delta G_R^\circ = 2\Delta G_f^\circ(\text{MgO}, s) + \Delta G_f^\circ(\text{SiO}_2, s) + 4\Delta G_f^\circ(\text{H}_2\text{O}, l) - \Delta G_f^\circ(\text{Mg}_2\text{Si}, s) - 8\Delta G_f^\circ(\text{OH}^-, \text{aq})$$

$$= 2 \times -569.3 \text{ kJmol}^{-1} - 1 \times 856.3 \text{ kJmol}^{-1} - 4 \times 237.1 \text{ kJmol}^{-1} + 75.31 \text{ kJmol}^{-1} + 8 \times 157.2 \text{ kJmol}^{-1}$$

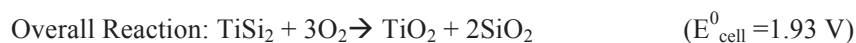
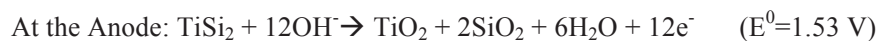
$$\Delta G_R^\circ = -1610.4 \text{ kJmol}^{-1}$$

$$\Delta G_R^\circ = -nFE^0$$

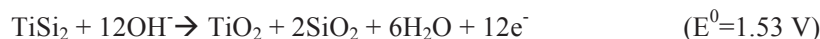
$$-1610.4 = -8 \times 96,485 \times E^0$$

$$E^0 = 2.09 \text{ V}$$

Titanium Silicide



Thermodynamic reaction to obtain anode half-cell:



$$\Delta G_f^\circ(\text{H}_2\text{O}, l) = -237.1 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{SiO}_2, s) = -856.3 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{TiO}_2, s) = -888.8 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{OH}^-, \text{aq}) = -157.2 \text{ kJmol}^{-1}$$

$$\Delta G_f^\circ(\text{TiSi}_2, s) = -127.0 \text{ kJmol}^{-1}$$

$$\begin{aligned}\Delta G^{\circ}_R &= \Delta G^{\circ}_f(\text{TiO}_2, s) + 2\Delta G^{\circ}_f(\text{SiO}_2, s) + 6\Delta G^{\circ}_f(\text{H}_2\text{O}, l) - \Delta G^{\circ}_f(\text{TiSi}_2, s) \\ &\quad - 12\Delta G^{\circ}_f(\text{OH}^-, aq) \\ &= -888.8 \text{ kJmol}^{-1} - 2 \times 856.3 \text{ kJmol}^{-1} - 5 \times 237.1 \text{ kJmol}^{-1} + 127.0 \text{ kJmol}^{-1} + 12 \\ &\quad \times 157.2 \text{ kJmol}^{-1}\end{aligned}$$

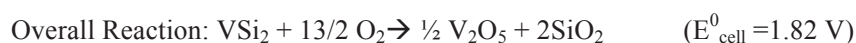
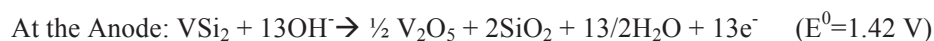
$$\Delta G^{\circ}_R = -1773.3 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_R = -nFE^0$$

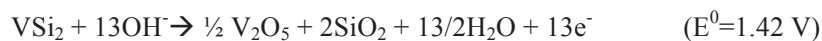
$$-1768.3 = -12 \times 96,485 \times E^0$$

$$E^0 = 1.527 \text{ V}$$

Vanadium Silicide



Thermodynamic reaction to obtain anode half-cell:



$$\Delta G^{\circ}_f(\text{H}_2\text{O}, l) = -237.1 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{SiO}_2, s) = -856.3 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{VSi}_2, s) = -39.37 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{OH}^-, aq) = -157.2 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{V}_2\text{O}_5, s) = -1205.9 \text{ kJmol}^{-1}$$

$$\begin{aligned}\Delta G^{\circ}_R &= \Delta G^{\circ}_f(\text{V}_2\text{O}_5, s) + 2\Delta G^{\circ}_f(\text{SiO}_2, s) + 5\Delta G^{\circ}_f(\text{H}_2\text{O}, l) - \Delta G^{\circ}_f(\text{CoSi}_2, s) \\ &\quad - 10\Delta G^{\circ}_f(\text{OH}^-, aq)\end{aligned}$$

$$\begin{aligned}&= \frac{1}{2} \times -1205.9 \text{ kJmol}^{-1} - 2 \times 856.3 \text{ kJmol}^{-1} - \frac{13}{2} \times 237.1 \text{ kJmol}^{-1} + 39.37 \text{ kJmol}^{-1} \\ &\quad + 13 \times 157.2 \text{ kJmol}^{-1}\end{aligned}$$

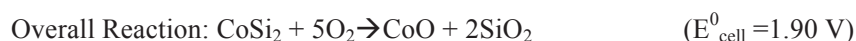
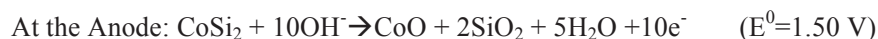
$$\Delta G^{\circ}_R = -1776.8 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_R = -nfE^{\circ}$$

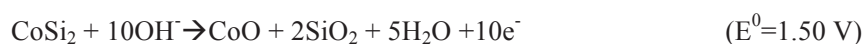
$$-1776.8 = -13 \times 96,485 \times E^{\circ}$$

$$E^{\circ} = 1.4166 \text{ V}$$

Cobalt Silicide



Thermodynamic reaction to obtain anode half-cell:



$$\Delta G^{\circ}_f(\text{H}_2\text{O}, l) = -237.1 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{SiO}_2, s) = -856.3 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{CoO}, s) = -214.2 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{OH}^-, aq) = -157.2 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_f(\text{CoSi}_2, s) = -97.6 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_R = \Delta G^{\circ}_f(\text{CoO}, s) + 2\Delta G^{\circ}_f(\text{SiO}_2, s) + 5\Delta G^{\circ}_f(\text{H}_2\text{O}, l) - \Delta G^{\circ}_f(\text{CoSi}_2, s) - 10\Delta G^{\circ}_f(\text{OH}^-, aq)$$

$$= -214.2 \text{ kJmol}^{-1} - 2 \times 856.3 \text{ kJmol}^{-1} - 5 \times 237.1 \text{ kJmol}^{-1} + 97.6 \text{ kJmol}^{-1} + 10 \times 157.2 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_R = -1442.7 \text{ kJmol}^{-1}$$

$$\Delta G^{\circ}_R = -nfE^{\circ}$$

$$-1442.7 = -10 \times 96,485 \times E^{\circ}$$

$$E^{\circ} = 1.495 \text{ V}$$

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