Electronic Supplementary Material (ESI) for Energy & Environmental Science

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 Ω·cm (University Wafers) was placed on the top of an alumina boat filled with magnesium powder (99.8 %, Alfa Aeser). The alumina boat was then placed in the center of the furnace. Finally, the chamber was heated to 650 ^{o}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 × 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 Aeser) 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 ^{o}C for $TiSi_2$

and VSi_2, 900 ^{o}C for $CoSi_2$, 700 ^{o}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 constructedsimilarly 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

At the Anode: $Mg_2Si + 8OH^- \rightarrow 2MgO + SiO_2 + 4H_2O + 8e^-$ ($E^0 = 2.09$ V)

At the Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ($E^0 = 0.40$ V)

Overall Reaction: $Mg_2Si + 2O_2 \rightarrow 2MgO + SiO_2$ ($E^0_{cell} = 2.49$ V)

Thermodynamic reaction to obtain anode half-cell:

$Mg_2Si + 8OH^- \rightarrow 2MgO + SiO_2 + 4H_2O$ ($E^0 = 2.09$ V)

$$\Delta G^{\circ}_{f}(H_2O, l) = -237.1\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(SiO_2, s) = -856.3\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(Mg_2Si,s) = -75.31\ kJmol^{-1}$$

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

$$\Delta G^{\circ}_{f}(MgO,s) = -569.3\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = 2\Delta G^{\circ}_{f}(MgOs) + \Delta G^{\circ}_{f}(SiO_2,s) + 4\Delta G^{\circ}_{f}(H_2O,l) - \Delta G^{\circ}_{f}(Mg_2Si,s) - 8\Delta G^{\circ}_{f}(OH^{-},aq)$$

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

$$\Delta G^{\circ}_{R} = \ -1610.4\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = -nfE^{0}$$

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

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

Titanium Silicide

At the Anode: $TiSi_2 + 12OH^{-} \rightarrow TiO_2 + 2SiO_2 + 6H_2O + 12e^{-}$ (E^0=1.53 V)

At the Cathode: $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ (E^0= 0.40 V)

Overall Reaction: $TiSi_2 + 3O_2 \rightarrow TiO_2 + 2SiO_2$ (E^0_{cell} =1.93 V)

Thermodynamic reaction to obtain anode half-cell:

$TiSi_2 + 12OH^{-} \rightarrow TiO_2 + 2SiO_2 + 6H_2O + 12e^{-}$ (E^0=1.53 V)

$$\Delta G^{\circ}_{f}(H_2O,l) = -237.1\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(SiO_2,s) = -856.3\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(TiO_2,s) = -888.8\ kJmol^{-1}$$

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

$$\Delta G^{\circ}_{f}(TiSi_2,s) = -127.0\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = \Delta G^{\circ}_{f}(TiO_2,s) + 2\Delta G^{\circ}_{f}(SiO_2,s) + 6\Delta G^{\circ}_{f}(H_2O,l) - \Delta G^{\circ}_{f}(TiSi_2,s) - 12\Delta G^{\circ}_{f}(OH^-,aq)$$

$$= -888.8\ kJmol^{-1} - 2 \times 856.3\ kJmol^{-1} - 5 \times 237.1\ kJmol^{-1} + 127.0\ kJmol^{-1} + 12 \times 157.2\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = -1773.3\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = -nfE^0$$

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

$$E^0 = 1.527\ V$$

Vanadium Silicide

At the Anode: $VSi_2 + 13OH^- \rightarrow \frac{1}{2} V_2O_5 + 2SiO_2 + 13/2H_2O + 13e^-$ (E^0=1.42 V)

At the Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (E^0= 0.40 V)

Overall Reaction: $VSi_2 + 13/2\ O_2 \rightarrow \frac{1}{2} V_2O_5 + 2SiO_2$ (E^0_{cell} =1.82 V)

Thermodynamic reaction to obtain anode half-cell:

$VSi_2 + 13OH^- \rightarrow \frac{1}{2} V_2O_5 + 2SiO_2 + 13/2H_2O + 13e^-$ (E^0=1.42 V)

$$\Delta G^{\circ}_{f}(H_2O,l) = -237.1\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(SiO_2,s) = -856.3\ kJmol^{-1}$$

$$\Delta G^{\circ}_{f}(VSi_2,s) = -39.37\ kJmol^{-1}$$

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

$$\Delta G^{\circ}_{f}(V_2O_5,s) = -1205.9\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = \Delta G^{\circ}_{f}(V_2O_5,s) + 2\Delta G^{\circ}_{f}(SiO_2,s) + 5\Delta G^{\circ}_{f}(H_2O,l) - \Delta G^{\circ}_{f}(CoSi_2,s) - 10\Delta G^{\circ}_{f}(OH^-,aq)$$

$$= \frac{1}{2} \times -1205.9\ kJmol^{-1} - 2 \times 856.3\ kJmol^{-1} - \frac{13}{2} \times 237.1\ kJmol^{-1} + 39.37\ kJmol^{-1} + 13 \times 157.2\ kJmol^{-1}$$

$$\Delta G^{\circ}_{R} = -1776.8\ kJmol^{-1}$$

$$\Delta G^{\circ}{}_{R} = -nfE^{0}$$

$$-1776.8 = -13 \times 96{,}485 \times E^{0}$$

$$E^{0} = 1.4166\ V$$

Cobalt Silicide

At the Anode: $CoSi_2 + 10OH^- \rightarrow CoO + 2SiO_2 + 5H_2O + 10e^-$ (E^0=1.50 V)

At the Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (E^0= 0.40 V)

Overall Reaction: $CoSi_2 + 5O_2 \rightarrow CoO + 2SiO_2$ (E^0_{cell} =1.90 V)

Thermodynamic reaction to obtain anode half-cell:

$CoSi_2 + 10OH^- \rightarrow CoO + 2SiO_2 + 5H_2O + 10e^-$ (E^0=1.50 V)

$$\Delta G^{\circ}{}_{f}(H_2O,l) = -237.1\ kJmol^{-1}$$

$$\Delta G^{\circ}{}_{f}(SiO_2,s) = -856.3\ kJmol^{-1}$$

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

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

$$\Delta G^{\circ}{}_{f}(CoSi_2,s) = -97.6\ kJmol^{-1}$$

$$\Delta G^{\circ}{}_{R} = \Delta G^{\circ}{}_{f}(CoO,s) + 2\Delta G^{\circ}{}_{f}(SiO_2,s) + 5\Delta G^{\circ}{}_{f}(H_2O,l) - \Delta G^{\circ}{}_{f}(CoSi_2,s) - 10\Delta G^{\circ}{}_{f}(OH^-,aq)$$

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

$$\Delta G^{\circ}{}_{R} = -1442.7\ kJmol^{-1}$$

$$\Delta G^{\circ}{}_{R} = -nfE^{0}$$

$$-1442.7 = -10 \times 96{,}485 \times E^{0}$$

$$E^{0} = 1.495\ V$$

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