Electronic Supplemental Information (ESI) for New Journal of Chemistry

A High-Capacity Iron Silicide Air Primary Battery in an Acidic Saline Electrolyte

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1. Material characterization

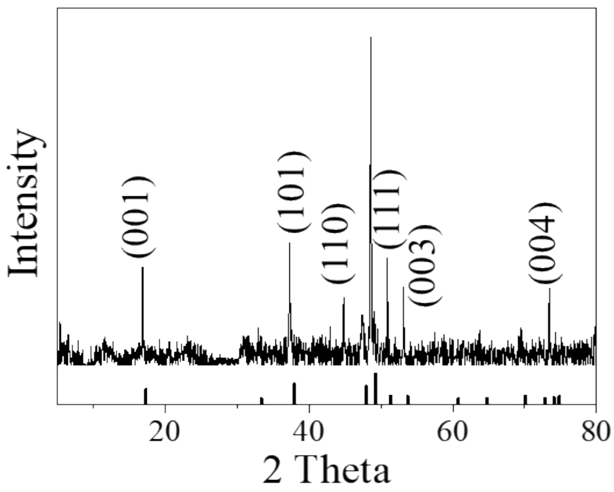

Fig. S1 XRD patterns of pretreated FeSi2 powder.

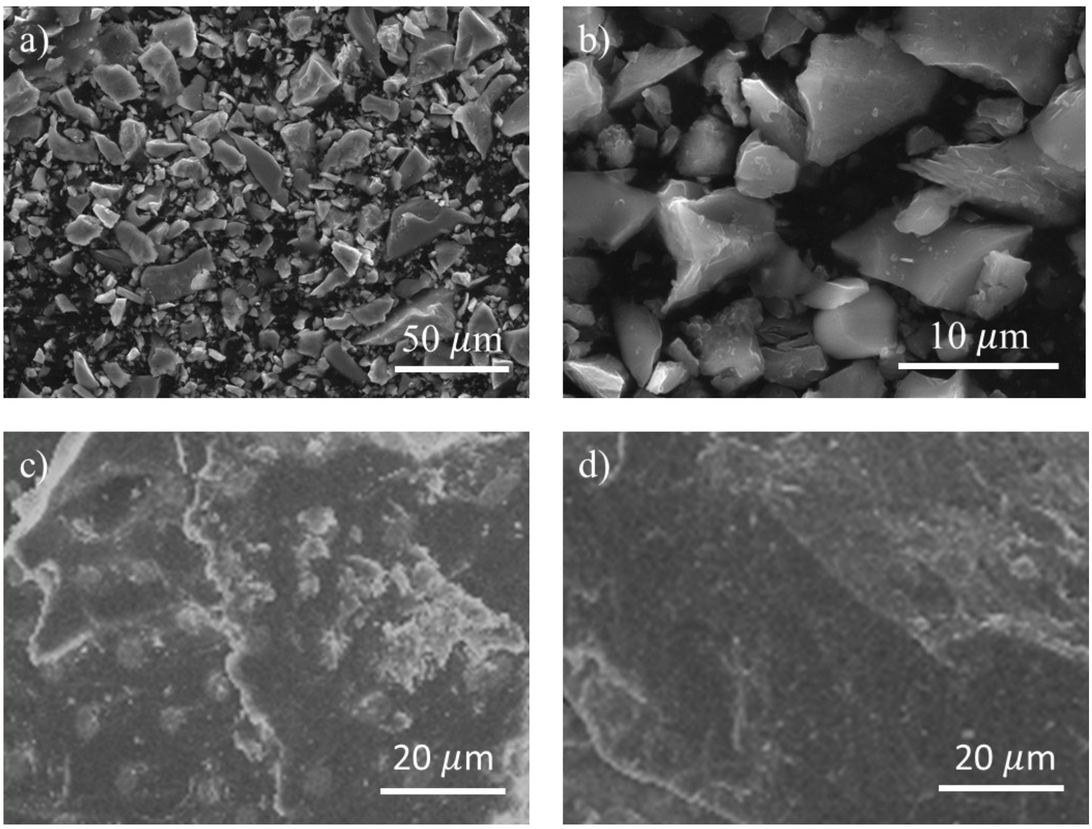

Fig. S2 SEM images of a) and b) $FeSi_2$ at different magnitude, c) $FeSi_2$ was immersed in 2 M H_2SO_4 for 48 hrs and d) $FeSi_2$ was immersed in 2 M H_2SO_4 which contained F^- ions for 48 hrs.

2. Corrosion rate

A corrosion-time plots obtained by ICP-AES technique of the solutions for iron corrosion can be found in research by M.A. Amin *et.al*. [1]

Find the mass of Fe dissolved and time

Mass of Fe dissolved = ~4.8 mg cm^{-2}

Time = ~11.5 hours

Corrosion rate = $\frac{4.8}{11.5}$ = ~0.42 mg cm^{-2} hr^{-1}

The corrosion rate of Fe in 1 M H^+ was 28 times that of $FeSi_2$ in ASF-2 and 89 times that of $FeSi_2$ in ASF-0.5.

Another corrosion experiment was carried out in the research by S.M. Lee *et.al*. [2]

The size of Zn gel anode used in the reference was 2.5 × 2 cm^2

Compare the H_2 evolution at 5 hrs for both Zn gel anode and $FeSi_2$ anode.

Area: 2.5 × 2 = 5 cm^2

Mass of Fe = 0.365 mg (in ASF-2)

Amount of Fe = 0.00652 mmol

Amount of H_2 = 0.00652 mmol

Volume of H_2 = 0.00652 × 22.4 = 0.146 mL (at STP)

The result indicates that the H_2 evolution from Zn gel anode (in 9 M KOH at 60 ℃) and $FeSi_2$ anode (in ASF-2 at 25 ℃) were ~0.56 mL and ~0.15 mL, respectively when both of them were immersed in electrolyte for 5 hours. Though temperature of electrolyte has significant effect on corrosion rate, we can conclude that they have similar corrosion rate (or similar magnitude).

3. **Calculation of theoretical cell potential** [3]

Anode: $FeSi_2 + 4H_2O \rightarrow Fe^{2+} + 2SiO_2 + 8H^+ + 10e^-$

$\Delta G_f^\theta(FeSi_2, s) = -22.6$ kcal mol^{-1}

$\Delta G_f^\theta(H_2O, l) = -56.687$ kcal mol^{-1}

$\Delta G_f^\theta(Fe^{2+}, aq) = -18.85$ kcal mol^{-1}

$\Delta G_f^\theta(SiO_2, s) = -204.75$ kcal mol^{-1}

$\Delta G_f^\theta(H^+, aq) = 0$ kcal mol^{-1}

ΔG_R^θ

$= \Delta G_f^\theta(Fe^{2+}, aq) + \Delta G_f^\theta(SiO_2, s) + \Delta G_f^\theta(H^+, aq) - \Delta G_f^\theta(FeSi_2, s) - \Delta G_f^\theta(H_2O, l)$

$= [(-18.85) + 2 \times (-204.75) + 0] - [(-22.6) + 4 \times (-56.687)]$

$= -179.00$ kcal mol^{-1} $\times$ 4.186 kJ kcal^{-1} = -749.3 kJ mol^{-1}

$\Delta G_R^\theta = -nfE^0$

$$E^\theta = -\frac{\Delta G_R^\theta}{nf} = -\frac{-749.3 \times 1000}{10 \times 96500} = +0.776 \text{ V}$$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\quad E^\theta = +1.229$ V

Overall equation: $2FeSi_2 + 5O_2 + 4H^+ \rightarrow 2Fe^{2+} + 4SiO_2 + 2H_2O$ $\quad E^\theta = 2.005$ V

4. **Calculation of theoretical and practical capacity**

Calculation of theoretical capacity:

Faraday's constant = 96500 C mol^{-1}

1 Ah = 1 A $\times$ 3600 s = 3600 C

1 mol of electrons: $\frac{96500}{3600}$ = 26.8 Ah

So theoretical capacity, $C_0 = 26.8 \times n \times \frac{m}{M}$

wherein, n is the amount of electron transition in the discharge process; m is the mass of active material in the anode, which is equal to 1 g in theoretical specific capacity calculation; M is the molar mass of active material.

Anode material	Theoretical capacity, Ah g^{-1}	Practical capacity, Ah g^{-1}	Density, g cm^{-3} [4]	Volumetric capacity, Ah L^{-1}	Ref.
Zn	0.82	0.645	7.134	4666	[5]
Fe	0.96	~0.5	7.87	~3935	[6]
FeB	2.41	1.2	~7	~8400	[7]
Si	3.82	1.206	2.3296	2809	[8]
$TiSi_2$	3.07	~1.8	4.0	~7200	[9]
$FeSi_2$	2.39	1.90	4.74	9006	This paper

Table S1 Summary of theoretical and practical capacity of different anode materials and their volumetric capacity from different references and this paper.

For $FeSi_2$:

$FeSi_2 + 4H_2O \rightarrow Fe^{2+} + 2SiO_2 + 8H^+ + 10e^-$

M = 112.03 g mol^{-1};

$n = 10$

$C_0 = 26.8 \times 10 \times \frac{1}{112.03} = 2.39$ Ah g^{-1}

Density of $FeSi_2$ is 4.74 g cm^{-3} [4]

Volumetric specific capacity = 2.39 $\times$ 4.74 = 11.33 Ah cm^{-3} = 11330 Ah L^{-1}

For FeB: [7]

$FeB + 9OH^- \rightarrow 0.5Fe_2O_3 + BO_3^{3-} + 4.5H_2O$

$M = 66.656$ g mol^{-1}

$n = 6$

$C_0 = 26.8 \times 6 \times \frac{1}{66.656} = 2.41$ Ah g^{-1}

Density of FeB is ~7 g cm^{-3} [4]

Volumetric specific capacity = 2.41 $\times$ 7 = 16.89 Ah cm^{-3} = 16890 Ah L^{-1}

Reference: Exceptional electrochemical activities of amorphous Fe–B and Co–B alloy powders used as high capacity anode materials

Practical gravimetric specific capacity = 1200 mAh g^{-1} = 1.200 Ah g^{-1}

Practical volumetric specific capacity = 1.200 Ah g^{-1} $\times$ 7 $\times$ 1000 = 8400 Ah L^{-1}

For Si:

$Si + 4OH^- \rightarrow Si(OH)_4 + 4e^-$

$M = 28.09$ g mol^{-1}

$n = 4$

$C_0 = 26.8 \times 4 \times \frac{1}{28.09} = 3.82$ Ah g^{-1}

Density of Si is 2.3296 g cm^{-3} [4]

Volumetric specific capacity = 3.82 $\times$ 2.3296 = 8.89 Ah cm^{-3} = 8890 Ah L^{-1}

Practical gravimetric specific capacity = 1206 mAh g^{-1} = 1.206 Ah g^{-1} [8]

Practical volumetric specific capacity = 1.206 Ah g^{-1} $\times$ 2.3296 $\times$ 1000= 2809 Ah L^{-1}

For $TiSi_2$

$TiSi_2 + 12OH^- \rightarrow TiO_2 + 2SiO_2 + 6H_2O + 12e^-$

M = 104.86 g mol^{-1}

n = 12

$C_0 = 26.8 \times 12 \times \frac{1}{104.86} = 3.07$ Ah g^{-1}

Density of $TiSi_2$ is 4.0 g cm^{-3} [4]

Volumetric specific capacity = 3.07 $\times$ 4.0 = 12.28 Ah cm^{-3} = 12800 Ah L^{-1}

Practical gravimetric specific capacity = 1800 mAh g^{-1} = 1.800 Ah g^{-1} [9]

Practical volumetric specific capacity = 1.800 Ah g^{-1} $\times$ 4.0 $\times$ 1000 = 7200 Ah L^{-1}

For Zn:

$Zn \rightarrow Zn^{2+} + 2e^-$

M = 65.38 g mol^{-1}

n = 2

$C_0 = 26.8 \times 2 \times \frac{1}{65.38} = 0.82$ Ah g^{-1}

Density of Si is 7.134 g cm^{-3} [4]

Volumetric specific capacity = 0.82 × 7.134 = 5.849 Ah cm^{-3} = 5849 Ah L^{-1} [5]

Reference:

For Fe:

$Fe + 2OH^{-} \rightarrow Fe(OH)_2 + 2e^{-}$

M = 55.85 g mol^{-1}

n = 2

$C_0 = 26.8 \times 2 \times \frac{1}{55.85} = 0.96$ Ah g^{-1}

Density of Fe is 7.87 g cm^{-3} [4]

Volumetric specific capacity = 0.96 × 7.87 = 7.56 Ah cm^{-3} = 7560 Ah L^{-1}

Practical gravimetric specific capacity = 500 mAh g^{-1} = 0.500 Ah g^{-1}

Practical volumetric specific capacity = 0.500 Ah g^{-1} × 7.87 × 1000= 3935 Ah L^{-1}

Reference

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