

Bismuth as a New Chloride-Storage Electrode Enabling the Construction of a Practical High Capacity Desalination Battery

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Supporting Information

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I. Calculation details

1. Volume expansion of Bi during Cl⁻ storage process (phase transition to BiOCl)

1) Unit cell volume of rhombohedral Bi

$$(a = 4.54 \text{ \AA}, b = 4.54 \text{ \AA}, c = 11.86 \text{ \AA}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ)$$

$$V_{\text{unit cell}} = 4.54 \text{ \AA} * 4.54 \text{ \AA} * \sqrt{3}/2 * 11.86 \text{ \AA} = 211.703 \text{ \AA}^3$$

Since there are 6 Bi atoms per unit cell,

$$V_{\text{unit cell}}/\text{atom}_{\text{Bi}} = 211.703 \text{ \AA}^3 / 6 = 35.283 \text{ \AA}^3$$

2) Unit cell volume of tetragonal BiOCl

$$(a = 3.89 \text{ \AA}, b = 3.89 \text{ \AA}, c = 7.37 \text{ \AA}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ)$$

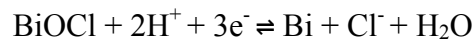
$$V_{\text{unit cell}} = 3.89 \text{ \AA} * 3.89 \text{ \AA} * 7.37 \text{ \AA} = 111.524 \text{ \AA}^3$$

Since there are 2 Bi atoms per unit cell,

$$V_{\text{unit cell}}/\text{atom}_{\text{Bi}} = 111.524 \text{ \AA}^3 / 2 = 55.762 \text{ \AA}^3$$

Therefore, the volume change of Bi during a phase transition to BiOCl is 158%.

2. Calculation of equilibrium redox potentials for Bi/BiOCl



1) Standard reduction potential

$$E^\circ = 0.160 \text{ V vs. SHE, which is equivalent to } -0.0372 \text{ V vs. Ag/AgCl (4 M KCl)}$$

2) Equilibrium potential in 0.6 M NaCl (pH 6.4)

$$\begin{aligned} E &= E^\circ - \frac{0.0591 \text{ V}}{n} \log a_{\text{Cl}^-} + 2\left(\frac{0.0591 \text{ V}}{n}\right) \log [H^+] \\ &= E^\circ - 0.0197 \text{ V} (\log a_{\text{Cl}^-}) - 0.0394 \text{ V (pH)} \\ &= E^\circ - 0.0197 \text{ V} \log (0.6) - 0.0394 \text{ V (6.4)} \\ &= 0.160 \text{ V} + 0.00437 \text{ V} - 0.25216 \text{ V} \\ &= -0.088 \text{ V vs. SHE} \\ &\text{or } -0.285 \text{ V vs. Ag/AgCl} \end{aligned}$$

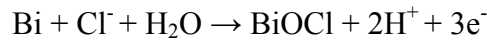
3) Equilibrium potential in 70 mM HCl (pH 1.15)

$$E = E^\circ - \frac{0.0591 \text{ V}}{n} \log a_{\text{Cl}^-} + 2\left(\frac{0.0591 \text{ V}}{n}\right) \log [H^+]$$

$$\begin{aligned}
&= E^\circ - 0.0197 \text{ V} (\log a_{\text{Cl}^-}) - 0.0394 \text{ V (pH)} \\
&= E^\circ - 0.0197 \text{ V} \log (0.07) - 0.0394 \text{ V (1.15)} \\
&= 0.160 \text{ V} + 0.02275 \text{ V} - 0.04531 \text{ V} \\
&= 0.13744 \text{ V vs. SHE} \\
&\text{or } -0.0596 \text{ vs. Ag/AgCl}
\end{aligned}$$

3. Capacity of Bi for Cl storage

When assuming complete conversion of Bi to BiOCl by the following reaction,



since one mole of Cl (MM= 35.453 g/mol) can be stored per one mole of Bi (MM= 208.9804 g/mol), the theoretical capacity of Cl storage in 1 g of Bi is calculated to be 169.6 mg/g_{Bi}. Storing one mole of Cl in one mol of Bi requires three moles of e⁻, which is equivalent to 289,455 C. Since Bi electrodes used in this study contain 1.25 mg of Bi (5.98 x 10⁻⁶ mol), the total charge necessary to completely convert Bi to BiOCl is calculated to be:

$$\text{Theoretical charge required to convert 1.25 mg of Bi to BiOCl} = 5.98 \times 10^{-6} \text{ mol}_{\text{Bi}} \times 289,455 \text{ C/mol}_{\text{Bi}} = 1.73 \text{ C}$$

However, the total charge experimentally observed to convert 1.25 mg of Bi to BiOCl was 0.2351 mAh, which is equivalent to 0.846 C. This means that during chlorination, only 48.9% of the Bi (0.611 mg) in the Bi electrode is electrochemically active and was converted to BiOCl. Therefore, although the theoretical capacity for Cl that can be stored in 1 g of Bi is 169.6 mg/g_{Bi}, the experimental capacity for Cl storage that is stored in 1 g of Bi using the Bi electrodes used in this study is calculated to be 82.9 mg/g_{Bi} (= 169.6 mg/g_{Bi} x 48.9 %).

4. Capacity for Cl storage by CDI

The capacity for Cl storage of CDI can be calculated from its capacity for NaCl storage reported in the previous study (S4), which is 13.5 mg/g_{carbon}. Assuming that the activated carbon electrodes used for the Na capture and the Cl capture have the same mass and surface area, the capacity of storing 13.5 mg of NaCl in 1 g of carbon is equivalent to storing 8.18 mg of Cl in 0.5 g of carbon and 5.32 mg of Na in 0.5 g of carbon. Therefore, the capacity for Cl storage can be calculated to be 16.36 mg/g_{carbon}.

Table S1. Standard Gibbs free energies of formation (ΔG_f°) for species involved with the Bi-Cl-H₂O system.

Species	ΔG_f° , kJ mol ⁻¹ (298.15 K and 1 bar)	
	Ref. S1	Ref. S2
Cl ⁻ (aq)		-131.23
OH ⁻ (aq)		-157.24
H ₂ O (l)		-237.13
Bi ³⁺ (aq)		82.80
BiOCl (s)		-322.10
Bi ₂ O ₃ (s)		-493.70
BiO ⁺ (aq)		-146.40
BiOH ²⁺ (aq)	-163.72	
Bi ₆ (OH) ₁₂ ⁶⁺ (aq)		-2350.7
Bi ₂ O ₄ (s)	-456.06	
Bi ₂ O ₅ (s)	-383.13	
Bi ₄ O ₇ (s)	-973.83	
BiCl ²⁺ (aq)		-61.27
BiCl ₂ ⁺ (aq)		-205.40
BiCl ₃ (s)		-315.00
BiCl ₄ ⁻ (aq)		-481.50

Table S2. Electrochemical reactions involved with the Bi-Cl-H₂O system with E and solubility equations at 25 °C.

	Reactions	E and Solubility
1	$\text{Bi}^{3+} + \text{H}_2\text{O} = \text{BiOH}^{2+} + \text{H}^+$	$\text{pH} = -1.645 + \log [\text{Bi}^{3+}] - \log [\text{BiOH}^{2+}]$
2	$6\text{BiOH}^{2+} + 6\text{H}_2\text{O} = \text{Bi}_6(\text{OH})_{12}^{6+} + 6\text{H}^+$	$\text{pH} = 1.588 + \log [\text{BiOH}^{2+}] - \log [\text{Bi}_6(\text{OH})_{12}^{6+}]$
3	$\text{Bi}_6(\text{OH})_{12}^{6+} = 3\text{Bi}_2\text{O}_3 + 3\text{H}_2\text{O} + 6\text{H}^+$	$\text{pH} = 4.620 + \log [\text{Bi}_6(\text{OH})_{12}^{6+}]$
4	$2\text{BiOCl} + \text{H}_2\text{O} = \text{Bi}_2\text{O}_3 + 2\text{Cl}^- + 2\text{H}^+$	$\text{pH} = 10.965 + \log [\text{Cl}^-]$
5	$\text{BiOH}^{2+} + \text{Cl}^- = \text{BiOCl} + \text{H}^+$	$\text{pH} = -4.757 - \log [\text{BiOH}^{2+}] - \log [\text{Cl}^-]$
6	$\text{Bi}^{3+} + \text{H}_2\text{O} + \text{Cl}^- = \text{BiOCl} + 2\text{H}^+$	$\text{pH} = -3.201 - 0.5 \log [\text{Bi}^{3+}] - 0.5 \log [\text{Cl}^-]$
7	$\text{BiCl}_2^+ + \text{H}_2\text{O} = \text{BiOCl} + \text{Cl}^- + 2\text{H}^+$	$\text{pH} = -0.946 + 0.5 \log [\text{Cl}^-] - 0.5 \log [\text{BiCl}_2^+]$
8	$\text{BiCl}_4^- + \text{H}_2\text{O} = \text{BiOCl} + 3\text{Cl}^- + 2\text{H}^+$	$\text{pH} = 0.249 + 1.5 \log [\text{Cl}^-] - 0.5 \log [\text{BiCl}_4^-]$
9	$\text{Bi}^{3+} + 3\text{e}^- = \text{Bi}$	$E = 0.286 + 0.0197 \log [\text{Bi}^{3+}]$
10	$\text{BiOH}^{2+} + \text{H}^+ + 3\text{e}^- = \text{Bi} + \text{H}_2\text{O}$	$E = 0.254 + 0.0197 \log [\text{BiOH}^{2+}] - 0.0197 \text{ pH}$
11	$\text{BiOCl} + 2\text{H}^+ + 3\text{e}^- = \text{Bi} + \text{H}_2\text{O} + \text{Cl}^-$	$E = 0.160 - 0.0197 \log [\text{Cl}^-] - 0.0394 \text{ pH}$
12	$\text{Bi}_6(\text{OH})_{12}^{6+} + 12\text{H}^+ + 18\text{e}^- = 6\text{Bi} + 12\text{H}_2\text{O}$	$E = 0.285 + 0.0033 \log [\text{Bi}_6(\text{OH})_{12}^{6+}] - 0.0394 \text{ pH}$
13	$\text{Bi}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- = 2\text{Bi} + 3\text{H}_2\text{O}$	$E = 0.376 - 0.0592 \text{ pH}$
14	$\text{BiCl}_2^+ + 3\text{e}^- = \text{Bi} + 2\text{Cl}^-$	$E = 0.197 - 0.0394 \log [\text{Cl}^-] + 0.0197 [\text{BiCl}_2^+]$
15	$\text{BiCl}_4^- + 3\text{e}^- = \text{Bi} + 4\text{Cl}^-$	$E = 0.150 - 0.0788 \log [\text{Cl}^-] + 0.0197 [\text{BiCl}_4^-]$
16	$\text{Bi}_4\text{O}_7 + 4\text{Cl}^- + 6\text{H}^+ + 2\text{e}^- = 4\text{BiOCl} + 3\text{H}_2\text{O}$	$E = 2.596 + 0.1184 \log [\text{Cl}^-] - 0.1775 \text{ pH}$
17	$3\text{Bi}_4\text{O}_7 + 3\text{H}_2\text{O} + 18\text{H}^+ + 6\text{e}^- = 2\text{Bi}_6(\text{OH})_{12}^{6+}$	$E = 1.846 - 0.0198 \log [\text{Bi}_6(\text{OH})_{12}^{6+}] - 0.1775 \text{ pH}$
18	$\text{Bi}_4\text{O}_7 + 2\text{H}^+ + 2\text{e}^- = 2\text{Bi}_2\text{O}_3 + \text{H}_2\text{O}$	$E = 1.299 - 0.0592 \text{ pH}$
19	$\text{Bi}_2\text{O}_4 + 2\text{Cl}^- + 4\text{H}^+ + 2\text{e}^- = 2\text{BiOCl} + 2\text{H}_2\text{O}$	$E = 2.073 + 0.0592 \log [\text{Cl}^-] - 0.1183 \text{ pH}$
20	$3\text{Bi}_2\text{O}_4 + 12\text{H}^+ + 6\text{e}^- = \text{Bi}_6(\text{OH})_{12}^{6+}$	$E = 1.697 - 0.1183 \text{ pH}$
21	$\text{Bi}_2\text{O}_5 + 2\text{Cl}^- + 6\text{H}^+ + 4\text{e}^- = 2\text{BiOCl} + 3\text{H}_2\text{O}$	$E = 1.840 + 0.0296 \log [\text{Cl}^-] - 0.0887 \text{ pH}$
22	$2\text{Bi}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^- = \text{Bi}_4\text{O}_7 + \text{H}_2\text{O}$	$E = 1.549 - 0.0592 \text{ pH}$

Table S3. Determination of Cl^- concentration in the solution during the chlorination of Bi measured by a chloride ion meter (see the experimental section for measurement conditions).

Charge passed (C)	Theoretically expected Cl^- concentration (g/L)	Measured Cl^- concentration (g/L)
0	2.127 g/L	2.14
25	2.025 g/L	2.03
50	1.923 g/L	1.92
75	1.821 g/L	1.83
100	1.719 g/L	1.73

FARADAIC EFFICIENCY: 100%

Table S4. Determination of Na^+ concentration in the solution after the sodiation of $\text{NaTi}_2(\text{PO}_4)_3$ measured by a sodium ion meter (see the experimental section for measurement conditions).

Charge passed (C)	Theoretically expected Na^+ concentration (g/L)	Measured Na^+ concentration (g/L)
0	1.379	1.38
17.4 C	1.242	1.27

FARADAIC EFFICIENCY: 80%

Table S5. Roughly estimated energy requirement of the Bi/Bi/NaTi₂(PO₄)₃ cell and the previously reported Ag/MnO₂ cell for desalination.

I. To remove Cl⁻ present in 1 L of 0.6 M NaCl*

	Ag/MnO ₂ (9) ^a	Bi/NaTi ₂ (PO ₄) ₃ (neutral/neutral) ^b	Bi/NaTi ₂ (PO ₄) ₃ (neutral/acid) ^c
Electrical Energy Requirement (kWh/m ³)	1.3	57.3	5.9

a. In reference (9), it is shown that 1.209 mg of Cl⁻ (4030 mg_{Cl}/L of 300 uL) was removed by 261 mJ (0.0000725 Wh) by the Ag/MnO₂ cell. Therefore, the energy consumption for desalination is calculated to be 1.3 kWh/m³ for removal of Cl⁻ in 1L of 0.6 M NaCl (= 21.23 g of Cl⁻).

b. This is for the case where both desalination and salination is performed in neutral conditions. In this case, due to the slow reduction kinetics of BiOCl to Bi in neutral condition, both the desalination and salination steps require energy input. As a result, the Bi/NaTi₂(PO₄)₃ cell cannot serve as a desalination battery and cannot offer a practical desalination system.

c. This is for the case where desalination is performed in neutral condition but salination is performed in acidic condition. The energy requirement is higher than Ag/MnO₂ cell. However, it is still comparable to the energy requirement for RO (4-6 kWh/m³)(ref) without considering energy consumption required for pre-treatment of water critical for RO. With this energy requirement together with the cheap cost of Bi, commercially viable desalination systems based on Bi/BiOCl electrode, which can complement RO, are expected.

II. To remove Na⁺ present in 1 L of 0.6 M NaCl^{d,*}

	Ag/MnO ₂ (9) ^d	Bi/NaTi ₂ (PO ₄) ₃ (neutral/neutral) ^e	Bi/NaTi ₂ (PO ₄) ₃ (neutral/acid) ^e
Electrical Energy consumption (kWh/m ³)	1.3	19.1	2.0

d. Since the Ag/MnO₂ cell removes 1 Na and 1 Cl per electron, the energy requirement for Cl⁻ removal is the same as the energy requirement for Na removal. However, The Bi/NaTi₂(PO₄)₃ cell removes 3 Na and 1 Cl per three electron. Therefore, energy requirement for Na removal is one third of the energy requirement for Cl removal.

* The calculation results shown here are only rough estimations based on the preliminary results shown in the current study and the result shown in reference 9 (Figure *). Ours (Figure7)

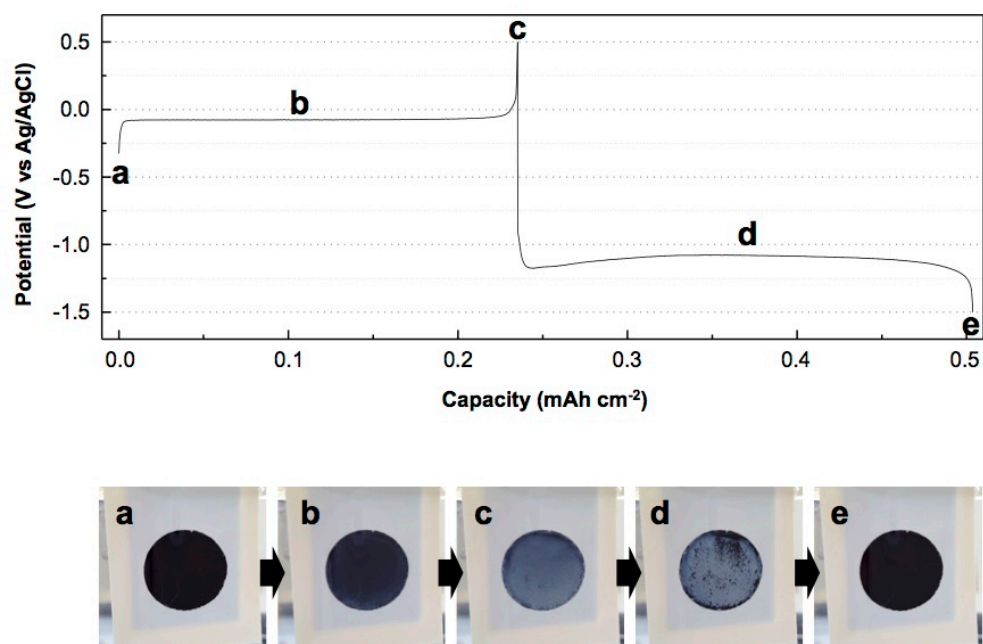


Figure S1. Photographs showing the surface color change of the Bi electrode during various stages of the chlorination and dechlorination processes.

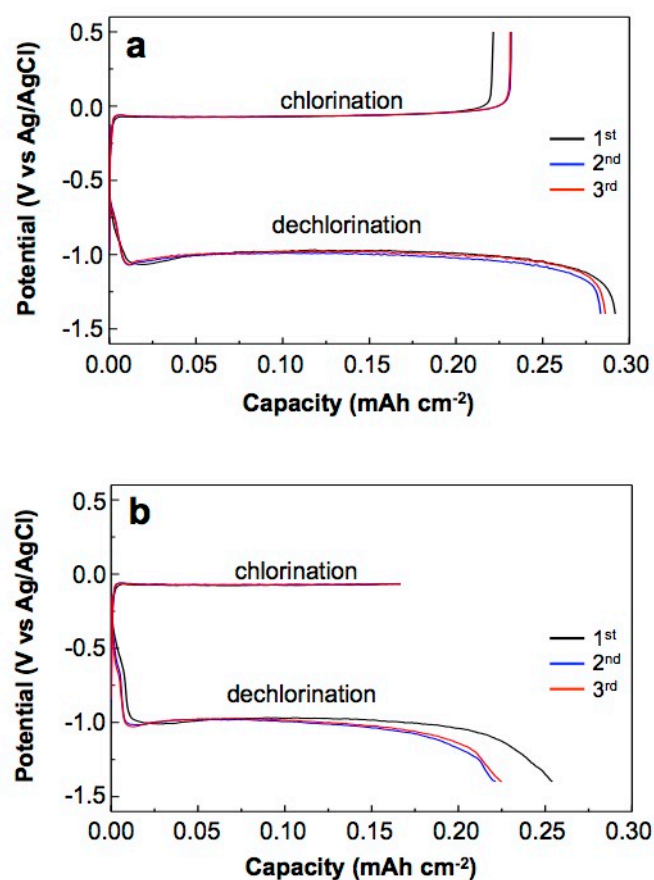


Figure S2. (a) Potential-capacity plots of the Bi electrode for the first three chlorination/dechlorination cycles at $\pm 2 \text{ mA cm}^{-2}$ in 0.6 M NaCl in the voltage range of 0.5 V and -1.4 V vs. AgAgCl and (b) potential-capacity plots of the Bi electrode for the first three chlorination/dechlorination cycles using the same conditions except that the initial chlorination capacity was restricted to $0.1756 \text{ mAh cm}^{-2}$, which is 80% of the initial chlorination capacity shown in (a).

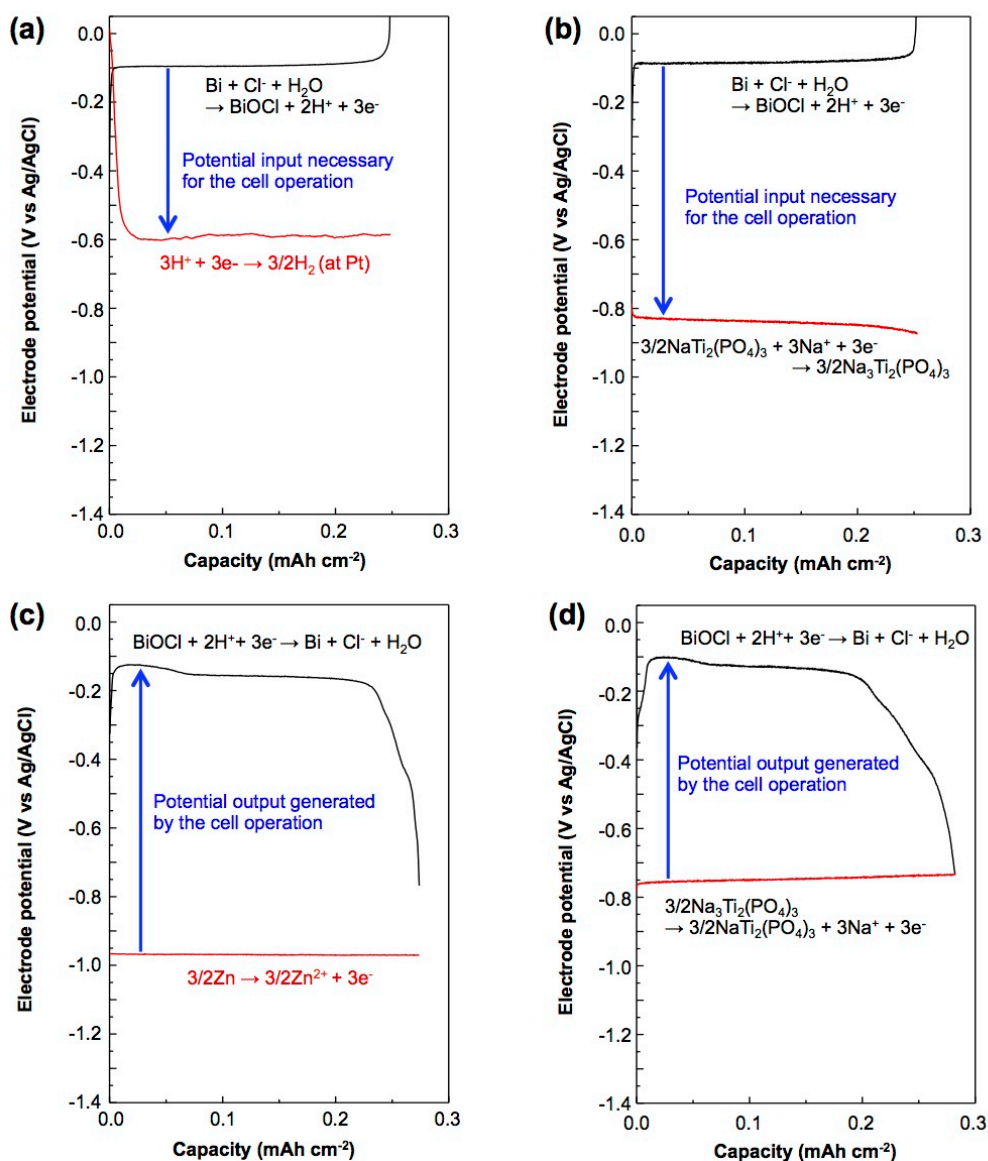


Figure S3. (a) The potential-capacity plots of the Bi electrode and the Pt electrode in 70 mM HCl during charging in comparison with (b) the potential-capacity plots of the Bi electrode in 70 mM HCl and the NaTi₂(PO₄)₃ electrode in 1 M Na₂SO₄ during charging; (c) the potential-capacity plots of the BiOCl electrode and the Zn electrode in 70 mM HCl during discharging in comparison with (d) the potential-capacity plots of the BiOCl electrode in 70 mM HCl and the Na₃Ti₂(PO₄)₃ electrode in 1 M Na₂SO₄ during discharging. All charging and discharging processes were performed galvanostatically at $\pm 1 \text{ mA cm}^{-2}$.

References

- (S1) M. Pourbaix, Atlas of electrochemical equilibria in aqueous solutions (NACE, Houston Texas, ed.2, 1974), pp. 1-644.
- (S2) D. D. Wagman, W. H. Evans, V, B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 1982, **11** 392.