Supporting Information

Highly Efficient H₂ Production and Size-Selective AgCl Synthesis via Electrolytic Cell Design

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Table of Contents

Cell Voltage Calculations.

The theoretical applied voltage for water splitting is 1.23 V. This conclusion applies only to the electrolyte with the same pH value in the anode and cathode chambers. However, assuming that OER is carried out in a neutral electrolyte (1.0 M KNO_3) and HER in an acidic electrolyte (1 M HNO_3) forming an asymmetric neutral-acidic electrolytic cell, the applied voltage for water splitting can be obtained by the following Nernst formula:

For water electrolysis in asymmetric neutral-acidic cell

OER at the anode (1M KNO_3, pH=7)

$$4OH^- - 4e^- \rightarrow 2H_2O + O_2$$
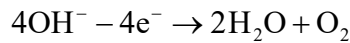
$$E_a = E^\theta_{O_2/OH^-} - 2.303 \frac{RT}{4F} \log\left[\frac{\alpha(OH^-)^4}{\alpha(H_2O)^2 \alpha(O_2)}\right] = 1.229V - 0.059V \times pH = 0.8153V$$
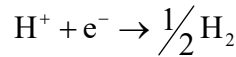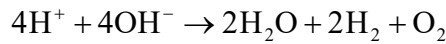
HER at the cathode (1M HNO_3, pH=0)

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$

$$E_c = E^\theta_{H^+/H_2} - 2.303 \frac{RT}{4F} \log\left[\frac{\alpha_{H_2}}{\alpha(H^+)^2_{H^+}}\right] = 0V - 0.0591 \times pH = 0V$$
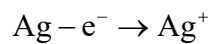
The overall reaction:

$$4H^+ + 4OH^- \rightarrow 2H_2O + 2H_2 + O_2$$

$$V_{theoretical\,required} = E_a - E_c = 0.815V$$

when the anode OER was replaced by silver oxidation reaction (AOR)

AOR at the anode (1M KNO_3 with 0.01 M KCl, pH=7):

$$Ag - e^- \rightarrow Ag^+$$

Ag^+ will react with Cl^- spontaneously:
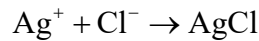
$$Ag^+ + Cl^- \rightarrow AgCl$$

$$E_a = E^\theta_{AgCl/Ag} - \frac{RT}{nF} \ln\left[\frac{\alpha_{Ag} \times \alpha_{Cl^-}}{\alpha_{AgCl}}\right] = 0.222V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{0.01}{1}\right] = 0.340V$$

$$E^\theta_{AgCl/Ag} = 0.222V$$

HER at the cathode (1M HCl, pH=0)

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$
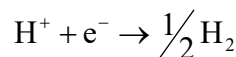
$$E_c = E^\theta_{H^+/H_2} - \frac{RT}{nF} \ln\left[\frac{1}{\alpha^2_{H^+}}\right] = 0V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{1}{1^2}\right]V = 0V$$

$$E^\theta_{H^+/H_2} = 0V$$

Overall reaction:

$$Ag + HCl \rightarrow AgCl + \frac{1}{2} H_2$$

$$V_{\text{theoretical required}} = E_a - E_c = 0.340V$$
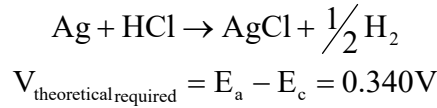
where R is 8.314 J K^{-1} mol^{-1} (molar gas constant), T is 298.15 K, n is 1 (the number of electrons transferred per mole of product), F is 96485 C mol^{-1} (Faradaic constant), and is the corresponding activity.

If AOR at the anode (1M KNO$_3$ with 0.025 M KCl, pH=7):

$$E_a = E^{\theta}_{\text{AgCl/Ag}} - \frac{RT}{nF} \ln\left[\frac{\alpha_{Ag} \times \alpha_{Cl^-}}{\alpha_{AgCl}}\right] = 0.222V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{0.025}{1}\right] = 0.317V$$

$$V_{\text{theoretical required}} = E_a - E_c = 0.317V$$

If AOR at the anode (1M KNO$_3$ with 0.05 M KCl, pH=7):

$$E_a = E^{\theta}_{\text{AgCl/Ag}} - \frac{RT}{nF} \ln\left[\frac{\alpha_{Ag} \times \alpha_{Cl^-}}{\alpha_{AgCl}}\right] = 0.222V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{0.05}{1}\right] = 0.299V$$

$$V_{\text{theoretical required}} = E_a - E_c = 0.299V$$

If AOR at the anode (1M KNO$_3$ with 0.075 M KCl, pH=7):

$$E_a = E^{\theta}_{\text{AgCl/Ag}} - \frac{RT}{nF} \ln\left[\frac{\alpha_{Ag} \times \alpha_{Cl^-}}{\alpha_{AgCl}}\right] = 0.222V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{0.075}{1}\right] = 0.289V$$

$$V_{\text{theoretical required}} = E_a - E_c = 0.289V$$

If AOR at the anode (1M KNO$_3$ with 0.1 M KCl, pH=7):

$$E_a = E^{\theta}_{\text{AgCl/Ag}} - \frac{RT}{nF} \ln\left[\frac{\alpha_{Ag} \times \alpha_{Cl^-}}{\alpha_{AgCl}}\right] = 0.222V - \frac{8.314 \times 298.15}{1 \times 96485} \ln\left[\frac{0.1}{1}\right] = 0.281V$$

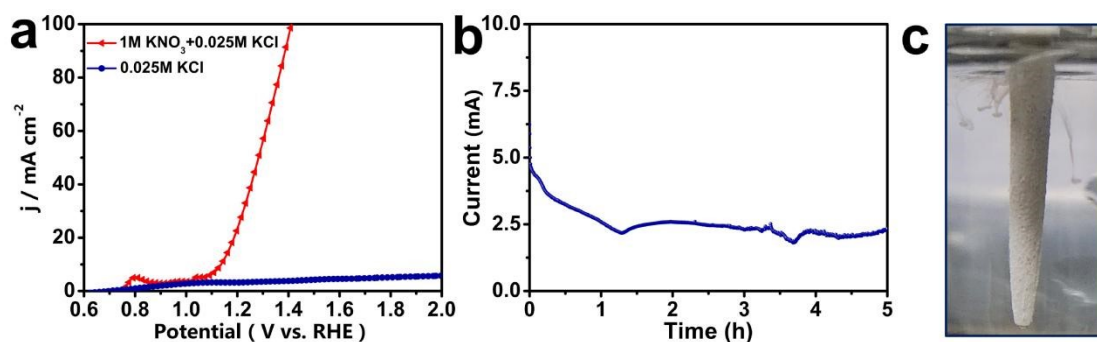$$V_{\text{theoretical required}} = E_a - E_c = 0.281V$$

According to theoretical calculation, the potential of practical application for asymmetric neutral-acidic cell using AOR instead of OER is much lower than that of water splitting.

Figure S1. (a) LSV curves with different electrolytes. (b) Chronoamperometry curve for silver in 0.025 M KCl at 2.5 V vs. RHE. (c) Photograph showing surface of the silver rod during the reaction. The silver electrode surface was covered with a thick white material, making it difficult to continue the reaction.
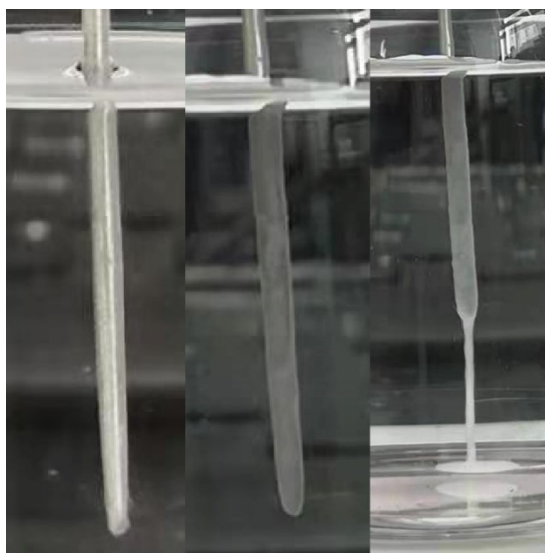
Figure S2. Photograph showing the changes of the silver rod during positive scanning from +0.7V (vs. RHE).

Figure S3. Photograph showing surface of the silver rod when the reaction is over.
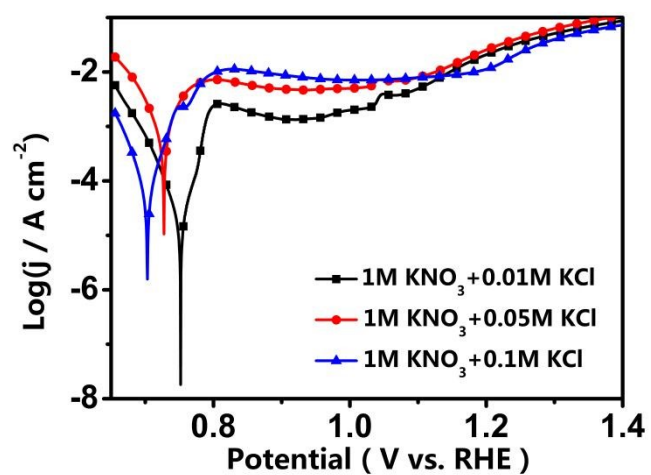
Figure S4. The polarization curves of silver electrode with different chloride ions concentration.
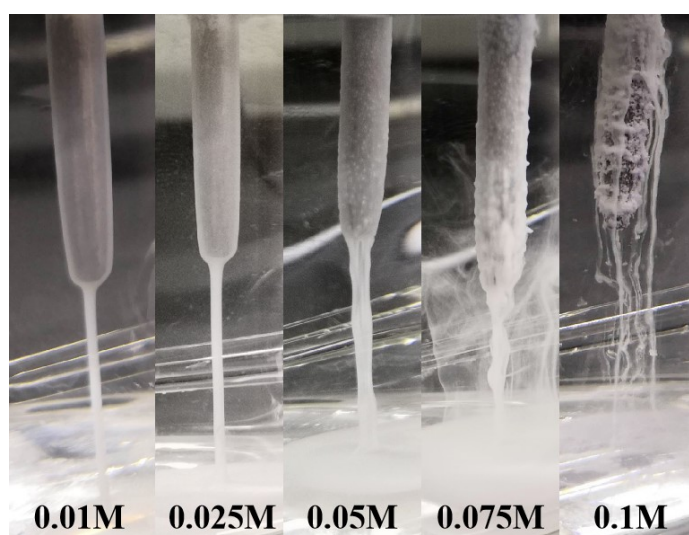
Figure S5. The phenomenon of silver electrode reaction with different chloride ions concentration.

Figure S6. Photograph of the actual electrochemical device.

Figure S7. (a) XRD pattern of Ag$_3$PO$_4$/AgCl. (b) XRD pattern of Ag$_2$O/AgCl. (c) SEM images of Ag$_3$PO$_4$/AgCl. (d) SEM images of Ag$_2$O/AgCl. Ag$_3$PO$_4$/AgCl appears as a flake and Ag$_2$O/AgCl as a polyhedron.
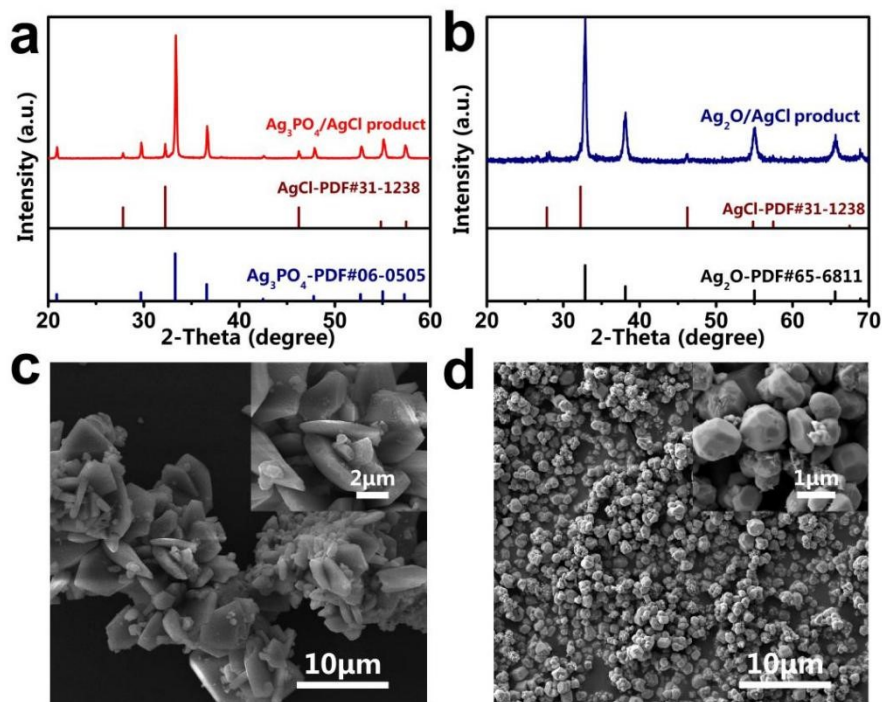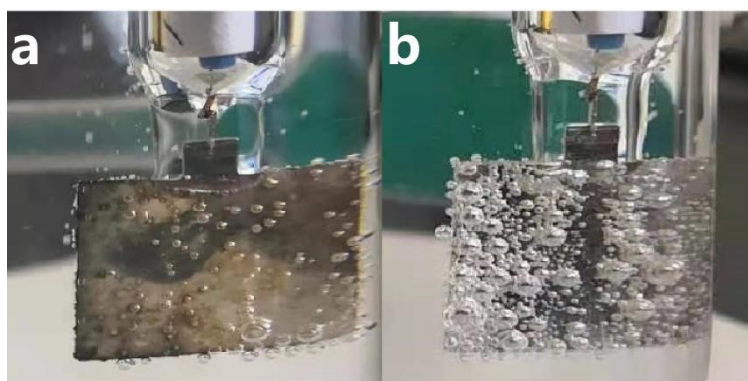

Figure S8. Photograph showing the difference of Pt sheet electrode surface with and without chloride ions in electrolyte during the reaction: (a) no chloride ions in the electrolyte, (b) 0.01M chloride ions in the electrolyte.
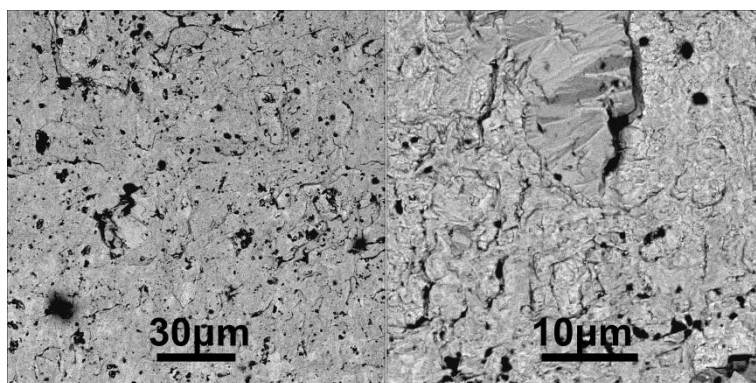
Figure S9. SEM images of silver rod after the reaction.
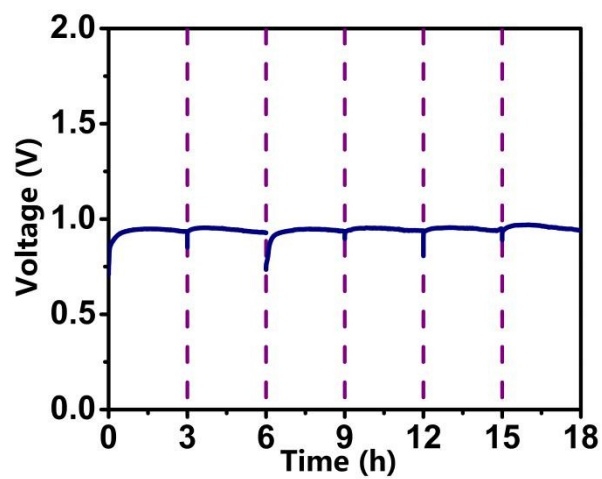
Figure S10. Durability measurement when silver and graphite rods were used as the anode and cathode, respectively. The measurements were carried out at a current of 10 mA.

Table S1: Comparison of the electrolytic voltage between our work and the overall water splitting

Electrode materials	Medium	E (overall reaction)	Reference
Anode：Sliver rod Cathode：Pt sheet	Anode：1M KNO_3+0.025M KCl Cathode：1M HCl	1.1 at 10 mA cm^{-2}	This work
Anode：Sliver rod Cathode：Graphite rod	1M HNO_3+0.01M KCl	0.95 at 10 mA cm^{-2} 1.37 at 250 mA cm^{-2}	This work
NiFe LDH /DG	1.0 M KOH	1.5 at 20 mA cm^{-2}	[1]
NiFeRu-LDH	1.0 M KOH	1.52 at 10 mA cm^{-2}	[2]
NiFe LDH	1.0 M KOH	1.54 at 10 mA cm^{-2}	[3]
NiVIr-LDH	1.0 M KOH	1.42 at 10 mA cm^{-2}	[4]
NiFe(OH)x/FeS	1.0 M KOH	1.42 at 10 mA cm^{-2}	[5]
FeP/Ni2P	1.0 M KOH	1.42 at 10 mA cm^{-2}	[6]
Ni_2P-NiP_2 HNPs‖NiFe-LDH	1.0 M KOH	1.48 at 10 mA cm^{-2}	[7]
N-Ni_3S_2/NF‖N-Ni_3S_2/NF	1.0 M KOH	1.48 at 10 mA cm^{-2}	[8]
Cu@NiFe LDH ‖ Cu@NiFe LDH	1.0 M KOH	1.54 at 10 mA cm^{-2}	[9]
MoS_2/Ni_3S_2	1.0 M KOH	1.56 at 10 mA cm^{-2}	[10]
$Ni_{0.1}Co_{0.9}P$	1.0 M PBS	1.89 at 10 mA cm^{-2}	[11]
CoO/$CoSe_2$	1.0 M PBS	2.18 at 10 mA cm^{-2}	[12]

References

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