

## Supporting information for the paper

### Energy-saving synthesis of potassium iodate *via* electrolysis of potassium iodine and O<sub>2</sub> in a membraneless cell

#### Experimental details

##### 1. Chemical reagents and Material

Potassium iodine (KI), potassium iodate (KIO<sub>3</sub>), potassium hydroxide (KOH), silver nitrate (AgNO<sub>3</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) were analytical grade and purchased from Beijing Chemicals Company, China. Polytetrafluoroethylene emulsion (PTFE 60 wt. %), acetylene black were purchased from Yi Lida Co. Ltd, China.

Three kinds of dimensionally stable anodes (DSAs) electrode including Platinum-coating titanium mesh (Pt/Ti), iridium oxide coating titanium mesh (IrO<sub>2</sub>/Ti) and Ruthenium Oxide coating nickel mesh (RuO<sub>2</sub>/Ti), were purchased from Xi'an Northwest Institute for Nonferrous Metal Research, China.

##### 2. Preparations of ORC and Ag-ORC electrodes

A porous oxygen cathode was prepared according to the following steps. 300mg PTFE emulsion (60 wt. %) and 100mg ammonium nitrate were dissolved in 1ml H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH (V/V 1:1). The solution was dipped into 400mg acetylene black powder. The solid mixture was roll-pressed into a 200 μm thick membrane. The membrane

was heated from room temperature to 280 °C with a rate of 2°C /min and maintained at 280 °C for 40 min, then cooled to room temperature naturally. The gas released by decomposition of  $\text{NH}_4\text{NO}_3$  created the porous structure in the membrane. The porous membrane was pressed with a nickel foam substrate as current collector at 10 MPa for 30s. This obtained cathode was labeled as ORC.

The mixing, roll-pressing in preparation of Ag-ORC was same as that in preparing ORC, except for using 120mg silver nitrate instead of 100mg ammonium nitrate. By thermal treatment,  $\text{AgNO}_3$  in the membrane change to  $\text{AgO}$ , and the released gases made the porous structure. After being pressed with a piece of ORC, the prototype electrode was cathodically polarized at -0.7V (vs. SCE) in 2M KOH for 10min, so that  $\text{AgO}$  in it changed to Ag particles, and an Ag-ORC was finished.

### 3. Cyclic voltammetry and Polarization test.

Electrochemical measurement, such as cyclic voltammetry (CV), potentiodynamic and potentiostatic polarization was carried out with an Electrochemistry Workstation (PARSTAT2273) in a conventional three-electrode system. A platinum plate (1.0cm ×1.0cm) was used as a counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. A saturated potassium chloride salt bridge was placed between the reference electrode solution and the cell. All solution was bubbled with nitrogen before electrochemical tests.

Cyclic voltammetry, potentiodynamic and potentiostatic polarization were carried out with an Electrochemistry Workstation (PARSTAT2273) in a conventional

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A platinum plate ( $2\text{mm}\times 5\text{mm}$ ) electrode was used as the working electrode in cyclic voltammetry at  $25^\circ\text{C}$ . ORC and Ag-ORC were used as working electrode in Potentiodynamic cathodic polarization at  $70^\circ\text{C}$ . Pt/Ti,  $\text{IrO}_2/\text{Ti}$ -,  $\text{RuO}_2/\text{Ti}$  were used as working electrode in Potentiodynamic anodic polarization at  $70^\circ\text{C}$ .

All solution was bubbled with nitrogen before electrochemical tests.

#### 4. Electrolysis experiment

The electrolysis method using HEC was tested in a cell separated by ion-exchanged membrane (NEOSEPTA-AMX, Asahi Kasei Chemicals Corporation) with Pt/Ti as cathode and  $\text{RuO}_2/\text{Ti}$  as anode ( $2.5\text{cm}\times 4.0\text{cm}$ ). The anolyte (50ml) was the mixed solution of 1M KI and 2M KOH, and the catholyte (50ml) was 2M KOH. The anolyte and the catholyte were pre-heated to  $70^\circ\text{C}$ , and circular flowed in rate of  $5\text{ml min}^{-1}$  respectively with the help of a pump, and before the anolyte being returned to the cell it was cooled down to lead  $\text{KIO}_3$  crystallize.

The electrolysis method using ORC or Ag-ORC was tested in a single-compartment cell with  $\text{RuO}_2/\text{Ti}$  as anode. The electrolyte (50ml) was the mixture solution of 1M KI and 2M KOH. Oxygen was continuously introduced into oxygen cathode gas chamber during the electrolysis. The electrolyte was pre-heated to

70°C, and circular flowed in rate of 5ml·min<sup>-1</sup> with the help of a pump, and before returning to the cell the electrolyte was cooled down to lead KIO<sub>3</sub> crystallize.

The yield for the production of KIO<sub>3</sub> was calculated as following (Eq. 1),

$$Y = \frac{n_{KIO_3, produced}}{n_{KI, initial}} \times 100\% = \frac{\frac{m_{KIO_3, powder}}{M_{KIO_3}} + c_{IO_3^-} \cdot V}{n_{KI}} \times 100\% \quad \text{Eq. 1}$$

Where  $n_{KI, initial}$  is the input amount of KI (that is 0.05mol in this study),  $n_{KIO_3, produced}$  is the amount of the produced KIO<sub>3</sub>, which is the addition of the crystallized KIO<sub>3</sub> powder and the remaining IO<sub>3</sub><sup>-</sup> in the electrolyte. The KIO<sub>3</sub> precipitation was washed by ice-water, and then the KIO<sub>3</sub> was dried at 80°C for two hours. The quantity of KIO<sub>3</sub> in precipitation and the concentration of IO<sub>3</sub><sup>-</sup> in the final electrolyte solution were determined by the iodometric titration method.<sup>1</sup>

In this study, only 90% of the electric quantity needed for 0.05mol KI transforming to KIO<sub>3</sub> was applied in the electrolysis tests, that is to say, the theoretical yield for KIO<sub>3</sub> is only 90%.

Current Efficiency (CE) was defined as the ratio of the practical amounts of KIO<sub>3</sub> to theoretical amounts of KIO<sub>3</sub>, which was calculated by Eq. 2.

$$CE = \frac{Q_{consumed, KIO_3}}{Q_{applied}} \times 100\% = \frac{n_{produced KIO_3} \cdot Z \cdot F}{Q_{applied}} \times 100\% \quad \text{Eq. 2}$$

Where Z is 6, the number of the transferred electrons for I<sup>-</sup> transforming to IO<sub>3</sub><sup>-</sup>,  $F=96485C \cdot mol^{-1}$ .  $Q_{applied}$  equals to 26051C calculated by Eq.3

$$Q_{\text{applied}} = 90\% \times Q_{\text{t}} = 90\% \times n_{\text{KI, initial}} ZF \quad \text{Eq. 3}$$

## 5. Legends of Figures and lists of Tables

**Fig.S1** Cyclic Voltammetry data for KI in alkaline media

**Fig.S2** Surface morphology of Ag-ORC

**Fig.S3** Potentiostatic cathodic polarization tests of Ag-ORC

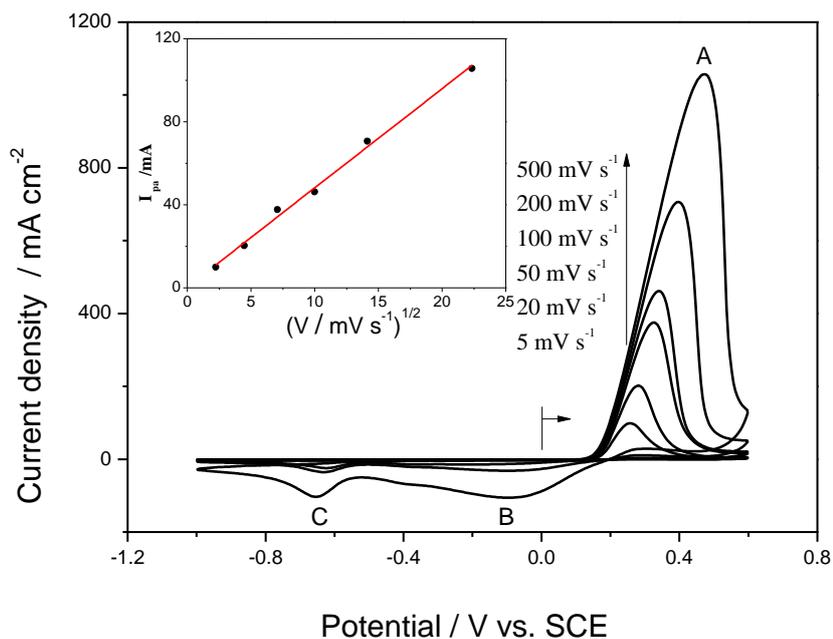
**Fig.S4** Potentiostatic cathodic polarization tests of ORC

**Fig.S5** Potentiodynamic anodic polarization of DSAs

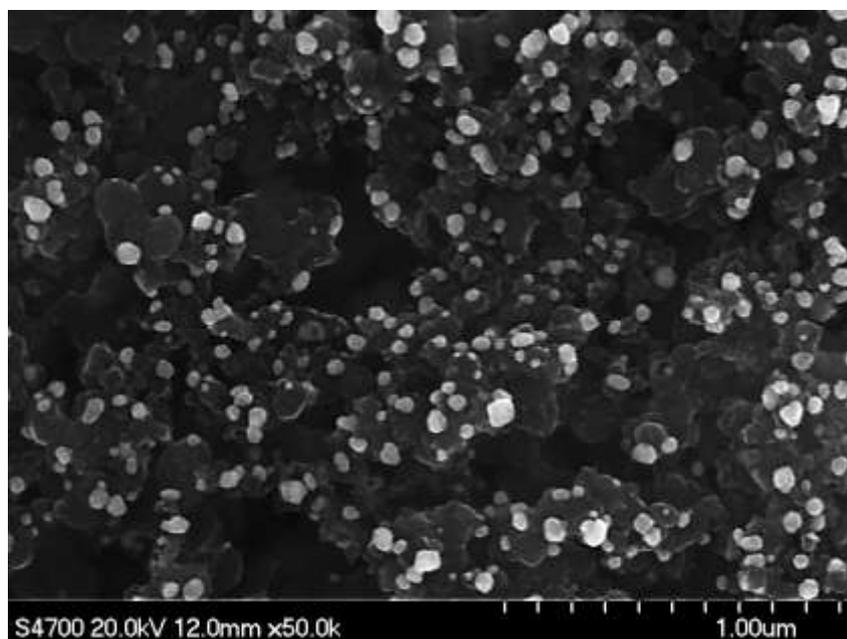
**Tab.S1** Electrolysis test of DSAs coupling with Ag-ORC

**Tab.S2** Electrolysis test at different temperature

**Tab.S3** The comparison of three methods for producing  $\text{KIO}_3$

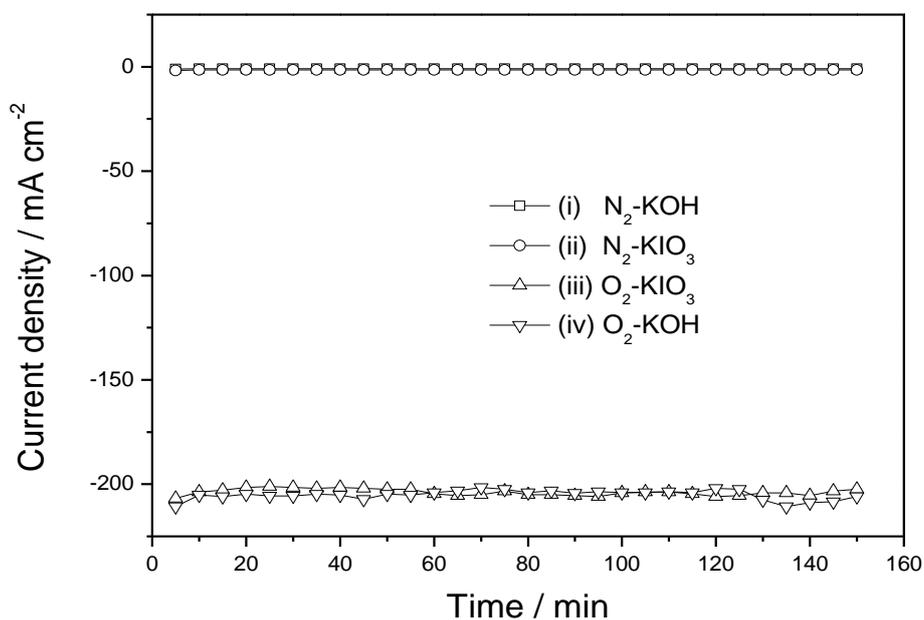


**Fig. S1** Cyclic voltammograms recorded in alkaline KI medium on Pt electrode at different scan rates from 5~500 mV s<sup>-1</sup>, temperature 25°C, electrolyte 1M KI and 2M KOH. The inset shows the relationship between  $I_{pa}$  and  $v^{1/2}$ .

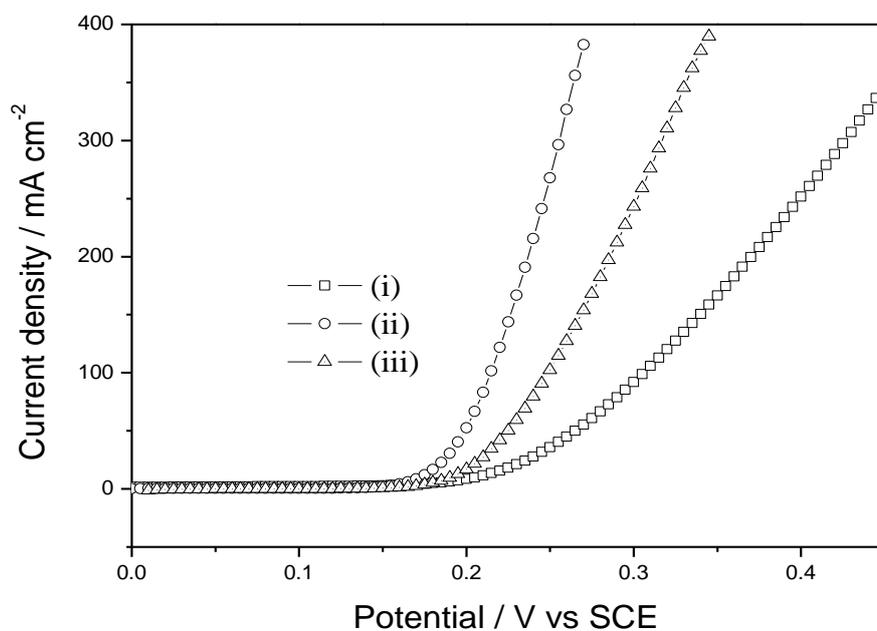


**Fig. S2** SEM images of Ag-ORC.

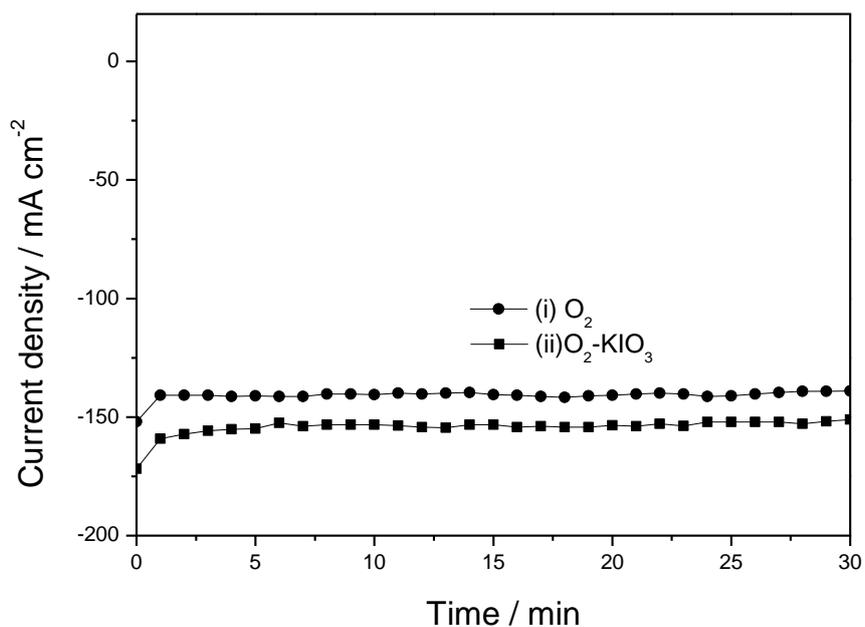
The morphology of the as-prepared Ag-ORC electrode was observed by a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 20.0 kV.



**Fig. S3** The Potentiostatic cathodic polarization curves of Ag-ORC immersed in 2M KOH at -0.33V. (i) in N<sub>2</sub> atmosphere, (ii) in N<sub>2</sub> atmosphere and 0.17M KIO<sub>3</sub>, (iii) in O<sub>2</sub> atmosphere and 0.17M KIO<sub>3</sub>, (iv) in O<sub>2</sub> atmosphere. Temperature 70 °C.



**Fig. S4** The Potentiostatic cathodic polarization curves (scan rate of 5mV/s) on DSAs immersed in 2M KOH in the presence of 1M KI and 0.17M KIO<sub>3</sub>. DSAs including: (i) IrO<sub>2</sub>/Ti, (ii) Pt/Ti, and (iii) RuO<sub>2</sub>/Ti. Temperature: 70 °C.



**Fig. S5** The Potentiostatic cathodic polarization curves of Ag-ORC immersed in 2M KOH at -0.61V, (i) in  $O_2$  atmosphere, (ii) in  $O_2$  atmosphere and 0.17M  $KIO_3$ . Temperature  $70^\circ C$

As shown by curve (i) in Fig S5, in absence of  $KIO_3$ , the current density due to reduction of  $O_2$  was nearly  $140 \text{ mA}\cdot\text{cm}^{-2}$ , while the current density achieved to  $154 \text{ mA}\cdot\text{cm}^{-2}$  in the presence of  $IO_3^-$  in electrolyte. And the extra current density was due to the reduction of  $IO_3^-$ , meaning that  $IO_3^-$  was produced on anode at current density of  $150 \text{ mA}\cdot\text{cm}^{-2}$  and simultaneously being reduced on ORC cathode at  $14 \text{ mA}\cdot\text{cm}^{-2}$ . As a result, the CE decreased by nearly 10% when the concentration of  $IO_3^-$  was 0.17M. And the concentration of  $IO_3^-$  was about 0.4M at the end period of electrolysis test, so the CE decreased to 79.7%.

### Electrolysis effects of different DSAs

Tab. S1 summarizes the electrolysis results by using different anodes but the same cathode of Ag-ORC. The cell voltage of Pt/Ti and  $RuO_2$ /Ti are lower than 0.72V,

and the CE of both are higher than 95%. The results are accords with the anodic potentiodynamic polarization (see Fig. S4). Which shows that RuO<sub>2</sub> and Pt are both more effective than IrO<sub>2</sub> for electro-oxidation of I<sup>-</sup>. Considering the cost and properties, we chose RuO<sub>2</sub>/Ti as the proper anode.

**Tab. S1** Electrolysis effects of different DSAs

NO.	Cathode	Anode	Average Cell Votalge (V)	CE (%)	Yield (%)
1		IrO <sub>2</sub> /Ti	0.791	87.9	79.1
2	Ag--ORC	Pt/Ti	0.698	95.9	86.3
3		RuO <sub>2</sub> /Ti	0.716	96.3	86.7

<sup>a</sup>  $j=150\text{mA/cm}^2$ , Temperature 343K, electrode area 10 cm<sup>2</sup>, electrode gap 2mm, electrolysis time 4.82h.

### Electrolysis effects at different Temperature.

The electrolysis at reaction temperature in range of 55 to 90°C was tested. As shown in Tab.S2. The cell voltage decreased obviously when the temperature increased, which can be explained that the diffusion rate of ions and the reaction rates on both of anode and cathode increased due to the higher temperature, which lead to the IR of electrolyte and the overpotential on electrodes decrease.

On the other hand, CE also decreased as the temperature increased (as shown in Tab.1 and Fig 1b), and CE was even lower than 90% at 90°C. Several facts may explain the phenomenon: (1) the produced IO<sub>3</sub><sup>-</sup> became easier to be reduced on cathode due to higher diffusion rate and reaction rate; (2) the side reaction on anode, *i.g.* oxygen evolution became more obviously at higher temperature.

Considering the effect of the reaction temperature on both of the cell voltage and CE, 70°C was chosen as the proper one.

**Tab.S2** Electrolysis effects at different Temperature.

No.	temperature °C	Average Cell Voltage (V)	Current efficiency (%)	Yield (%)
1	55	0.865	95.9	86.3
2	60	0.819	96.8	87.1
3	70	0.716	96.3	86.7
4	80	0.687	93.4	84.1
5	90	0.674	88.7	79.8

In the single-compartment cell with Ag-ORC as the cathode and RuO<sub>2</sub>/Ti as the anode, temperature 70°C,  $j=150\text{mA cm}^{-2}$ , electrode area  $10\text{cm}^2$ , electrode spacing 2mm.

### The comparison of three methods for producing KIO<sub>3</sub>

Based on the references<sup>2, 3</sup> and the theoretical calculation, the comparison among the three methods for producing KIO<sub>3</sub>, namely chemical oxidation, electrolysis using HEC and electrolysis using ORC was summarized in Tab.1.

**Tab.S3** The comparison of three methods for producing KIO<sub>3</sub>

Processes	Reaction equation	Yield * (%)	Oxidant /current efficiency	Oxidant /electricity for 1t KIO <sub>3</sub>
Chemical oxidation**	$11\text{KClO}_3 + 3\text{H}_2\text{O} + 6\text{I}_2 \xrightarrow{\text{H}^+ 70-90^\circ\text{C}} 6\text{KH}(\text{IO}_3)_2 + 5\text{Cl}_2\uparrow + 3\text{KCl}$ $\text{KH}(\text{IO}_3)_2 + \text{KOH} \rightarrow 2\text{KIO}_3 + \text{H}_2\text{O}$	~90	~90%	580kg KClO <sub>3</sub>
Electrolysis Using HEC	$\text{KI} + 6\text{H}_2\text{O} \xrightarrow{\text{electricity OH}^- 60-80^\circ\text{C}} \text{KIO}_3 + 3\text{H}_2\uparrow$	~87	~97%	1700Kwh
Electrolysis Using ORC	$2\text{KI} + 3\text{O}_2 \xrightarrow{\text{electricity OH}^- 60-80^\circ\text{C}} 2\text{KIO}_3$	~86	~96%	560Kwh

\* The yield for KIO<sub>3</sub> by chemical oxidation is obtained by adding stoichiometric or more amount of KClO<sub>3</sub>, while the yields for KIO<sub>3</sub> by both electrolysis processes are obtained when only 90% of theoretical electric quantity is applied. \*\* I<sub>2</sub> is the main form in acidic media, while I<sub>2</sub> transfer to KI and KIO<sub>3</sub> spontaneously in basic media. In order to distinguish the reactants, pure KI is used as initial reactants in basic media.

## Reference

1. W. Horwitz, A. Senzel, H. Reynolds and D. Park, *Official methods of analysis of the Association of Official Analytical Chemists*, AOAC, 1975.
2. Y. W. Zhang, and A. M. Wang, *China well and salt*, 2008, **198**, 13-14
3. Z. S. Yang, *Inorganic chemicals industry (Chinese)*, 1999, **31**, 23-25.