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Energy-saving synthesis of potassium iodate *via* electrolysis of potassium iodine and O_2 in a membraneless cell†

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An electrochemical process for producing potassium iodate based on oxidation of KI coupled with oxygen reduction reaction in a newly designed cell is reported. By using an Ag-modified oxygen reduction cathode, the proposed cell needed no ion exchange membrane, and the current efficiency for KIO_3 was confirmed to be over 96%, the corresponding cell voltage was only 0.7–0.8 V.

Potassium iodate (KIO_3) is used as an iodizing additive in salt[1,2] as well as the additive in other foods[3] and a primary standard substance in redox titration.[4] KIO_3 can be synthesized through chemical oxidation of KI (or I_2) by oxidants such as potassium chlorate, nitric acid or hydrogen peroxide.[5,6] Strongly acidic medium is necessary for these oxidants to display high oxidizing ability, but I_2 is easily lost in acidic solution, which makes the yield of IO_3^- decrease. Moreover, the chemical waste due to oxidant causes environment pollution.

Electrochemical approaches, which are able to avoid using hazardous compounds and media,[7–9] tune the potential or electro-catalyst for the required reaction,[10,11] and decrease the chemical waste,[12–14] have been widely investigated in green synthesis recently. Electrochemical synthesis of KIO_3 has been applied[15,16] in which the oxidation of KI is coupled with hydrogen evolution on the cathode (that is, hydrogen-evolution cathode (HEC), such as Pt, Ni, RuO_2, *etc.*). An ion exchange membrane (see Fig. 1(a)) must be installed in the cell, because the produced IO_3^- on the anode may diffuse to the cathode to be reduced again. However, an ion exchange membrane is not only expensive, but also easy to be fouled due to the precipitation of metal iodate. Moreover, the voltage of this method is reported to be higher than 2.0 V, leading to high energy consumption.

In this paper we report a simple and energy-saving process for electrochemical synthesis KIO_3 from O_2 and KI, which uses an oxygen reduction cathode (ORC) in a membraneless cell, with corresponding cell voltage of only 0.7–0.8 V. The schematic diagrams of the HEC cell and the ORC cell are shown in Fig. 1.

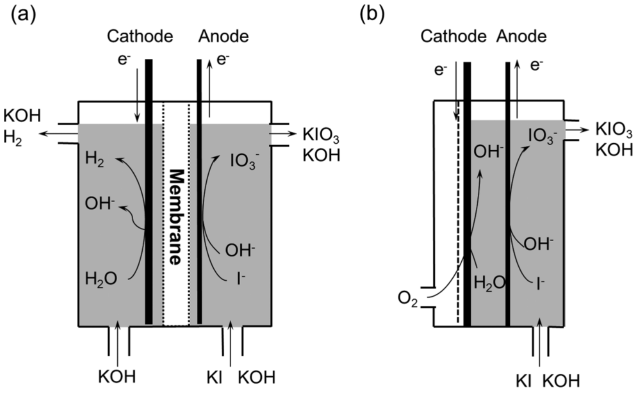

Fig. 1 The schematic diagrams of the electrochemical cells for (a) using a hydrogen evolution cathode, and (b) using an oxygen-reduction cathode.

In order to explain why an ion-exchange membrane is needed in the electrolytic cell using HEC, the oxidation of KI and reduction of KIO_3 were studied by cyclic voltammetry on a Pt plate electrode (2 mm × 5 mm) to establish the reaction mechanism. Fig. 2 shows the cyclic voltammograms (CVs) obtained in alkali medium for (i) the oxidation of I^-, (ii) the reduction of IO_3^-, and (iii) the oxidation of I^- and the reduction of IO_3^-, (iv) the oxygen and hydrogen evolution without I^- or IO_3^-.

The strong anodic peaks in range of 0.15–0.6V (*vs.* SCE, same below) are attributed to the oxidation of I^-. The peak currents are linear with the square root of the potential scan rate (Fig. S1, ESI†), indicating that the electrochemical oxidation of I^- is limited by diffusion. Since there is only one anode peak and its current density is much stronger than those of cathode peaks in curve (i), the reaction path from I^- to IO_3^- is deduced that the electrochemical-chemical (E-C) model[17,18] is more predominant to the direct six-electron-transfer path[19] (as shown in eqn (1)). That is, I^- is more likely oxidized to I_2 on anode through two-electron-transfer path followed by disproportionation of I_2 to form I^- and IO_3^-.

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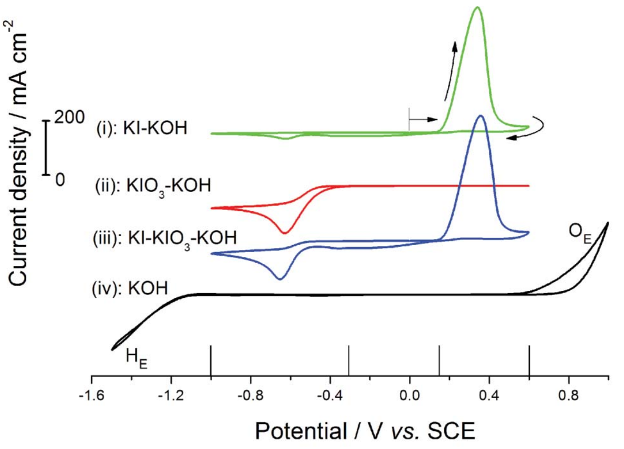

Fig. 2 Cyclic voltammograms obtained on a platinum electrode in 2 M KOH for (i) 1 M KI, (ii) saturated KIO_3, (iii) 1 M KI and saturated KIO_3, (iv) without KI and KIO_3. Scan rate of 100 mV s^{-1}, temperature 25 °C.

$$6I^- \xrightarrow{-6e^-} 3I_2 \xrightarrow{+6OH^-} IO_3^- + 5I^- + 3H_2O \qquad \text{(predominant)}$$
$$6I^- \xrightarrow{-6e^- +6OH^-} IO_3^- + 5I^- + 3H_2O \qquad (1)$$

The fact that oxygen evolution occurs at a potential more positive than that of I^- oxidation means that the anodic current efficiency for producing KIO_3 would be satisfied.

The weak and wide cathodic peaks in range of –0.3–0.15 V are attributed to the reduction of intermediate of I_2. Because the disproportionation of I_2 is rapid in alkaline medium, the reduction peak of I_2 to I^- (B, –0.2 V) can only be observed at high scan rate (Fig. S1†).

The cathodic peaks in range from –0.85 to –0.3 V are attributed to the reduction of IO_3^-. Since hydrogen evolution occurs at the potential negative than –1.2 V, which is more negative than that of reduction of IO_3^-, the reduction of IO_3^- is preferential to hydrogen evolution. So if IO_3^- diffuses to the surface of HEC, it is destined to be reduced. That is just the reason why an ion exchange membrane is necessary in electrochemical cells using HEC.

Oxygen reduction cathodes (ORCs) are the electrodes on which oxygen is able to be reduced to H_2O_2 or OH^-. Besides the application of ORC in fuel cells,[20,21] ORCs have been tried to use in chlor-alkali membrane cell[22,23] to replace HECs, and the cell voltage could reduce from 3.2–3.5 V to 2.1–2.4 V due to the potential of oxygen reduction is higher than that of hydrogen evolution. The porous ORCs used in this study were prepared by thermal treatment of homemade carbon-PTFE paper. Some of the ORCs were modified by Ag particles through *in situ* electrochemical reduction method, labeled as Ag-ORC (for preparation method and the SEM image of Ag-ORC, see ESI, Fig. S2†).

The potentiodynamic cathodic polarization curves of ORC in alkaline medium on N_2 or O_2 atmosphere with or without KIO_3 in solution are shown in Fig. 3a. As shown by curve A4, the cathodic current due to O_2 reduction could be observed when the potential is more negative than –0.35 V, and the current density increases to more than 200 mA cm^{-2} at the potential of –0.65 V. The corresponding current density of the curve recorded in N_2 atmosphere in the presence of IO_3^- (curve A2) is due to the reduction of IO_3^-, which is more than 17 mA cm^{-2} at the potential of –0.65 V. It is inferred that if oxygen is sufficient and the potential of the ORC is controlled in the range of –0.3 to –0.4 V, the reduction of IO_3^- on the cathode would be avoided. However, the corresponding current density in range of 10–20 mA cm^2 is so low that it is uneconomic to do so in practice. Current density due to O_2 reduction increases greatly at more negative potential, while the reduction of IO_3^- also becomes more obvious. For example, the current due to the reduction of IO_3^- is nearly 10% of the total at the potential of –0.65 V.

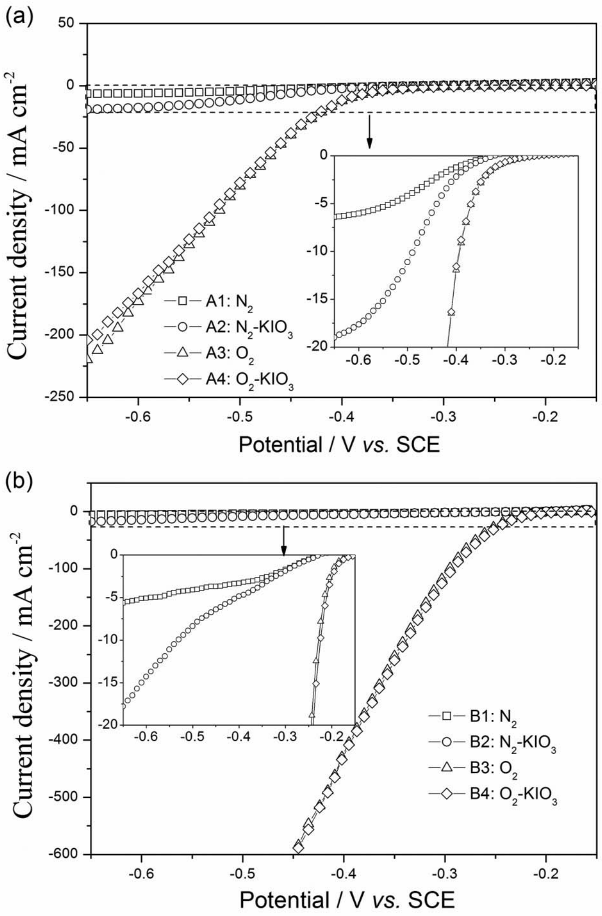

Fig. 3 The potentiodynamic cathodic polarization curves of (a) ORC and (b) Ag-ORC in 2 M KOH. A1 and B1: in N_2 atmosphere, A_2 and B_2: in N_2 atmosphere and 0.17 M KIO_3, A3 and B3: in O_2 atmosphere and 0.17 M KIO_3, A4 and B4: KOH in O_2 atmosphere. scan rate 5 mV s^{-1}, temperature 70 °C.

The reduction of IO_3^- on cathode could be further decreased if an Ag-ORC was used. As shown in Fig. 3b, the cathodic current due to the reduction of O_2 on Ag-ORC could be observed when the potential was –0.2 V, and the current density increased to 200 mA cm^{-2} even at –0.33 V, which can be explained that the overpotential of the electrode reaction of O_2 to OH^- on Ag-ORC decreased greatly.[23,24] While the current density due to the reduction of IO_3^- at –0.33V was only 1–2 mA cm^{-2}, which means the ratio of IO_3^- reduction current to the total reductive current

Table 1 Electrochemical oxidation of KI to produce KIO_3 by coupling with different cathodes

No	Cathode	Anode	Average cell voltage (V)	CE (%)	Yield[c] (%)
1	HEC[a]	RuO_2/Ti	2.185	96.7	87.0
2	ORC[b]		0.992	79.5	71.6
3	Ag-ORC[b]		0.716	96.3	86.7

[a] The cell using HEC was two-compartment cell divided by membrane. [b] The cell using ORC and Ag-ORC was single-compartment cell without membrane. [c] All electrolysis tests were conducted until 90% of the theoretical electric quantity was applied, so the value of the theoretical yield of KIO_3 is 90%. Temperature 70 °C, $j = 150$ mA cm^{-2}, electrode area: 2.5 cm × 4.0 cm, electrode spacing 2 mm.

was only about 1%. This was also confirmed by the potentiostatic polarization tests at the applied potential of –0.33 V (Fig. S3†). So if KIO_3 is produced in a cell using an Ag-ORC, the membrane could be abandoned as well as the cell voltage is lowered greatly.

To verify the above results, electrochemical synthesis of KIO_3 was carried out in laboratory scale (for electrolysis details, see ESI†). KIO_3 crystalline was obtained by cooling down the electrolyte, and the filtrate was recycled to the cell. The difference between HEC and ORC was demonstrated by coupling with the same anode (RuO_2/Ti; for information about other DSAs, see Fig. S4 and Table S1†) as shown in Table 1. The average cell voltage of a membrane cell using HEC was 2.185 V, while the cell voltage of a single-compartment electrolytic cell using ORC was 0.992 V, and even 0.716 V if an Ag-ORC was used. As for current efficiency (CE), since the reduction of IO_3^- was avoided efficiently by employing ion-exchange membrane, the CE in the cell with HEC could reach 96.7%. In the cell using ORC, CE decreased to 79.5% owing to the reduction of IO_3^- (see Fig S5†). However, the CE was improved to 96.3% by using Ag-ORC, because the overpotential of O_2 reduction was decreased obviously in the presence of Ag particles.

The effects of current density on CE are summarized in Table 2. As current density increased, the cell voltage raised and the CE decreased. It can be explained that the CE on both anode and cathode decreased at larger current density because the competitive reaction of oxygen evolution and the reduction of IO_3^- becomes more significant. Considering the high space-time yield obtained at higher current density, a current density of 150 to 200 mA cm^{-2} is a proper choice.

It is noticed that the accumulation of nano-silver particles leads the deterioration of Ag-ORC after dozens of electrolysis tests. But except for this disadvantage, three major advantages of the proposed process in relation to the challenges of green chemistry are summarized as follows:

(i) Energy-saving: the cell voltage of the proposed electrolysis method is only 0.7–0.8V that is 60–65% less than that of traditional electrolysis method.

(ii) Green and safe chemical: potassium iodate is produced by electrolysis of potassium iodine and O_2 without byproducts, which is also atom economic.

(iii) Improved equipment: the electrolysis cell needs no membrane to separate anode and cathode compartment.

These advantages are also great benefits for the application of a laboratory advance to the larger scale.

Table 2 Electrolysis effects of different current density

No.	Current density (mA cm^{-2})	Time (h)	Average cell voltage (V)	CE (%)	Yield (%)
1	100	7.24	0.654	97.1	87.4
2	150	4.82	0.716	96.3	86.7
3	200	3.62	0.778	95.4	85.9
4	250	2.89	0.863	88.9	80.0

In the single-compartment cell with Ag-ORC as the cathode and RuO_2/Ti as the anode, other conditions were the same as mentioned in Table 1.

Conclusions

In summary, a green and economic electrochemical synthesis of KIO_3 is reported in which the catalyzed oxygen reduction is designed to couple with the oxidation of KI to KIO_3. Ion exchange membrane is avoided in proposed cell with Ag-ORC, and the current efficiency for KIO_3 was confirmed to be over 96%, the corresponding cell voltage was only 0.7–0.8 V. This process is energy saving, atom economic, and environmental friendly.

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