Energy-saving synthesis of potassium iodate via electrolysis of potassium iodine and \( \text{O}_2 \) 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 KIO₃ was confirmed to be over 96%, the corresponding cell voltage was only 0.7–0.8 V.

Potassium iodate (KIO₃) is used as an iodizing additive in salt as well as the additive in other foods and a primary standard substance in redox titration. KIO₃ can be synthesized through chemical oxidation of KI (or I₂) by oxidants such as potassium chlorate, nitric acid or hydrogen peroxide. Strongly acidic medium is necessary for these oxidants to display high oxidizing ability, but I₂ is easily lost in acidic solution, which makes the yield of IO₃⁻ decrease. Moreover, the chemical waste due to oxidant causes environment pollution.

Electrochemical approaches, which are able to avoid using hazardous compounds and media, tune the potential or electro-catalyst for the required reaction, and decrease the chemical waste, have been widely investigated in green synthesis recently. Electrochemical synthesis of KIO₃ has been applied in which the oxidation of KI is coupled with hydrogen evolution on the cathode (that is, hydrogen-evolution cathode (HEC), such as Pt, Ni, RuO₂, etc.). An ion exchange membrane (see Fig. 1(a)) must be installed in the cell, because the produced IO₃⁻ 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 KIO₃ from O₂ 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.

In order to explain why an ion-exchange membrane is needed in the electrolytic cell using HEC, the oxidation of KI and reduction of KIO₃ 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 IO₃⁻, and (iii) the oxidation of I⁻ and the reduction of IO₃⁻, (iv) the oxygen and hydrogen evolution without I⁻ or IO₃⁻.

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 IO₃⁻ is deduced that the electrochemical-chemical (E-C) model is more predominant to the direct six-electron-transfer path (as shown in eqn (1)). That is, I⁻ is more likely oxidized to I₂ on anode through two-electron-transfer path followed by disproportionation of I₂ to form I⁻ and IO₃⁻.

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Cyclic voltammograms obtained on a platinum electrode in 2 M KOH for (i) 1 M KI, (ii) saturated KIO₃, (iii) 1 M KI and saturated KIO₃, (iv) without KI and KIO₃. Scan rate of 100 mV s⁻¹, temperature 25 °C.

The fact that oxygen evolution occurs at a potential more positive than that of I⁻ oxidation means that the anodic current efficiency for producing KIO₃ 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 I₂. Because the disproportionation of I₂ is rapid in alkaline medium, the reduction peak of I₂ 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 IO₃⁻. Since hydrogen evolution occurs at the potential negative than −1.2 V, which is more negative than that of reduction of IO₃⁻, the reduction of IO₃⁻ is preferential to hydrogen evolution. So if IO₃⁻ 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 H₂O₂ or OH⁻. Besides the application of ORC in fuel cells, ORCs have been tried to use in chlor-alkali membrane cell 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 N₂ or O₂ atmosphere with or without KIO₃ in solution are shown in Fig. 3a. As shown by curve A4, the cathodic current due to O₂ 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 N₂ atmosphere in the presence of IO₃⁻ (curve A2) is due to the reduction of IO₃⁻, 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 IO₃⁻ 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 O₂ reduction increases greatly at more negative potential, while the reduction of IO₃⁻ also becomes more obvious. For example, the current due to the reduction of IO₃⁻ is nearly 10% of the total at the potential of −0.65 V.

The reduction of IO₃⁻ 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 O₂ 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 O₂ to OH⁻ on Ag-ORC decreased greatly. While the current density due to the reduction of IO₃⁻ at −0.33 V was only 1–2 mA cm⁻², which means the ratio of IO₃⁻ reduction current to the total reductive current of −0.65 V.
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 KIO₃ 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 KIO₃ was carried out in laboratory scale (for electrolysis details, see ESI†). KIO₃ 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 (RuO₂/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 cell voltage of a single-compartment electrolytic cell using ORC, because the overpotential of O₂ reduction was decreased greatly.

The effects of current density on CE are summarized in Table 2. As current density increased, the cell voltage raised obviously in the presence of Ag particles. 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 0.7–0.8 V that is 60–65% less than that of traditional electrolysis method.

(ii) Green and safe chemical: potassium iodate is produced by electrolysis of potassium iodide and O₂ 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.

Conclusions

In summary, a green and economic electrochemical synthesis of KIO₃ is reported in which the catalyzed oxygen reduction is designed to couple with the oxidation of KI to KIO₃. Ion exchange membrane is avoided in proposed cell with Ag-ORC, and the current efficiency for KIO₃ 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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References