Int. J. Electrochem. Sci., 10 **(2015)** 6422 - 6432

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Synthesis of Periodate Combined with Indirect Oxidation of Chlorine on RuO_x/Ti Electrode

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Received: 2 May 2015 / *Accepted:* 23 May 2015 / *Published:* 24 June 2015

This study investigated a cyclic electrochemical synthesis method of periodate using RuO_x/Ti electrode as the anode and in analyte containing NaOH and NaCl. Scanning electron microscopy (SEM) images have shown that crystal nucleus of periodate were formed and evenly distributed on the surface of RuO_x/Ti electrode by pretreatment. The main product of $NaIO_4$ was generated by direct oxidation on anodic surface and indirectly oxidizing with the chlorine / hypochlorite in anodic chamber. A reaction mechanism among oxygen, chlorine and periodate formation on RuO_x/Ti electrode in alkali electrolyte has been proposed. In addition, single-factor assay revealed that the optimal current density and concentration of NaCl were 80 $mA.cm^{-2}$ and 0.05 $mol.L^{-1}$, respectively. Galvanostatic electrolyses and voltammetric experiments were carried out and indicated that the percent of conversation was as high as 85% and correspondingly the electrical energy consumption was saved up to 9.1% as compared to electrolysis in acid solution. Moreover, it was found that the cyclic electrolysis technique with flowing solution has avoided the corrosion of RuO_x/Ti electrode, decreased the energy consumption by the crystal deposition of periodate and increased the yield of space-time.

Keywords: RuO_x/Ti electrode; Periodate; Indirect oxidation; Alkaline-chlorination process; Cyclic system.

1. INTRODUCTION

Periodate is widely used in organic and bioorganic chemistry due to its strong oxidizability [1-4]. It is applied to oxidize vicinal diol to dialdehyde in organic phase with phase transfer catalysis [5-

7], where it is reduced to iodate and regenerated by electrochemical and chemical methods [8-11]. Electrochemical method is generally preferred than chemical method due to the high energy efficiency, ease of operation, a fast reaction rate and environmental compatibility. In contrast, chemical method is dangerous and toxic which requires the use of massive chlorine in concentrated alkaline solution[12].

In electrochemical process, various anode materials such as lead dioxide (PbO_2) electrode, boron-doped diamond (BDD) electrode and dimensionally stable anode (DSA, e.g. RuO_x / Ti or RuO_x-IrO_x / Ti) were investigated[13]. Among them, PbO_2 anode is the most attractive electrode due to its high oxygen evolution over-potential, low cost, excellent electrocatalytic performance, and good corrosion resistance in electrochemical oxidation process[14-16]. However, it was found that under high oxidation potential a few amount of mud was formed causing an increase of the energy consumption and product pollution[17]. Although the electrochemical lifetime of BDD electrode is larger than PbO_2 anode, BDD electrode is limited due to its high cost [18-20]. In contrast, DSA possessed superior stability and oxidation performance, which has been extensively applied to chlor-alkali industry [21-23].

Previous studies have attempted to combine the direct oxidation on anode with indirect oxidation by chemical reagent which was existed or formed in electrolyte, such as the use of hypochlorite in electrochemical denitrification [24-28] and electrochemical degradation of phenols[29-32]. It is noteworthy that hypochlorite was easily obtained and kept in chlor-alkali industry by chlorine evolution. This study aimed to produce periodate on a pretreated RuO_x / Ti anode by direct electro-synthesis in alkaline solution and by means of synergistic effect of chlorine in a cyclic system. Furthermore, current density and concentration of NaCl were measured so as to obtain the low energy consumption and high yield of periodate.

2. EXPERIMENTAL

2.1 Electrochemical cell

Experiments were carried out in a two-compartment cell with a cation exchange membrane (F6801, Asahi Kasei Chemicals Corporation) as separator, with RuO_x/Ti electrode as the anode and RuO_x- IrO_x /Ti electrode as cathode. The effective areas of both anode and cathode were 5 cm^2. All electrochemical measurements were carried out at 45 °C.

Electrolytes were analytic grade produced by Beijing Chemicals Company and sample preparations were made using deionized water. The solution in anodic compartment was consisted of 0.3 $mol.L^{-1}$ $NaIO_3$ and 1 $mol.L^{-1}$ NaOH while in cathodic compartment was filled with 1 $mol.L^{-1}$ NaOH.

2.2. Morphology characterization

The morphology coupled with an energy-dispersive spectroscope (EDS) of the RuO_x/Ti electrodes was investigated by scanning electron microscope (SEM, Zeiss SUPRA 55 with an accelerating voltage of 20 kV).

2.3. Voltammetric experiment

All electrochemical measurements were performed with an Electrochemistry Workstation (PARSTAT2273). The potentiodynamic anodic polarization test was carried out in a conventional three-electrode system with saturated calomel electrode (SCE) as a reference electrode which was placed in anode cell compartment. The minimum potential of the scanning range was 0.0 V, the maximum potential was 3.0 V and the sweep rate was 50 mV.s^{-1}. The electrolysis test was carried with different constant current density.

2.4. Electrolysis system

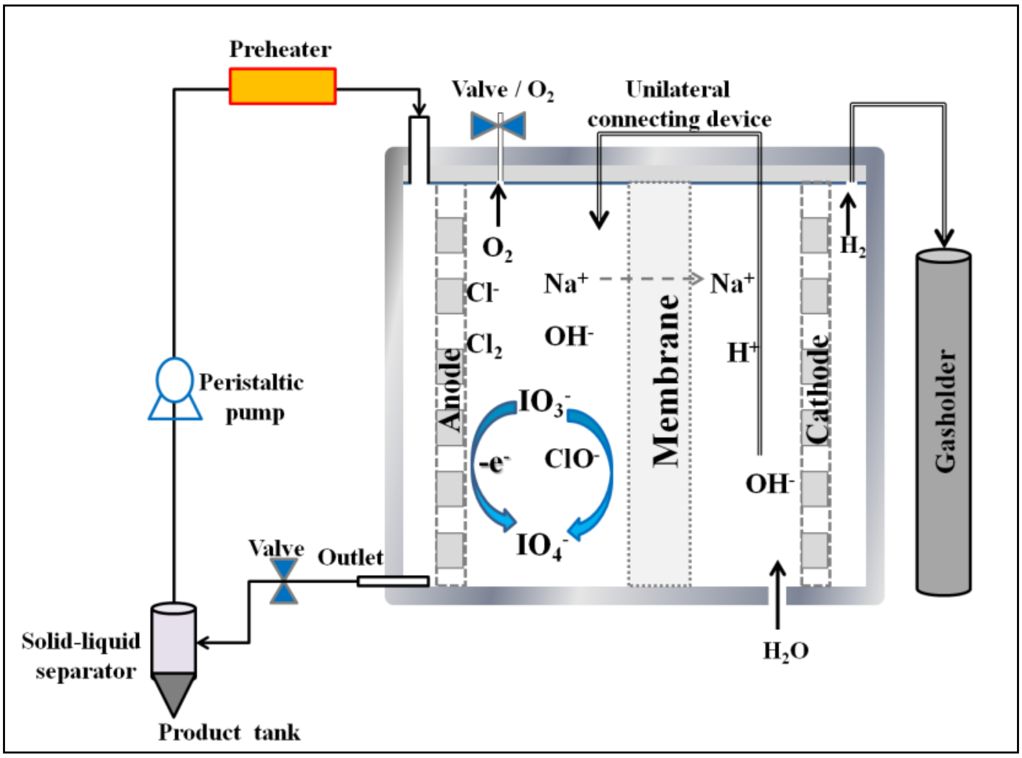


Figure 1. Schematic diagram of electrolysis process

The experimental apparatus and the schematic diagram of the cyclic process for generating periodate are illustrated in Figure 1. Compared to conventional electro-synthesis process with intermittent technique to obtain final products, in our method, only 10 mins was adopted to run and the solution in anodic chamber should be recycled after the separation of periodate and the addition of new solution.

3. RESULTS AND DISCUSSION

3.1 Morphologies and crystal structure of anode with different pretreatments

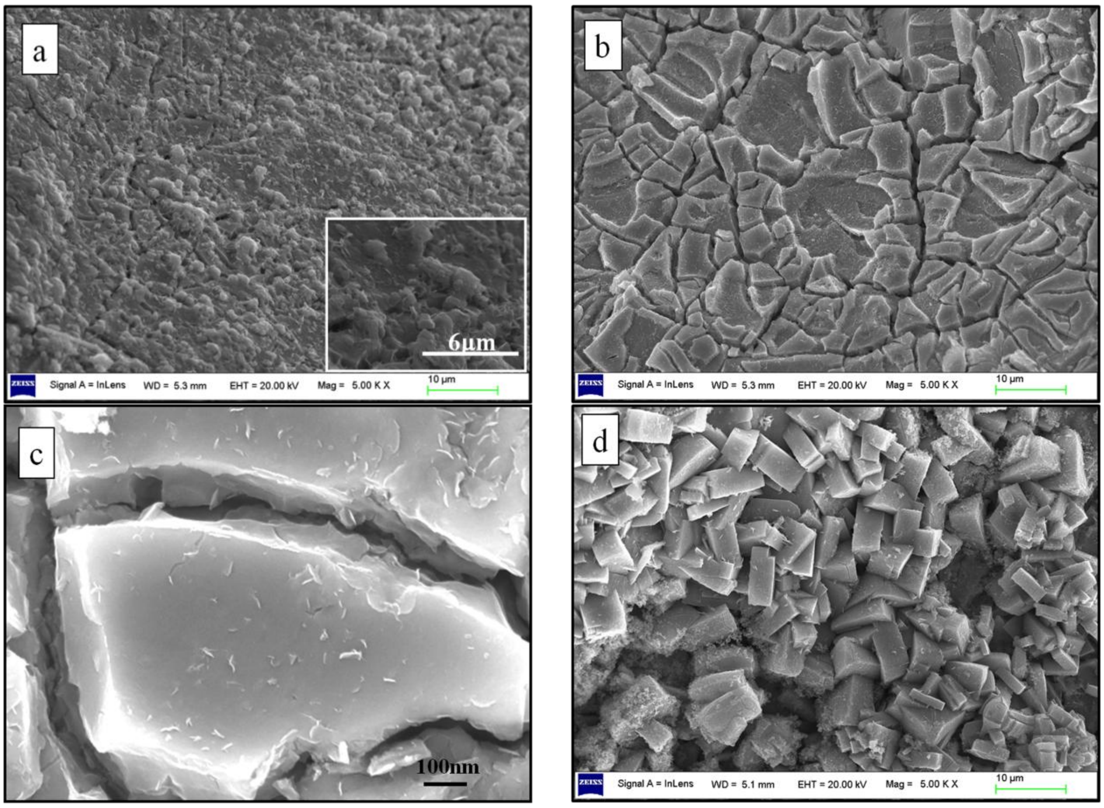


Figure 2. SEM surface images of different RuO_x/Ti electrode. (a) RuO_x/Ti electrode without pretreatment after electrolysis; (b,c) Pretreated RuO_x/Ti electrode before use; (d) RuO_x/Ti electrode with activating pretreatment after electrolysis.

The morphology and structure of RuO_x/Ti electrode can be a major factor in achieving a high discharge capacity. In order to study the influence of pretreatment, the microstructures of RuO_x/Ti anodic layer were examined by SEM technique (at 5000 times scale) as it is described in Figure 2. The SEM reveals that two different kinds of morphologies of RuO_x/Ti electrodes were obtained after electrolysis in the presence of iodate even at the same condition (electrolysis time: 10 mins, current density: 80 $mA.cm^{-2}$) with or without special pretreatment. Furthermore, as shown in Figure 2a, a flat and rough surface was obtained after electrolysis in anolyte but without any pretreatment. However, product of periodate was hardly detected in anolyte due to the low yield of periodate. Coupled with EDS datas also indicated that only trace amount of I element (0.94%, *Seeing in Supporting information*) was adsorbed on the surface of RuO_x/Ti electrode. While a pretreatment was used on RuO_x/Ti electrode at high current density of 120 $mA.cm^{-2}$ in the anolyte without iodate, the surface of RuO_x/Ti electrode became rimous (Figure. 2b). Due to the rimous cavity ranging from 100 nm to 500 nm distributed on the electrode (Figure. 2c), the active working area was significantly improved.

It was clearly seen that the surfaces of RuO_x/Ti electrode was composed of crystal grains of typical cubic shape (Figure. 2d), and EDS spectrums of RuO_x/Ti electrode confirmed that the contents of I element was increased from 0.94% to 9.07% (*Seeing in Supporting information*) by pretreatment. Based on these results, it could be concluded that the RuO_x/Ti electrode was successfully activated by the formation of a nano sized cavity.

3.2. Electrochemical properties in anolyte

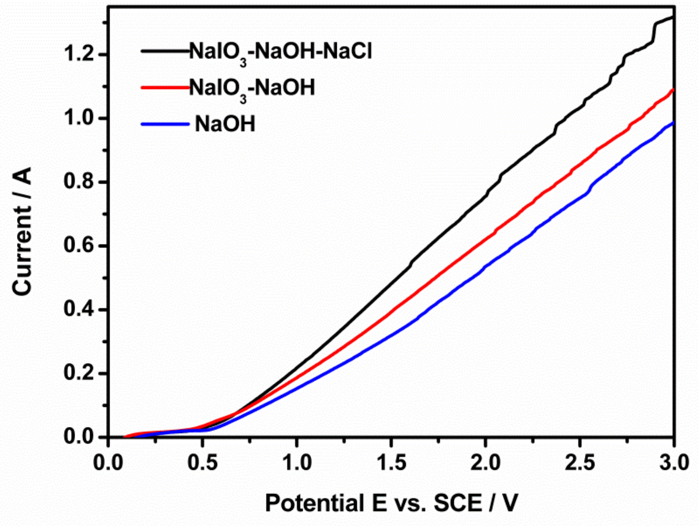


Figure 3. Linear sweep voltammograms of RuO_x/Ti electrode in different electrolytes (NaOH, $NaIO_3$-NaOH and $NaIO_3$-NaOH-NaCl) scaning from 0.2V to 3.0V *vs.* SCE at scan rates of 50 $mV.s^{-1}$

Figure.3 shows the linear sweep voltammograms of RuO_x/Ti electrode in different electrolytes. The curves at high current density between 1.6V to 3.0V have an irregular fluctuation in particular with the addition of NaCl in anolyte, which is caused by the presence of bubbles on the surface of the working electrode.

The main reactions of electrolysis in anode chamber are as follows:

$$H_2O \rightarrow (OH)_{ad} + H^+ + e^- \tag{1}$$

$$(OH)_{ad} \rightarrow (O)_{ad} + H^+ + e^- \tag{2}$$

$$(O)_{ad} \rightleftharpoons O_2 \tag{3}$$

where two arrows indicate a kinetically reversible (i.e. fast) step.

$$IO_3^- + (OH)_{ad} \rightarrow IO_4^- + H^+ + e^- \tag{4}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{6}$$

$$HClO \rightarrow H^+ + ClO^- \tag{7}$$

$$ClO^- + IO_3^- \rightarrow IO_4^- + Cl^- \tag{8}$$

According to the given mechanism, the first step (Eqs.1-3) is the water oxidation which is useless electric energy consumption. In NaOH solution, the fluctuation was due to the oxygen evolution at 2.55V (Eqs.3) and no obvious potential change even after the addition of $NaIO_3$ in the NaOH solution. Moreover, it was found that the addition of $NaIO_3$ increased the current intensity owning to the reaction of Eqs. (4). However, the potential of fluctuation was shifted negatively when NaCl existed in the anolyte on accounting of additional chlorine evolution (Eqs. 5) except oxygen evolution. In the presence of chloride ion during electrolysis, chlorine was formed on the surface of anode (about 1.58 V) and then dissolved in water to produce HOCl with hydrolysis reaction (Eqs.5-7). HOCl is a strong oxidant that oxidized the iodate in anolyte and replenished in the medium with the electrochemical reaction of NaCl. Eqs.8 represents the indirect oxidation of iodate[33], meanwhile, direct oxidation also occurs on the anode (Eqs.4). It is well known that chlorine evolution is more likely to react on RuO_x/Ti electrode than others, and chlorine stably existed as the form of NaClO. So, iodate is easy to be oxidized into periodate on RuO_x/Ti electrode in alkali solution.

3.3. Effects of NaCl dosage and current density on oxidation of iodate

3.3.1 NaCl dosage

Table 1. The additive influnce of NaCl with different concentrations

No.	C (Cl^-) mol.L^{-1}	Yield (%)	Current Efficiency (%)	Average cell voltage (V)	Consumption (Kw . h / Kg)
1	0.00	24.06	19.30	4.18	5.43
2	0.05	35.04	27.81	3.86	3.48
3	0.10	34.66	27.14	3.46	3.20
4	0.20	29.77	24.46	3.68	3.77

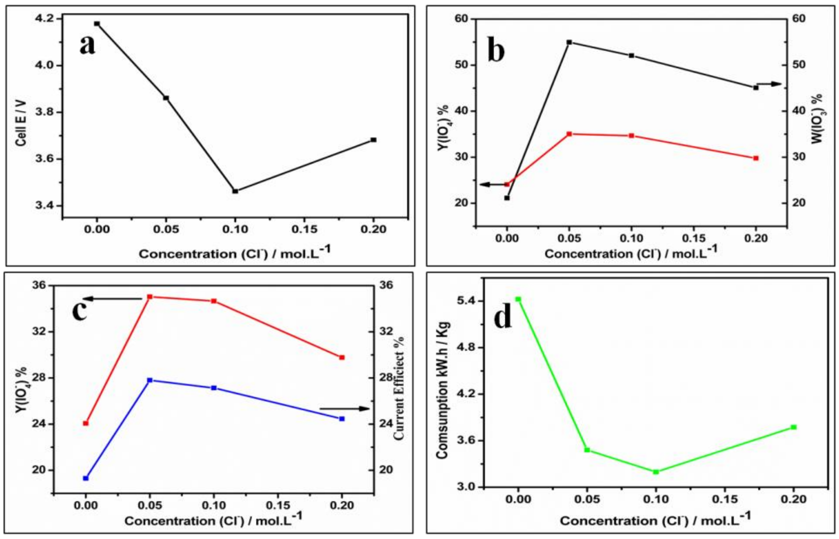


Figure 4. Electrolysis effects of different concentrations of NaCl. (a) cell voltage, (b)yield of IO_4^- and conversion rate of IO_3^-, (c) yield of IO_4^- and current efficiency and (d) electric energy consumption.

As was mentioned previously, NaCl could be oxidized to form a strong oxidant of HOCl, promoting the oxidation reaction and decreasing consumption[22]. As shown in Figure. 4 and Table 1, the cell voltage and consumption decreased with the increasing dosages of NaCl between 0 mol.L^{-1} to 0.1 mol.L^{-1}. With 0.2 mol.L^{-1} NaCl as supporting electrolyte, the redundant bubbles of Cl_2 were obtained but failed to dissolve in alkali anolyte adequately leading to an obvious decrease of the yield and CE. Moreover, the escaped Cl_2 from electrolyzer which is harmful to environmental and human health did also increase the electric energy consumption and accelerated corrosion of electrodes. With 0.05 mol.L^{-1} and 0.1 mol.L^{-1} NaCl as supporting electrolyte for electrolysis about 10 minutes, the phenomenon of bubbles and white solid on anode were easily observed in accordance with the high yield and current efficiency as compared to direct oxidation without NaCl.

3.3.2. Current density

Table 2. Electrolysis effects of different current density

No.	Current density (mA.cm^{-2})	Yield (%)	Current Efficiency (%)	Average cell voltage (V)	Consumption (Kw . h / Kg)
1	60	27.07	24.12	3.53	4.89
2	80	31.58	21.11	3.74	4.44
3	100	31.08	16.62	4.81	5.80
4	120	43.11	19.21	6.08	5.29

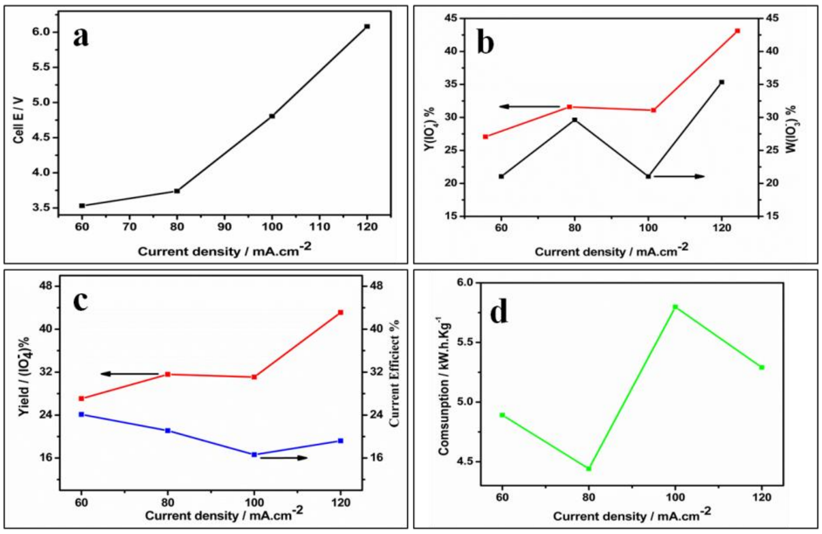


Figure 5. Electrolysis effects of different current density. (a) cell voltage, (b)yield of IO_4^- and conversion rate of IO_3^-, (c) yield of IO_4^- and current efficiency and (d) electric energy consumption.

The effects of the current density on CE, yield, cell voltage and consumption are summarized in Table 2. It is indicated that as the current density increased, the cell voltage raised and the CE decreased (Figure 5). It can be explained that the CE on both anode and cathode decreased at larger current density because the competitive reaction of oxygen, chlorine, hydrogen evolutions and the oxidation of IO_3^- becomes more significant. Considering the high spacetime yield and low consumption, the current density of 80 to 100 mA cm^{-2} is a proper choice (Figure 5). It is noticed that the accumulation of periodate crystals on the surface of anode lead to the increase of the cell voltage and electric energy consumptions after dozens of electrolysis tests. Fortunately, the cyclic system with flowing solution has restrained the growing contents of periodate crystal.

3.4 Applied electrochemical performance

Table 3. The comparison of material or energy consumption of three methods for producing periodate

Methods	Mechanism	Conversation rate / %	Consumption
Chemistry[12]	$NaIO_3 + 4NaOH + Cl_2 \rightarrow Na_3H_2IO_6 + 2NaCl + H_2O$ $Na_3H_2IO_6 + 2HNO_3 \rightarrow NaIO_4 + 2NaNO_3 + H_2O$	62	Equipment corrosion acid, alkali, heat
Electrolysis in acid solution[11]	$NaIO_3 + 2H_2O \rightarrow NaIO_4 + 2H_2\uparrow + 2O_2\uparrow$	42	2946Kw.h / t
Electrolysis in alkali solution and cyclic system	$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2\uparrow + 2H_2\uparrow$ $NaIO_3 + 2H_2O \rightarrow NaIO_4 + 2H_2\uparrow + 2O_2\uparrow$ $NaIO_3 + Cl_2 + NaOH \rightarrow NaIO_4 + NaCl + HCl$	85	2700Kw.h / t

To questions and disadvantages of conventional process, three major advantages of the proposed system in this study are summarized in Table 3. Compared to chemical process using amounts of concentrated acid, alkali and heat, a green and safer way was applied to produce periodate by electrolysis of iodate and HClO which is formed by dissolving Cl_2 in the half-closed system. Besides that, the cyclic system with flowing solution was adopted for extending the life of electrode material and membrane by avoiding the adsorption of bubbles and accumulation of periodate crystal on the surface of anode and membrane. Combining the indirect oxidation of chlorine with direct oxidation on anode, the conversion rate of iodate is 85% than 42% by electrolysis in acid electrolyte and the consumption is saved up to 9.1%

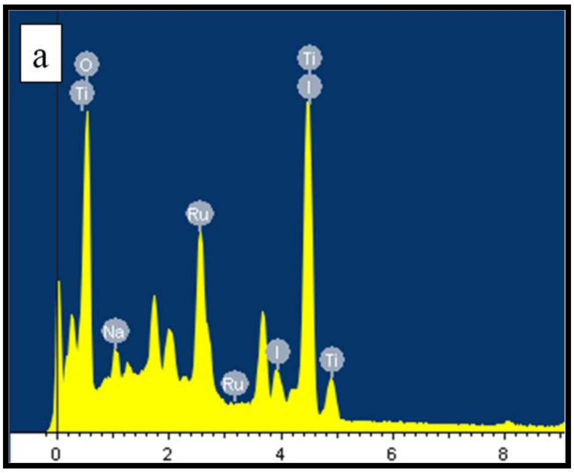
4. CONCLUSION

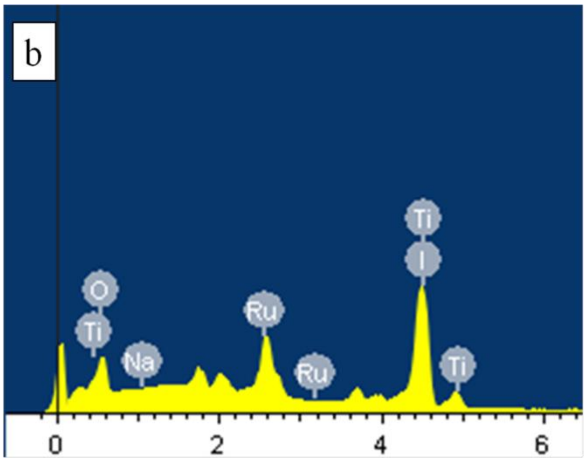
In the current study, a green and economic electrochemical synthesis of periodate in cyclic system is reported. The RuO_x/Ti electrode was pretreated by oxidation in alkali solution and in anolyte containing iodate, respectively. SEM images have shown that $NaIO_4$ crystal were formed and evenly distributed on the surface of RuO_x/Ti electrode. The electrochemical test and the proposed mechanism indicated that the addition of NaCl increase the synthesis of periodate in indirect oxidation by the formation of HClO. In addition, considering the practicability and operational cost, the optimal value of the current density and NaCl dosage were recommended as 80 mA.cm^{-2} and 0.05 mol.L^{-1}, respectively. Comparing to the conventional approach to generate periodate, the conversation percent (85%) and consumption (2700Kw.h / t) were superior in this study. Accordingly, the cyclic electrochemical system with indirect oxidation effect was significantly saved the electric energy consumption up to 9.1% and improved the purity of product. This study may have a useful implication for the laboratory and industrial applications.

SUPPORTING INFORMATION:

Table S1. EDS datas of RuO_x/Ti electrodes after electrolysis in anolyte with different pretreatments

	Na	O	I	Ti	Ru
Untreated	2.00	85.16	0.94	8.15	3.75
Pretreated with high current density	0.37	76.89	0.76	15.90	6.08
Activating pretreatment	11.78	74.22	9.07	3.93	1.00





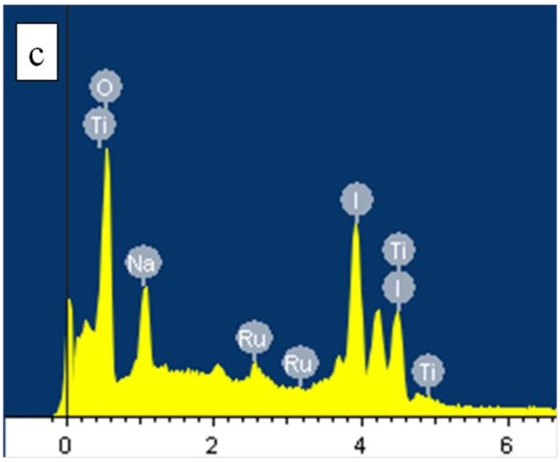


Figure S1. EDS spectrums of RuO_x/Ti electrodes after electrolysis in anolyte ($1 mol.L^{-1}$ NaOH, $5 mmol.L^{-1}$ NaCl and $0.3 mol.L^{-1}$ $NaIO_3$) with different pretreatments. (a) Only cleaning RuO_x/Ti electrode in ultrapure water, (b) electrolyzing 60 mins on RuO_x/Ti electrode with the constant current density of $120 mA / cm^{-2}$ in anolyte without $NaIO_3$, (c) activating pretreatment 10 mins in anolyte on (b).

ACKNOWLEDGEMENT
The authors greatly appreciate the support from the National Natural Science Foundation of China (No. 51374016) and the Fundamental Research Funds for the Central Universities of China (No. ZY1415, JD1415).

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