Factors Affecting the Anodic Oxidation of Isopropyl Alcohol in the Presence of Double Redox Mediators

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The operating conditions of electrooxidation of isopropyl alcohol in the presence of the double mediators were studied. The results indicated that electricity passed, concentrations of ruthenium dioxide, sodium chloride, isopropyl alcohol and temperature were the main factors affecting the current efficiency while current density was the minor. The results also revealed that both current efficiency and selectivity of acetone were 100% at the best operating conditions, i.e. $6 \times 10^{-4} \text{M RuO}_2$, 1M NaCl, 0.4M IPA, 25 mA cm$^{-2}$ and 288K.

1 INTRODUCTION

The electrooxidation of secondary alcohol by double redox mediators in a two-phase system has been studied\cite{1,12}. Comparatively, lower energy consumption and higher current efficiency were reported by the application of a single or a double redox mediators. In general, the oxidation of alcohol to produce aldehyde or ketone was carried out by traditional chemical reactions \cite{2,7}. The excess oxidant is necessary for a traditional process which the side reaction may occur and it is difficult to recycle the oxidants. The factors affected on the oxidation of alcohol by electrochemical method was seldom mentioned\cite{8,11,13}. Some authors published the oxidation of alcohol in the presence of an organic or inorganic single redox mediator \cite{8,12,13}. The oxidation of alcohol by double mediators in a two-phase system was also reported \cite{1,10}. However, the factors affecting the anodic oxidation of alcohol in the presence of double redox mediators are unclear. The anodic oxidation of isopropyl alcohol by double mediators in single-phase system is not reported. Furthermore, both the mechanism and kinetics of anodic oxidation of alcohol in the presence of double mediators are not clear\cite{10,11}. Electrosynthesis of organic compounds in the presence of redox mediator, not only the higher current efficiency and selectivity of products can be obtained but also no pollutant is created and lower energy is required. In general, lower potential and less energy consumption of a electrolysis process are required in the presence of Cl/Ru$^{4+}$ double mediators\cite{9}. Furthermore, Ru$^{4+}$ can be easily recycled in a double-mediator system. The lower potential and less energy consumption of an electrolysis process are required in industry\cite{3}. Traditionally, it is difficult to oxidize the secondary alcohol directly by electrolysis process\cite{5}. Both the selectivity and current efficiency of ketone by anodic oxidation of isopropyl alcohol(IPA) in the presence of single mediator are poor\cite{9}. Oxidation of the secondary alcohol in the presence of double redox mediators in two-phase system has been preliminary studied\cite{10,11}. Unfortunately, the operating conditions of producing ketone from isopropyl alcohol is not reported. Systematically, anodic oxidation of isopropyl alcohol in the presence of double redox mediators is carried out in this study.

2 EXPERIMENTAL

The oxidation of isopropyl alcohol was carried out in an electrochemical set up as shown in Fig.1. The platinum electrode was pretreated by dipping in basic, acidic solutions and then washing with distilled water for many times. The desired amount of RuO$_2$ and NaH$_2$PO$_4$ were added into 2 M NaCl aqueous solution in the electrolysis cell. The reactant ,IPA, was added in the electrolyte solution in the electrochemical cell as shown in Fig.2. Both agitation rate and temperature were
controlled at the desired values. When the system was at steady state, the current was supplied at a desired value from the power supply (Amel-550). The products were periodically sampled and analyzed by a gas chromatography (Shimadzu GC-9A).

3 RESULTS AND DISCUSSION

3.1 Effect of electricity passed

Figure 3 shows the results of the effect of electricity passed on the current efficiency of acetone. The current efficiency of acetone reached 68% for a $5 \times 10^{-3}$ F electricity passed. Increasing electricity passed from $5 \times 10^{-3}$ to $2 \times 10^{-2}$ F the current efficiency decreases from 68 to 40%. At the beginning of a run, the surface of working electrode is fresh and the oxidation rate of chloride anion is fast. When the run lasted, some impurity on the surface of working electrode was found, and the anodic oxidation rate of chloride anion slowed down. At constant current, the cell voltage increased with time. Besides, side reaction might occur, such as electrolysis of water. On the other hand, acetone will be catalyzed in acid condition to produce diacette alcohol as shown in Fig.3. The current efficiency of acetone decreased with electricity passed.

3.2 Effect of concentration of ruthenium dioxide

The current efficiency of acetone increased from 42 to 90% by increasing the concentration of ruthenium dioxide from zero to $7.54 \times 10^{-4}$ M as shown in Fig.4. The selectivity of acetone was significantly affected by the concentration of ruthenium dioxide. The maximum selectivity of acetone was 100% at $3.76 \times 10^{-4}$ M of ruthenium dioxide as shown in Fig.4. The results showed that aldol condensation of acetone occurred at a lower concentration of ruthenium dioxide resulting a lower selectivity of product.

3.3 Effect of concentration of sodium chloride

Increasing concentration of sodium chloride from 0.2 to 2M the current efficiency increased from 63 to 88% and conversion increased from 6 to 17% as shown in Fig.5. Further increasing the sodium chloride concentration to 3M, the current efficiency and conversion slightly decreased. At a fixed current density, the applied cell voltage is higher resulting electrolysis of water or side reaction which decreased the current efficiency. At lower concentration of sodium chloride the conductivity is lower than that at high NaCl concentration.

3.4 Effect of concentration of IPA
Figure 6 shows the effect of concentration of isopropyl alcohol on current efficiency and conversion of acetone. Increasing the concentration of isopropyl alcohol from 0.1 to 0.4 M the current efficiency increased from 76 to 100%. 17% best conversion is obtained at 0.21 M IPA.

3.5 Effect of current density

Figure 7 shows the effect of current density on current efficiency. The higher the current density supplied the lower the current efficiency was. At high current density, electrolysis of water might occur resulting a lower current efficiency.

3.6 Effect of temperature

Effect of temperature on current efficiency of acetone is shown in Fig. 8. The results show that increasing the temperature decreases current efficiency. The vapor pressure of RuO$_4$ increased with temperature, the concentration of RuO$_4$...
decreased with temperature after a period of a run. Consequently, the current efficiency was lower at a higher temperature.

4 CONCLUSIONS
The anodic oxidation of isopropyl alcohol could be easily obtained in the presence of double redox mediators. Both current efficiency and selectivity

of product were 100% at the best operating conditions, i.e. $6\times10^{-4}$ M RuO$_2$, 1 M NaCl, 0.4 M IPA, 25 mA cm$^{-2}$ and 288 K. The factors which mainly affect the current efficiency include electricity passed, temperature, concentrations of ruthenium dioxide, sodium chloride and isopropyl alcohol while current density is minor.

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REFERENCES