Influence of Solution Conductivity on Contact Glow Discharge Electrolysis

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Abstract Using a thin platinum anode in contact with an electrolytic solution, normal electrolysis develops spontaneously to contact glow discharge electrolysis (CGDE) at sufficiently high voltage. During this transition, midpoint voltage (V_D) is an important critical value. From V_D on, plasma is sustained by direct current glow discharge between the electrode and the electrolyte surface. And H_2O_2 is the main non-faradaic yield. In this study, effects of conductivity on V_D and the concentration of H_2O_2 have been investigated in Na_2SO_4 and $NaCl$ solution. The results indicate that V_D decreases with the increasing conductivity. And the value of V_D and the concentration of H_2O_2 in $NaCl$ solution are less than those in Na_2SO_4 solution. The concentration of H_2O_2 increases steadily and then decreases to maintain a stationary value.

Keywords Contact glow discharge electrolysis · Conductivity · Midpoint voltage · Hydrogen peroxide

Introduction

Electrochemical discharge phenomenon was first described in literature more than 150 years ago [1]. It is also termed in literature as plasma electrolysis [2], electrode effects [3–6] (anode or cathode effects depending on which electrode the phenomena takes place) or contact glow discharge electrolysis (CGDE) [7–9]. There have been extensive studies on electrochemical discharge because of increasing interest for its application. Nowadays, electrochemical discharge has been used in a variety of fields such as hydrogen production

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[10], micro-machining [11], nanoparticle synthesis [12], wastewater treatment [13, 14] and so on.

In recent years, much attention has been paid to CGDE for its simpler equipment and operation. In CGDE, plasma is sustained by direct current glow discharge between the electrode and the electrolyte surface [7–9]. Using a thin platinum anode in contact with an electrolytic solution, the conventional normal electrolysis develops spontaneously to CGDE if the applied voltage is raised to a critical value called the midpoint voltage (V_D) [15]. CGDE involves normal electrolysis, solvent vaporization near an electrode by Joule heating, hydrodynamic instabilities with vapor sheathing the electrode and glow discharges across the vapor sheath [8].

Chemical yields of anodic CGDE originate from the primary reaction zones, which consist of the plasma around the anode and the liquid phase near the plasma-anolyte interface. In the reaction zone within the plasma around the anode, H_2O vapor molecules are ionized or activated, and then bombarded each other to break up by charge transfer. The ultimate result is the production of free $\cdot OH$ and $\cdot H$ radicals. On the other hand, in the liquid-phase reaction zone near the plasma-anolyte interface, several liquid H_2O molecules break up into H_2 and H_2O_2 plus O_2 by being bombarded by each $H_2O_{gas}^+$ from the anodic plasma [8, 15]. As a mixture of these active species, $\cdot OH$, $\cdot H$, H_2O_2 and $H_2O_{gas}^+$ diffuse out of the primary zone and into the bulk electrolyte. They can interact among themselves and with any active substrate in the solution. Consequently, CGDE can be used to induce some unusual chemical changes in the solution.

Although CGDE has been systematically investigated in recent years, some issues remain unclear. For example, Hickling [16] concluded that the value of V_D was 410 V; while Susanta et al. [15] reported that V_D was 420 V, which was unaffected by the electrolyte's composition, concentration, temperature and surface tension. The effects of conductivity on the value of V_D and non-faradaic yield (H_2O_2) have not been investigated. In this study, we did a series of experiments to address these problems.

Experimental

Experimental apparatus was shown in Fig. 1. The anode was a platinum wire (0.3 mm) held in the brass support sealed into a glass tube. The cathode was a stainless steel stick placed in another glass tube (5 cm diameter), which was covered at the bottom by a sinter glass disk of medium porosity. Dissolved oxygen was removed from the electrolyte. The platinum wire was immersed into the solution to a depth of approximately 1.0 mm. In addition, the reaction cell was placed in a temperature-controlled water bath and the temperature of electrolyte was remained at 30°C. Electrolytic solutions with certain conductivity were prepared by dissolving sodium sulfate or sodium chloride in the distilled water. The solution was gently stirred with a magnet bar during the reaction. The pressure in the reactor was atmospheric. The voltage was applied through a direct current power supply (variable voltage 0–1,000 V and current 0–300 mA).

A Cary 50 UV–vis spectrometer (Varian, America) was used to determine the concentration of H_2O_2 in the process of CGDE. The determination of H_2O_2 was based on the reaction of H_2O_2 with titanyl ions giving yellow-colored complex of pertitanic acid [17]:

Fig. 1 Schematic diagram of the CGDE reactor **a** glass tube; **b** cathode; **c** anode; **d** water bath; **e** electrolytic solution; **f** magnetic bar; **g** gas outlet and sampling port

Results and Discussion

I–V Characteristic

A series of experiment was conducted in sodium sulfate solution to investigate the characteristic of anodic CGDE. I–V (Current vs. Voltage) curve was shown in Fig. 2, and four different regions were obviously identified. In section AB, the current was approximately in proportion to the applied voltage. Ohm's law was obeyed in section AB and conventional electrolysis occurred with small bubbles of gas leaving the anode. When the voltage continued increasing, a sharp decrease was observed at point B and the trend was maintained in BC region, with current being inverse proportional to the applied voltage. In this region, bubbles adhered to the anode surface and insulated a fraction of the surface, making it inactive. When the bubbles underwent the process of formation and collapse, the oscillation of the current occurred. At point C, the stabilized vapor sheath appeared around the anode. In section CD, the compact vapor sheath built up around the anode and progressively covered the anode surface. Current continued to slow down, reaching minimum at point D. From point D on, the current started to increase steadily with the rising voltage

Fig. 2 I–V curve (Medium: Na_2SO_4 ; conductivity: 2.92 mS cm^{-1})

Fig. 3 I-V curve (Medium: NaCl; conductivity: 2.93 mS cm^{-1})

and violet glow appeared in the anode. In section DE, glow discharge became yellow. The voltage at point D was called the midpoint voltage (V_D) [15].

The CGDE experiment was also conducted in NaCl solution. Its initial conductivity was close to that of Na_2SO_4 solution. I-V characteristic of CGDE in NaCl solution was shown in Fig. 3 and the curve pattern was similar to that in Na_2SO_4 solution. However, the current fluctuation was more obvious in NaCl solution in section BC. The current at point B was higher than that of Na_2SO_4 solution. V_D (460 V) in NaCl solution was less than that (495 V) in Na_2SO_4 solution, though.

Effect of Conductivity on V_D

To investigate the effect of conductivity on V_D , CGDE was conducted in Na_2SO_4 solution with its conductivity changing from 0.91 to 8.66 mS cm^{-1} . As seen in Fig. 4, V_D clearly decreased, from 570 to 425 V, with the increase of conductivity in Na_2SO_4 solution. The result was connected with the characteristic at point D, where the vapor sheath covered the anode and current transport happened through glow discharge. At point D, the critical factor for the onset of glow discharge across the vapor sheath was a sufficient potential drop to cause an appreciable conduction through the gas phase. When the conductivity of the electrolyte increased, the ion migration was enhanced and relatively lower voltage could sustain sufficient potential drop. Therefore, V_D decreased with the increase of conductivity.

Fig. 4 Variation of V_D with conductivity of solution

Fig. 5 Variation of pH and conductivity in Na₂SO₄ and NaCl solution in CGDE (Voltage: 500 V)

The CGDE experiments were also conducted in NaCl solution with its conductivity in the range of 0.97–4.65 mS cm⁻¹. V_D changed from 525 to 440 V, as shown in Fig. 4. V_D also decreased with the increasing conductivity and the trend was similar to that in Na₂SO₄ solution. However, V_D in NaCl solution was lower than those in Na₂SO₄ solution, even though the initial conductivity of two solutions was the same. That is, V_D was affected by the electrolyte's composition and concentration, which was different from those reported previously [15].

Figure 5 displayed the change of pH and conductivity in Na₂SO₄ and NaCl solution in CGDE. The pH of NaCl solution was less than that of Na₂SO₄ solution, while the conductivity of NaCl solution was higher than that of Na₂SO₄ solution in the process of CGDE. A possible explanation was that the following reactions occurred.

When CGDE was performed in NaCl solution, Cl^- could be transformed to chlorine radical. Two chlorine radicals reacted with each other to form one molecular of chlorine. HClO formed in reaction (4) then reacted with H_2O_2 to produce H^+ [18, 19]. The concentration of H^+ in NaCl solution was higher than that in Na₂SO₄ solution during the process of CGDE, even when the initial conductivity was the same. Because the ionic mobility of H^+ was much higher than other ions, NaCl solution has a higher conductivity than Na₂SO₄ solution during the process of CGDE. Therefore, even starting with the same initial conductivity, V_D in NaCl solution was less than that in Na₂SO₄ solution during the process of CGDE.

Effect of Conductivity on the Concentration of H_2O_2

H_2O_2 was the main non-faradaic product in CGDE. The measurement of H_2O_2 was useful to those reactions utilizing H_2O_2 in CGDE. The concentration of H_2O_2 was determined with the increasing voltage in Na₂SO₄ solution and the result was shown in Fig. 6. It was found that H_2O_2 started to form near 450 V and underwent a sharp rise after 495 V. 495 V was none other than the value of V_D on this condition. That is to say, H_2O_2 with higher

Fig. 6 Variation of H_2O_2 with increasing voltage in CGDE (Na_2SO_4 : 2.92 mS cm^{-1})

Fig. 7 The concentration of H_2O_2 in Na_2SO_4 and NaCl solution (Voltage: 500 V, NaCl : 2.93 mS cm^{-1} , Na_2SO_4 : 2.92 mS cm^{-1})

concentration was formed only when the voltage was beyond the value of V_D . So, 500 V is chosen as the applied voltage in the subsequent study, which was higher than V_D of each electrolyte.

The concentration of H_2O_2 in Na_2SO_4 solution and NaCl solution was also determined during CGDE, which was shown in Fig. 7. H_2O_2 accumulating in anolyte increased linearly with the treatment time of CGDE. The concentration of H_2O_2 in NaCl solution was less than that in Na_2SO_4 solution, as expected based on our previous explanation. When CGDE was performed in NaCl solution, HClO consumed H_2O_2 accumulating in the solution, therefore causing the decrease of H_2O_2 concentration.

We also studied the effect of conductivity on the formation of H_2O_2 by measuring the concentration of H_2O_2 in Na_2SO_4 solution with the conductivity changing from 2.92 to 7.61 mS cm^{-1} . As shown in Fig. 8, higher conductivity caused more production of H_2O_2 at the beginning of CGDE. The concentration of H_2O_2 was approximately in proportion to the conductivity of solution. After 10 min treatment of CGDE, the concentration of H_2O_2 was highest in 7.61 mS cm^{-1} Na_2SO_4 solution. However, with the treatment time increasing to 20 min, the relationship between concentration of H_2O_2 and the conductivity changed. The concentration of H_2O_2 increased steadily and then decreased to maintain a stationary value. The highest amount of H_2O_2 was formed in 5.38 mS cm^{-1} Na_2SO_4 solution. We reasoned that when the applied voltage (500 V) and the conductivity of solution was 2.92 mS cm^{-1} , plasma was not fully formed and the amount of reactive species produced was not enough. However, when the conductivity increased to 7.61 mS cm^{-1} , V_D decreased. Plasma

Fig. 8 Variation of concentration of H_2O_2 with conductivity of Na_2SO_4 solution

became full and sufficient H_2O_2 accumulated in anolyte, and underwent decomposition to O_2^{E} due to its further reaction with $\cdot\text{OH}$ [15].

When the formation and decomposition of H_2O_2 reached balance, the concentration of H_2O_2 finally maintained at a stationary value. For those reactions utilizing H_2O_2 in CGDE, the optimum conductivity of Na_2SO_4 was around 5.38 mS cm^{-1} since the highest amount of H_2O_2 was formed at that point.

Conclusions

V_D was affected by the electrolyte's composition and concentration. And V_D decreased with the increasing conductivity of solution. Higher amount of H_2O_2 was formed only when the applied voltage was above V_D . V_D and the concentration of H_2O_2 in NaCl solution were less than those in Na_2SO_4 solution. The concentration of H_2O_2 increased steadily with the increasing conductivity, and then decreased to maintain a stationary value. The concentration of H_2O_2 in 5.38 mS cm^{-1} Na_2SO_4 solution was found to be the highest.

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