The effect of electrolyte constituents on contact glow discharge electrolysis

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ABSTRACT

Ordinary electrolysis developed spontaneously to contact glow discharge electrolysis (CGDE) at sufficiently high voltage, with glow discharge taking place around a thin platinum anode which was in contact with electrolyte solution. During this transition, the critical voltage (V_D) was an important parameter for the onset of CGDE. The results indicated that V_D decreased with the increasing conductivity and then maintained a certain value. The different dimension and material of cathode had little effect on V_D . When the electrolyte conductivity was 5.0 mS/cm, V_D was hardly affected by electrolyte composition. And the concentrations of H_2O_2 producing in the anolyte were close in different inert electrolyte. However, the concentrations of H_2O_2 in NaCl, NaAc, Na_2CO_3 and $NaHCO_3$ solution were lower than that in Na_2SO_4 solution. And the concentration of H_2O_2 in the anolyte was also decreased by adding a minute amount of CH_3OH .

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1. Introduction

Nowadays, electrochemical discharge has been used in a variety of fields such as hydrogen production, micro-machining, nanoparticle synthesis, wastewater treatment and so on [1]. It was 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]. The understanding of electrochemical discharge continued with the increasing interest for its application. Kellogg focused on the anode effect in aqueous electrolyte and discovered the characteristic transition region, then named kellogg's region [10]. Hickling and Ingram investigated the factors governing the breakdown of conventional electrolysis and found the chemical effect of CGDE was closely similar to resemble the alpha radiolysis of water [11]. Vogt investigated the parameters of influencing the onset of electrode effect and presented mathematical models for the incremental ohmic resistance [12], the formation of gas film and bubble coverage fraction [3,6]. They found that deteriorated wetting of the electrode–electrolyte interface and decreasing rate of bubble release were two other important effects of electrochemical discharge, besides local evaporation of the electrolyte by Joule heating [1].

In recent years, much attention has been paid to CGDE for its production of $\bullet OH$. In CGDE, plasma was sustained by direct cur-

rent glow discharge between the electrode and the electrolyte surface [7–9]. Using a thin platinum anode in contact with an electrolyte solution, the conventional electrolysis could develop spontaneously to CGDE when the applied voltage was sufficiently high [13]. During the transition process, I – V (current vs voltage) curve was characteristic to CGDE. Sengupta and Singh studied the onset, location and chemical effect of CGDE in H-type reactor [7]. They found that V_D depended on the polarity of the electrode (420 V for the anode and 160 V for the cathode in aqueous solution) and was unaffected by the electrolyte composition, concentration, temperature and surface tension. However, our recent research indicated that V_D decreased with the increasing conductivity when the conductivity of electrolyte changed from 0.91 to 8.66 mS cm^{-1} [14]. It was necessary to proceed towards completely understanding the onset of CGDE. At the same time, it was well established that CGDE generate active radicals ($\bullet OH$, H_2O_2 , etc.) which made it particularly suitable for decontamination purpose. Many papers have presented results on destruction efficiencies of phenols [15,16], organic dyes and production efficiencies of hydrogen peroxide [17–19]. However, the effect of electrolyte composition has not been systematically studied so far. In this study, we did a series of experiments in order to further address these problems.

2. Experimental

Experimental apparatus was similar to that in our previous work [14]. The anode was a platinum wire (0.30 mm) held in the brass support sealed into a glass tube. The cathode was a graphite stick (diameter: 3.92 mm) placed in another glass tube, which was cov-

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ered at the bottom by a sinter glass disk of medium porosity. Electrolyte solutions with certain conductivity were prepared by dissolving electrolyte in the distilled water. 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. The solution was gently stirred with a magnet bar during the reaction. The voltage was applied through a direct current power supply (variable voltage 0–1000 V and current 0–300 mA).

To reduce the amount of sampling and improve the reliability of results by replicate determination of multiple samples, spectrophotometry was carried on microplates by Multiskan Spectrum (Thermo Scientific, America) after confirming a Cary 50 UV-vis spectrometer (Varian, America). It was used to determine the concentration of H_2O_2 producing 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 [20]:

3. Results and discussion

3.1. I - V characteristic

A series of experiment was conducted in different electrolyte solution to investigate the characteristic of anodic CGDE. Fig. 1 illustrated the typical I - V curve in Na_2SO_4 solution. In the mean stationary I - V characteristics, several different regions were identified:

$0 < V < V_A$: ohmic region; electrolysis of water took place and conventional electrolysis occurred with small bubbles of gas leaving the anode.

$V_A < V < V_B$: limiting current region (or region of current saturation); bubbles were coalescing to the anode and the bubble coverage fraction increased. V_B was termed as the breakdown voltage in reference.

$V_B < V < V_D$: transition region; V_D was the critical voltage (also termed as midpoint voltage in reference). The transition region was also divided into three parts as follows.

$V_B < V < V_C$: a sharp decrease was observed. A vapor sheath appeared and progressively covered the anode surface. The bub-

Fig. 1. I - V curve of CGDE in Na_2SO_4 solution (conductivity: 8.20 mS/cm).

Fig. 2. Variation of characteristic voltage with the conductivity of Na_2SO_4 solution.

bles in vapor sheath underwent the process of formation and collapse, the oscillation of the current occurred.

$V_C < V < V_{C'}$: the stabilized vapor sheath appeared around the anode. The current became stable.

$V_{C'} < V < V_D$: the compact vapor sheath built up around the anode and progressively covered the anode surface.

$V > V_D$: glow discharge electrolysis region; the vapor sheath covered all active bubble nucleation sites of the anode; current transport happened through glow discharge. The current started to increase steadily with the rising voltage and violet glow appeared in the anode. In section DE, glow discharge became yellow.

Since CGDE was still an electrochemical process and the glow discharge was transferred by ions, it was evident that the conductivity of the solution had an influence on the onset of CGDE. In this study, CGDE were conducted in Na_2SO_4 solution with its conductivity changing from 1.00 to 12.47 mS/cm, and in Na_2HPO_4 solution with its conductivity in the range of 2.01–12.00 mS/cm. The results were shown in Fig. 2 and Fig. 3, respectively. It was found that the characteristic value of V_A , V_B , V_C and $V_{C'}$ decreased with increasing conductivity in Na_2SO_4 solution and Na_2HPO_4 solution. However, V_D decreased with the increase of conductivity, and then maintained a certain value. This result demonstrated that the

Fig. 3. Variation of characteristic voltage with the conductivity of Na_2HPO_4 solution.

conductivity was one of important factors influencing the onset of CGDE. The increment of conductivity resulted in a higher current density at the same applied voltage and the power dissipation in the vicinity of the anode became relatively higher. The vapor sheath and the glow discharge were easy to generate. Another critical factor for the onset of CGDE was a sufficient potential drop to cause an appreciable conduction through the gas phase. The critical voltage should be sufficiently high to sustain the potential drop through glow discharge. Therefore, the onset of CGDE was correlated with both the voltage and the conductivity of the solution.

3.2. Effect of conductivity on V_D

Since V_D was the critical voltage for the onset of CGDE, much attention had been paid on the parameters influencing on it. It had been found in the previous work that V_D decreased with the increase of conductivity in the range of 0.91–8.66 mS/cm [14]. In this study, V_D in Na_2SO_4 solution was investigated in the range of 1.00–11.38 mS/cm as shown in Fig. 4. When the conductivity of Na_2SO_4 solution changed from 1.00 mS/cm to 5.99 mS/cm, V_D decreased from 542 V to 438 V. When the conductivity of Na_2SO_4 solution was 7.00, 8.20, 9.25, 10.48 and 11.38 mS/cm, the values of V_D were 432, 431, 425, 420 and 425 V, respectively [7]. The magnitudes of V_D were close to 420 V, obtained from Sengupta's experimental result. That is, when the conductivity of solution was in the range of 7.00–11.38 mS/cm, the effect of conductivity on V_D was largely not significant.

In the case of Na_2HPO_4 solution, when the conductivity changed from 2.01 to 9.02 mS/cm, V_D decreased from 526 V to 415 V. When the conductivity of Na_2HPO_4 solution was 9.97, 10.99 and 12.00 mS/cm, the values of V_D were 408, 409 and 408, respectively. V_D in both electrolyte solutions decreased with increasing their conductivity, and then maintained a certain value. In addition, in the range of 4.00–8.00 mS/cm, V_D in Na_2SO_4 solution and Na_2HPO_4 solution were so close that two curves were overlapped which was shown in Fig. 4. The difference of V_D existed in the lower conductivity (<4.00 mS/cm) and in the higher conductivity (8.00–12.00 mS/cm).

In addition, the magnitudes of V_D were compared with those in the previous study, as shown in Fig. 5. In the range of 2.00–9.00 mS/cm, the magnitudes of V_D were close. The diameters of stainless steel cathode (in the previous study) and graphite cathode were 2 and 3.92 mm, respectively. That is to say, the effect of electrode dimension and cathode material on V_D was so little in this

Fig. 4. Variation of V_D with the conductivity of electrolyte.

Fig. 5. The effect of cathode dimension and material on V_D in Na_2SO_4 solution.

range, which was consistent with Sengupta's experimental results [7].

At the same time, CGDE was also conducted in different electrolyte with the same conductivity, as shown in Table 1. When the conductivity of solution was 5.00 mS/cm, all values of V_D were very close in different electrolytes. Therefore, it could be concluded that V_D was unaffected by the electrolyte's composition if the conductivity of solution was given a specific value in a certain range. This result was consistent with the Sengupta's experimental results [7].

3.3. Effect of electrolyte composition on chemical reactivity of plasma

To characterize the chemical reactivity of plasma, the concentration of H_2O_2 was determined as a typical indicator of long living chemical compound. The effect of conductivity on the concentration of H_2O_2 has been investigated in our previous work [14]. The concentration of H_2O_2 increased with CGDE treatment time. The concentration of H_2O_2 producing in the anolyte increased with the increase of conductivity, and then maintained at a stationary value. In this study, we investigated the concentrations of H_2O_2 in different electrolytes with the same conductivity 5.00 mS/cm. Table 1 listed the concentrations of H_2O_2 producing in different electrolytes after 20 min CGDE treatment. The concentrations of H_2O_2 accumulating in anolyte were 59.22 mg/L, 60.65 mg/L in Na_2SO_4 , Na_2HPO_4 solution, respectively. The concentrations of

Table 1

The effect of electrolyte composition on CGDE under the same conductivity (5.00 mS/cm).

Electrolyte	V_D (V)	$C_{\text{H}_2\text{O}_2}$ (mg/L)
Na_2SO_4	451	59.22
Na_2HPO_4	451	60.65
Na_2CO_3	456	47.87
NaHCO_3	450	43.35
NaCl	450	22.56
NaAc	452	41.26
$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{HPO}_4$	450	63.26
$\text{Na}_2\text{SO}_4 + \text{CuSO}_4$	452	64.01
$\text{Na}_2\text{SO}_4 + \text{NaAc}$	453	64.66
$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CO}_3$	455	62.56
$\text{Na}_2\text{SO}_4 + \text{NaHCO}_3$	459	59.60
$\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$	458	63.85
$\text{Na}_2\text{SO}_4 + \text{NaOH}$	458	64.02
$\text{Na}_2\text{SO}_4 + \text{NaCl}$	452	56.58
$\text{Na}_2\text{SO}_4 + \text{CH}_3\text{OH}$	450	46.71

H₂O₂ in these two different electrolyte solutions were very close, since Na₂SO₄ and Na₂HPO₄ were inert electrolyte, which did not react with the active species of the plasma.

In NaCl solution, the concentration of H₂O₂ was 22.56 mg/L which was lower than that in Na₂SO₄ solution. It was because when the CGDE was performed in NaCl solution, Cl[−] could be transformed to chlorine radical. Two chlorine radicals reacted with each other to form molecular chlorine (Cl₂). HClO formed in reaction (4) then consumed H₂O₂ in anolyte [20]. Therefore, the concentration of H₂O₂ in NaCl solution was lower than that in Na₂SO₄ solution.

In NaAc solution, the concentration of H₂O₂ was just 41.26 mg/L because Ac[−] consumed part of •OH which resulted in the decrease of the concentration of H₂O₂. Na₂CO₃ and NaHCO₃ were often employed as inhibitor for •OH. The rate constants between Na₂CO₃, NaHCO₃ and •OH were $8.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The concentration of H₂O₂ in Na₂CO₃ and NaHCO₃ solution were 47.87 and 43.35 mg/L, respectively; which were lower than that in Na₂SO₄ solution.

CGDE was also conducted in mixed electrolyte solution. The concentrations of H₂O₂ in Na₂SO₄ solutions containing small amount of Na₂CO₃, NaHCO₃, Na₂HPO₄, CuSO₄, H₂SO₄, NaOH, NaAc and NaCl were 62.56 mg/L, 59.60 mg/L, 63.26 mg/L, 64.01 mg/L, 63.85 mg/L, 64.02 mg/L, 64.66 mg/L and 56.58 mg/L, respectively. That is, the presence of a small quantity of other electrolyte in solution had slight influence on the concentration of H₂O₂.

When a little amount of methanol was in the present of Na₂SO₄ solution, the concentration of H₂O₂ was 46.71 mg/L, which was also lower than that without methanol. It was because CH₃OH could capture •OH due to the following reaction [21]:

In practice, methanol was often chosen as the typical hydroxyl radical scavenger.

4. Conclusions

In CGDE, V_D decreased with the increasing conductivity of solution, and then maintained a certain value. When the con-

ductivity was 5.00 mS/cm, V_D was unaffected by the electrolyte's composition. The different dimension and material of cathode had insignificant effect on V_D. And the concentrations of H₂O₂ in the anolyte were approximately close in Na₂SO₄ and Na₂HPO₄ solution. The concentrations of H₂O₂ in NaCl, NaAc, Na₂CO₃ and NaHCO₃ solution were lower than that in Na₂SO₄ solution. The presence of a small quantity of these electrolytes in Na₂SO₄ solution had slight influence on the concentration of H₂O₂. The presence of CH₃OH in Na₂SO₄ solution decreased the concentration of H₂O₂ in the anolyte.

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