Comparative Study on Application of Bimetallic Pt-Based Alloy Electrocatalysts in Advanced Chlor-Alkali Electrolysis

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Abstract

Application of an oxygen-depolarized cathode will contribute to energy saving in chlor-alkali electrolysis. For this purpose, the development of high-performance cathode with the best electrocatalyst is essential. Using bimetallic Pt-based alloy electrocatalysts including PtPd and PtAg carbon-supported in oxygen-depolarized cathode chlor-alkali cell has been shown to have the high cell performance. This study presents application of PtRu carbon supported electrocatalyst oxygen-depolarized cathode and performance comparison of cells with carbon-supported PtRu, PtPd and PtAg electrocatalysts cathodes using the same DSA-Cl₂ anode. Results show that there are quite similarity between the effects of various factors on the caustic current efficiency (CCE) in a zero-gap oxygen-depolarized chlor-alkali cells employing carbon-supported PtPd, PtRu and PtAg electrocatalysts. Besides, it seems that the PtPd/C electrocatalyst cathode has relatively higher performance than the other cathodes with PtAg/C and PtRu/C electrocatalysts in zero-gap chlor-alkali cells.

Keywords: Oxygen-Depolarized, Chlor-Alkali, CCE, Electrocatalyst, Performance, Saving Energy

1. Introduction

Chlorine as one of the most important bulk chemicals in the world is produced by the brine electrolysis. Chlorine is not only used in the day-to-day life but also is an essential part of the chemical building block that results a myriad of reactions and products in the major plastic, pharmaceutical, inorganic, fine chemical and specialty industries. The chlorine production can therefore be regarded as an indicator of the country’s chemical industry state of development. It is an energy intensive process, where consumes electrical power between 2100 and 3300 kWh·t⁻¹ Cl₂ depending on the operating parameters and the type of the process. There are three major processes based on mercury, diaphragm and membrane cells for the electrolysis. The membrane cell is the most recent advanced technology with less environmental contamination and electrical power consumption. Despite the fact that the overall energy intensity has been reduced due to the successive introduction of ion exchange membrane cells instead of the “unclean” mercury and diaphragm process, the issue of energy consumption is still a main issue.

Replacing the conventional hydrogen-evolving cathode by oxygen-depolarized cathode in CA membrane cell reduced the cell voltage [1-5] and consequently 30% energy consumption reduction at 4 kA·m⁻² [4-5] and CO₂ emission reduction i.e. global environment improvement.

The conventional and advanced chlor-alkali cells carbon dioxide emissions are compared for a range of primary energy sources that could be used to generate power [6] (Figure 1). Another difference is the hydrogen generation (a low value byproduct) in chlor-alkali cells with conventional hydrogen-evolving cathodes compared to the oxygen-depolarized cathodes. The utilization of waste hydrogen in conventional chlor-alkali plants with fuel cells has recently become quite popular. The fuel cells can return only around 50% of the clean hydrogen energy, whereas most of the “dirty” fossil fuel energy is consumed to generate the hydrogen. Also, installation of the fuel cell stacks translates into yet another capital investment. Therefore utilizing the hydrogen “burning” fuel cells in the existing conventional chlor-alkali plants will never compete the oxygen-depolarized cells tech-
The current chlorine/caustic manufacturing methods will eventually be replaced by the advanced chlor-alkali technology.

The key element of the advanced chlor-alkali cell is the oxygen-depolarized cathode. An oxygen-depolarized cathode should be designed to facilitate an intimate interaction between oxygen, catholyte and electrocatalyst particles at the three phase boundaries (gas/liquid/solid), in order to reduce oxygen effectively. Due to harsh condition in saturated oxygen and concentrated caustic of chlor-alkali membrane cell media, the oxygen-depolarized cathodes are more susceptible to performance loss than the conventional hydrogen-evolving cathodes. Another drawback of oxygen-depolarized cathodes in chlor-alkali cells is the peroxide stability. However the peroxide eventually decomposes to the hydroxide and has no role on energy loss, but the peroxide adverse potential effects on cathode stability [7] and caustic handling issues make it a troublesome byproduct. Different materials with different structures (carbon-based or carbon free electrodes) may be used to construct oxygen-depolarized cathodes. The impact of electrocatalysts to bring about high activity (i.e. high current densities) at lower cell voltages and stable oxygen-depolarized cathode performance over the period of time is of utmost importance. The frequently used catalysts in oxygen-depolarized cathodes are platinum [2-5,7-9] and silver [1,8-9] either carbon supported or as pure metal. Due to high cost of platinum, different techniques such as Pt-based alloy electrocatalysts have been developed to reduce loading Pt. The alloyed electrocatalysts composed of two different metal elements have drawn a greater interest than monometallic ones. The reason may be possible catalytic activity improvement. The employment of Pt-based alloy electrocatalysts including PtPd and PtAg carbon-supported in oxygen-depolarized chlor-alkali cathodes has been already reported [10,11]. In this study, the oxygen-depolarized cathode implementation containing a carbon supported PtRu electrocatalyst is reported. Its cathode performance that is caustic current efficiency is compared with PtPd and PtAg carbon supported oxygen-depolarized cathode performance. The preparations of Pt-alloy electrocatalyst cathodes and their characterizations are also described in brief.

2. Experimental Preparation and Set up

2.1. The Cathode Preparation

The employed cathodes have the same structure but different Pt-alloy electrocatalysts as reaction layers. The cathodes structure consists of a gas diffusion layer, a reaction layer and a current collector as shown in Figure 2. The gas diffusion layer is a very thin conductive porous sheet comprising 65% - 70% carbon (721 m²·gr⁻¹ surface area supplied by Iranian Co.) and 35% - 30% PTFE powder (Aldrich Co.). The conductive porous sheet was prepared by thorough mixing of carbon and PTFE powder, extruding the uniform mixture into a sheet and then expanding it on a silver-plated nickel mesh as a current collector. The carbon supported PtPd and PtRu electrocatalysts are synthesized by sodium borohydride reduction method [12,13]. The carbon supported PtPd, PtRu and PtAg are loaded over the gas diffusion layer of each cathode with 0.53, 0.64 and 0.6 mg·cm⁻² density, respectively as reaction layer.

2.2. Cathode Performance Measurement

The cell performance evaluation is carried out in the laboratory scale zero-gap type CA membrane set-up. The cell includes an ion-exchange membrane (Flemion®892, Asahi Glass Co.) which divides the cell into a chamber with standard coated titanium plate (DSA®-Cl₂) as anode and another chamber with a prepared oxygen-depolarized as cathode. The prepared cathode was in close contact with the ion-exchange membrane and the electrocatalyst layer facing to the cathode chamber. In the zero-gap design, which is used throughout this study, flooding
by caustic solution is prevented, voltage and peroxide formation are reduced [4,5]. During the brine electrolysis, the anolyte is continuously fed into the jacketed heater anode chamber with a digital thermometer to monitor its temperature. Moreover, the anolyte pH was controlled by the feed pH and its circulation. The anode and cathode chamber overflows are conducted to different separators for further depleted reactant separation and recirculation. The preheated humidified oxygen at atmospheric pressure is used as cathode chamber feed. The cell current is kept constant and the corresponding cell voltages are measured. In order to measure the caustic produced, caustolyte samples were collected and titrated against 1.0 M HCl solution. These data are then used for calculation of the caustic current efficiency.

3. Results and Discussions

3.1. Cathode Characterization

The cathodes surfaces of bimetallic Pt-based alloy electrocatalysts are investigated using scanning electron microscope (SEM) with a XL30 Philips Co. microscope (Figure 3). The SEM cathodes surfaces of the loaded bimetallic Pt-based alloy electrocatalysts indicate totally different particles sizes and also their relatively uniform dispersion. The likely reason may be the way of painting to load electrocatalysts particles.

The oxygen-depolarized cathodes must be sufficiently hydrophobic to prevent the intrusion of catholyte into electrode pores and consequently, prevent electrode flooding. Hydrophobicity evaluation was made through water contact angle measurements and the results confirm the cathodes surfaces hydrophobicity as is shown in Figure 4. The hydrophobic surfaces have water contact angles larger than 90°. As is expected, the result indicate that water contact angle on the cathode surface increases as cathode PTFE/carbon composition changes from 30/70 to 35/65. Generally, the cathodes that are loaded with bimetallic Pt-based alloy electrocatalysts show high electronic conductivity, sufficient hydrophobicity and mechanical strength.

3.2. Cathode Performance

One of the valuable responses which are directly proportional to total energy consumed by an electrolysis cell is the current efficiency. The caustic current efficiency (CCE) as cell performance was thus measured according to the procedure described in Section 2 and calculated based on the following equation [14]:

\[
CCE(\%) = \frac{m(t) - m(t = 0)}{It/nF} \times \frac{MW_{NaOH}}{MW_{NaCl}}
\]  

The five process parameters affecting the advanced chlore-alkali cells performance include current density, Brine concentration, Anolyte pH, cell temperature and oxygen flow rate in the presence of different cathodes loaded with carbon supported PtRu, PtPd and PtAg and the same DSA-Cl₂ anode based on our pervious works [10,11] are compared as shown in Figures 5-9.

The CCE of the cells using PtRu/C, PtPd/C and PtAg/C electrocatalysts increases with cell temperature increase as seen in Figure 5. This may be due to the fact that cell temperature has impacts on the rate of oxygen reduction and the electrolyte conductivity [15]. Besides, the CCE increase is more sensible in the PtRu/C and...
PtAg/C electrocatalyst cathodes than the cathode with PtPd/C electrocatalyst layer with temperature increase. The cell with PtPd/C cathode shows a minimum CCE at a cell temperature of 90°C. This result indicates that the cell temperature effect on cell performance using PtPd/C electrocatalyst cathode is less than other cells.

The cells CCE (PtRu/C, PtPd/C and PtAg/C electrocatalysts) are plotted against anolyte pH in Figure 6. The results show that the CCE increases as the brine acidity decrease (i.e. increasing anolyte pH). It is probable that the increase of brine PH increases H3O+ charge pass through membrane and therefore lowering the membrane resistance and caustic concentration [16]. The result is the cells CCE decrease.

The oxygen flow rate effect on CCE is likely related to ease of caustic removal from the cathode pores at high oxygen flow rate. The corresponding results of the cells using PtRu/C, PtPd/C and PtAg/C electrocatalysts are depicted in Figure 7 and the increase of oxygen flow rate enhances the CCE. The results show that the PtPd/C cathode CCE at low oxygen flow rate is higher than the other cathodes (PtRu/C and PtAg/C) in chlor-alkali cell.

The CCE increases with brine concentration as a consequence of lower caustic crossover [17] for all cathodes (i.e. PtRu/C, PtPd/C and PtAg/C) as Figure 8 shows. The cell with PtRu/C cathode shows higher CCE at brine concentration of 300 g/l. Figure 9 shows the CCE decreases as the current density increases from 1 to 4 kA/m² for all mentioned (PtRu/C, PtPd/C and PtAg/C) cathodes. This is the result of the different 2- or 4-electron oxygen reduction reactions kinetics [17,18]. At the same current density, the PtPd/C electrocatalyst cell shows higher CCE compared to the other cathode cells.

The oxygen reduction reaction is a complex process involving four coupled proton and electron transfer steps. Several of the elementary steps involve intermediate reactions leading to a wide choice of reaction pathways.
The exact sequence of the reactions is still not known and all reaction steps, intermediate reactions and their kinetic parameters must be identified, which is clearly challenging. Relatively stable HO_2^- ion formation may stop the oxygen reduction reaction in alkaline electrolytes that easily converts to dioxide. Although there is no consensus on the exact reaction sequence, two overall pathways direct 4-electron and peroxide pathway may take place in alkaline media [19]:

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \\
\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{OH}^- + \text{HO}_2^- \\
\text{HO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow 3\text{OH}^- 
\end{align*}
\]

The produced peroxide may also undergo catalytic decomposition as follows:

\[
2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2
\]

Platinum is the most commonly used and active catalyst for oxygen reduction reaction and all of the platinum-group metals reduce in alkaline media according to the direct 4-electron process [20,21]. Pt-based alloys have been studied and generally exhibit higher activity and stability than pure Pt. The enhanced Pt-alloy electrocatalytic activity is explained by a number of phenomena, such as: 1) Pt-Pt bond length reduction, favoring the oxygen adsorption, 2) Pt 5d orbital electron density 3) the surface oxide layers [22].

The enhanced oxygen reduction reaction activity on Pt/Pd as an effect of stronger oxygen adsorption on Pt surfaces has been cited by others as inhibiting factor during O_2 reduction in alkaline media. Examination of the Pt monolayers on the various metal substrates (such as Ag, Pd and Ru) revealed that Pt(III) was already close to optimal, in terms of d-band center (in determining oxygen reduction reaction activity). Pd/Pt is the only system that shows slightly higher activity [23].

4. Conclusions

Commercial progression difficulties of the chlor-alkali membrane cells using oxygen-depolarized cathodes are investigated. The oxygen-depolarized cathode’s main drawback is loss performance under harsh conditions in chlor-alkali cell. Using bimetallic PtRu carbon-supported electrocatalysts in oxygen-depolarized cathode chlor-alkali cell has shown an appropriate way to improve or enhance the performance of chlor-alkali membrane cells. The employment of bimetallic Pt-based alloy electrocatalysts including PtRu, PtPd and PtAg carbon-supported in oxygen-depolarized chlor-alkali cells is compared with each others. There are quite similarity between the effects of various factors on the CCE in a zero-gap oxygen-depolarized chlor-alkali cell employing carbon-supported PtPd, PtRu and PtAg electrocatalysts. It seems that the PtPd/C electrocatalyst cathode has relatively higher performance than the other cathodes with PtAg/C and PtRu/C electrocatalysts in zero-gap chlor-alkali cells.

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