

Comparative Study of the Pt and Ru Carbon Support's Affection on the Caustic Current Efficiency in a Zero-gap Advanced Chlor-alkali cell

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Abstract: The progress of the membrane chlor-alkali technology and its additional optimization resulted in a meaningful reduction of energy consumption in chlor-alkali process. Pt is the normally electro-catalyst in the most applicable of oxygen diffusion cathodes, but there are many problems in this case including flooding and production of peroxide. These problems cause to explosion and destroy the structure's pore media of the gas diffusion cathode. The peroxide phenomena cause to decrease the caustic current efficiency and many other problems. In this research the effects of various process parameters on caustic current efficiency (CCE) in a zero-gap oxygen-depolarized chlor-alkali cell employing a State-of-the-art Ru carbon support, which the Pt is replaced with Ru, were studied and the results comparison with silver plated nickel screen electrode (ESNS®). For doing a thorough research, we selected the process parameters from both cathodic and anodic compartments. Seven process parameters were studied including anolyte pH, temperature, flow rate and brine concentration from the anode side, oxygen temperature and flow rate from the cathode side and the applied current density. The effect of these parameters on CCE was determined quantitatively. The result of experiment shows the best performance for the Ru as an electro-catalyst in the gas diffusion cathode for advanced chlor alkali process.

Key words: Advanced chlor-alkali; Electro-catalyst; caustic current efficiency; gas diffusion cathodes; Process parameters; Comparison; Ru carbon support; ESNS®

INTRODUCTION

The progress of the membrane chlor-alkali technology and its additional optimization resulted in a meaningful reduction of energy consumption in chlor-alkali process. The state-of-the-art membrane reactors operate at voltages as low as 3.2V at a typical current density of 0.4 A/cm² (Mirzazadeh *et al.*, 2008; Yamaguchi *et al.*, 1999). Brine electrolysis is still one of the most energy-intensive industrial operations, despite the tremendous efforts of the chlor-alkali industry to reduce the energy consumption. It is accepted that the developed membrane technology has reached the theoretical end-point on energy consumption. Therefore, more optimization of this process is not expected to result in a significant cut of the energy consumption. Nevertheless, by replacing the hydrogen-evolving cathode in a membrane cell with an oxygen-depolarized cathode, the cell voltage and energy consumption can be reduced by as much as 30% at 0.4 A/cm² (Mirzazadeh *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004). The electrochemical reduction of oxygen in an alkaline environment has been the topic of many researches and the successful employment of silver (Mirzazadeh *et al.*, 2008; Beckmann and Luke, 2000; Furuya and Aikawa, 2000) and platinum (Mirzazadeh *et al.*, 2008; Furuya and Aikawa, 2000, Federico *et al.*, 2000) catalysts in oxygen-depolarized chlor-alkali cathodes has already been reported. While an oxygen-depolarized chlor-alkali cell significantly lowers energy consumption per unit weight of chlorine and caustic, optimization of process parameters to achieve maximum current efficiency is remained almost untouched. The only published work that is somewhat related to this issue was carried out by researchers at Los Alamos National Laboratory to minimize peroxide formation in an ACA cell using ELAT® cathodes (Mirzazadeh *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004). As far as we know, there have been a few published literatures on a thorough investigation of the effects of operating parameters on the CCE of ACA membrane cells by Mohammadi *et al.*, (2008). Besides, no open literature was found to explore thoroughly the performance of the newly developed gas diffusion cathode as a composition of 65 percents carbon and 35 percents PTFE by weight with Ru electro catalyst which extruded at 360- 420

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°C and normally pressure during thirty minutes. This paper thus presents part of our research on the implementation of oxygen-depolarized cathodes in a modified commercial membrane cell using the newly developed gas diffusion cathode as a composition of 65 percents carbon and 35 percents PTFE by weight with Ru electro catalyst which is made by our research and comparison it with the ESNS[®] cathode which is produced by E-Tek Inc. The study focuses on selected performance characteristic of the cell (CCE). As our study to implement gas diffusion electrode in chlor-alkali cell arose from fuel cell research, the arrangement of our ACA cell and PEM type fuel cell is relatively analogous. For example, while the most of oxygen depolarized chlor-alkali cells (Mohammadi *et al.*, 2008; Beckmann and Luke, 2000; Federico *et al.*, Sakata *et al.*, 1999; Saiki *et al.*, 1999) can be classified as finite gap (where the cathode side is divided by the gas-diffusion cathode into separate oxygen and caustic compartments) we implemented a fuel cell-like, zero-gap arrangement. In this configuration, there are no independent oxygen and caustic compartments and the oxygen cathode stays in intimate contact with the ion-exchange membrane. In this way, both the flooding of the cathode by the NaOH solution and the ohmic drop has been meaningfully reduced (Mohammadi *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004).

MATERIALS AND METHODS

Chemicals Used:

The materials that were used for the making of cathode are as follows: PTFE, graphitized carbon black with 1400 m²/gr specific surface area by supplied by Iranian Co, Acid Chloro Rutheniumic was purchased from ALDRICH Co. The brine was prepared from analytical grade NaCl (Merck Inc.) using deionized water produced in ipp. All other chemicals used for analysis were also analytical grade. The general material for titration and iodine metric.

Method of Cathode Preparation:

As a substrate of the electrode catalyst layer, 200 μm thick conductive porous PTFE sheets comprising 65 wt% carbon and 35 wt% PTFE were used. The conductive porous PTFE sheet with a porosity of 80% was prepared by thoroughly mixing carbon carrier powder and PTFE powder, extruding into a sheet and expanding to obtain the desired thickness. The resulting conductive porous PTFE sheet was composed of carbon carriers netted with three-dimensional fibrous PTFE, and showed high electronic conductivity, gas diffusibility, water repellency and tear strength. The ruthenium catalyst was supported on carbon carriers by impregnating the conductive porous PTFE sheet with H₂RuCl₆ using a mixed solution of water and ethanol containing 5 wt.% H₂RuCl₆, drying and reducing H₂RuCl₆ into Ru in nitrogen containing 3% hydrogen. The ruthenium supported conductive porous PTFE sheet cut into appropriate size was used as an electrode catalyst layer. The electrode catalyst layer was attached to a nickel expanded mesh current collector coated with conductive adhesive made of carbon black powder and dispersion of FEP (copolymer of tetra-fluoro ethylene and ethylene). Porous PTFE film of 10 μm thickness was used as a water-repellent layer that prevented electrolyte solution from leaking in the air chamber and supplied enough oxygen to produce OH⁻ ions to the electrode catalyst layer. The electrode catalyst layer, the current collector and the water-repellent layer were stacked as shown in Fig. 1 and pressed at a temperature of 300°C to bond each other. This process allowed the formation of a one-body oxygen reduction gas diffusion electrode (Morimoto *et al.*, 2000).

Experimental Set-up:

The electrochemical cell was a divided filter-press type (Micro-flow cell, Electro cell AB, Sweden) with 10 cm² (3.3 cm×3 cm) electrode area (Fig. 2) that was modified to allocate gas diffusion electrode. The cell used in this study employed a commercially available, 10 cm² gas diffusion electrodes with Ru electro catalyst which is made by our research as a composition of 65 percents carbon and 35 percents PTFE by weight with Ru electro catalyst which extruded at 360- 400 °C and normally pressure during thirty minutes. The catalyst layer contained carbon-supported Ruthenium with a total Ru loading of 0.64 mg cm⁻². The nickel screen side of the cathode remained in intimate contact with the carboxylic side of the ion exchange membrane (Flemion[®] 892, Asahi Glass Co.). The anode was a standard coated titanium plate (DSA[®]-Cl₂). The cell flow fields were made from 2mmTeflon. The cell performance evaluation was carried out in an ACA set-up developed in our laboratory. Fig. 3 shows the process flow diagram of the set-up used in this study. The anolyte feed tank was heated by jacketed heater and its temperature was monitored by digital thermometer. Anolyte pH was measured by an on-line pH-meter inserted in anolyte feed tank. The anolyte was recirculated in separate hydraulic circuit throughout the experiment by magnetic pump according to Fig. 3. The overflow from the anolyte compartment

of the electrolysis cell was sent to a gas–liquid separator. During electrolysis, Cl₂ gas produced was absorbed by 2M NaOH solution in TK-103 and then TK-104, respectively. The cathode chamber was fed with oxygen at atmospheric pressure. The oxygen stream was heated and humidified by a jacketed bubble column humidifier (HF). The oxygen temperature and extend of humidification was adjusted before entering the cathode compartment. In order to minimize corrosion, the cathode gas feed line was equipped with two valves that would stop the oxygen flow and replace it with nitrogen upon a power loss. Constant currents were applied to the cell and the corresponding cell voltages were measured by a multi meter. After each test, the set-up was washed thoroughly with deionized water drained and dried. Preliminary tests showed in order to produce determinable chlorine and caustic, the electrolysis run time should be at least 150 min.

TK-102 (NaOH product tank). TK-103, 104 (chlorine absorption tanks). SP-101, 102 (gas–liquid separator). FM-101 (liquid flow meter). FM-102 (oxygen flow meter). T-101, 102 (temperature indicator). PH-101 (on-line pH meter).

DC-101 (DC power supply). H-101, 102 (jacketed electrical heater). P-101 (anolyte magnetic pump). H.I. (humidification indicator). PG (pressure gauge). HF (humidifier). M.F.Cell (membrane flow cell).

Analysis:

CCE was determined from titration of the sodium hydroxide samples with standardized 1.0M HCl (from HCl 37% by weight) solution (Fisher) against phenolphthalein. The peroxide content in the NaOH solution was found spectrophotometrically. (UV-Visible spectrophotometer – SHIMADZU). Fresh samples of sodium hydroxide were mixed with a known amount of potassium ferricyanide solution in aqueous NaOH. The peroxide content was determined from a decrease of ferricyanide absorption at 418 nm (Mohammadi *et al.*, 2008 Aziz *et al.*, 1964). Due to the very weak acidic properties of hydrogen peroxide (pK_a = 11.75 (Mohammadi *et al.*, 2008; Ardon *et al.*, 1965), the volume of the acid used to neutralize the NaOH sample corresponded to the sum of the sodium hydroxide present in the sample and the NaOH produced as a result of hydro peroxide anion (HO₂⁻) protonation (Mohammadi *et al.*, 2008; Lipp *et al.*, 2005). Since the latter quantity was also equal to the amount of NaOH that would form because of HO₂⁻ decomposition, the CCE quoted in this study are corrected for peroxide.

RESULTS AND DISCUSSION

Effect of Brine Concentration:

The effect of brine concentration on CCE was studied and the results are shown in Fig. 4. As seen, like conventional membrane cells (Jalali and Thesis, 2005) and like ACA zero-gap cells with ELAT® (Mohammadi *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004), the CCE increases linearly with brine concentration within the experimental range studied. At low brine concentrations, the low CCE is due to the membrane swelling and permeability. Consequently, more water is transported through the membrane yielding lower caustic concentration (Mohammadi *et al.*, 2008; Keating and Gerner, 1997). As could be expected, the CCE also increases with brine concentration because of decreased caustic crossover through the membrane. One may suspect the partial oxygen evolution (Czarnetzki *et al.*, 1992; Fern'andez *et al.*, 2002) on the DSA® anode to contribute to the above phenomena. This reaction produces hydronium cations and its relative contribution to the measured current increases with the decrease in brine concentration (Czarnetzki *et al.*, 1992; Fern'andez *et al.*, 2002).

As shown in this figure the gas diffusion layer with Ru electro-catalyst in the reaction layer have the best average performance in comparison with ESNS cathode.

Effect of Anolyte pH:

This is the first time that the effect of anolyte pH on CCE of an ACA cell is being studied. The corresponding results are represented in Fig. 5. The results show that CCE increases with increasing anolyte pH within the experimental range studied. It is believed that an increase in brine acidity (decrease in pH) may produce an increased H₃O⁺ flux across the membrane, which may result in a low membrane resistance, low CCE and low NaOH concentration. However, like conventional membrane cells reported earlier (Mohammadi *et al.*, 2008; Jalali and Thesis, 2005) the chlorine current efficiency decreases with increasing brine pH due to the production of by products such as hypochlorite and chlorate in anolyte at higher pH's (Bergner and Appl, 1990).

As shown in this figure the gas diffusion layer with Ru electro-catalyst in the reaction layer have the best average performance in comparison with ESNS cathode.

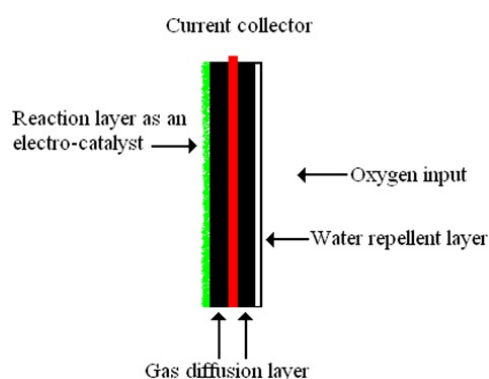


Fig. 1: Structure of the oxygen reduction cathode

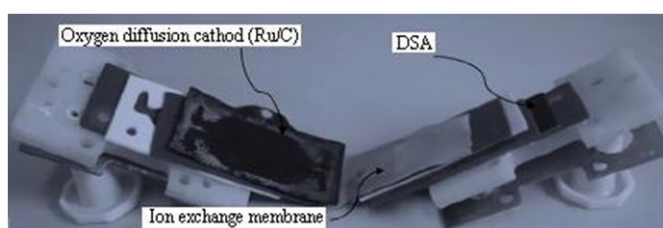


Fig. 2: Components of the membrane cell used in this study

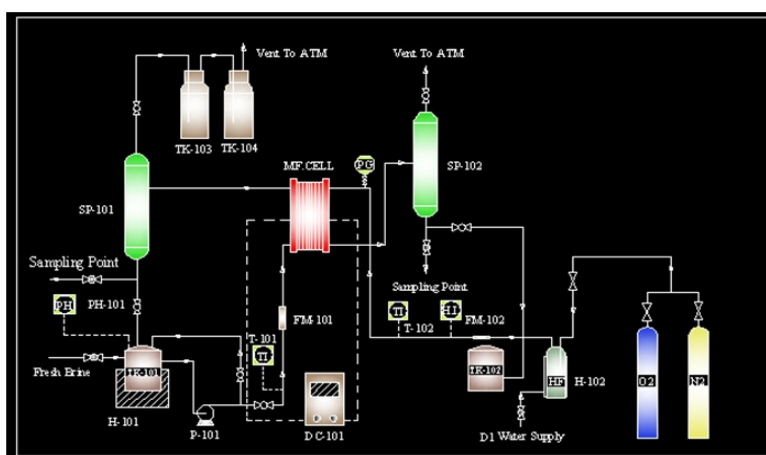


Fig. 3: Process flow diagram of the ACA set-up utilized: TK-101 (brine recirculation tank). TK-102 (NaOH product tank). TK-103, 104 (chlorine absorption tanks). SP-101, 102 (gas-liquid separator). FM-101 (liquid flow meter). FM-102 (oxygen flow meter). T-101, 102 (temperature indicator). PH-101 (on-line pH meter). DC-101 (DC power supply). H-101, 102 (jacketed electrical heater). P-101 (anolyte magnetic pump). H.I. (humidification indicator). PG (pressure gauge). HF (humidifier). M.F.Cell (membrane flow cell).

Effects of Anolyte and Oxygen Temperature:

The non-isothermal effect of an ACA cell was studied for the first time and the results are shown in Figures 6 and 7. The result shows that CCE increases with temperature in both cases. At low temperatures, the rate of oxygen reduction is low and this lowers CCE profoundly (Jalali and Thesis, 2005). Another point that should mention is that the electrical conductivity of the electrolyte is a function of concentration and temperature. At high temperatures, the high conductivity of anolyte solution lowers the cell voltage and therefore energy consumption of the chlor-alkali set-up will be low as conventional membrane cells (Jalali and Thesis, 2005). Consequently the economic and energy factors are in favor of the technology that utilizes higher temperatures.

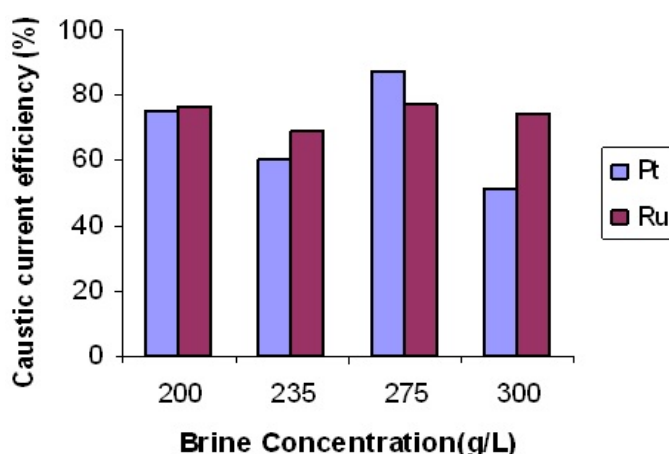


Fig. 4: The effect of brine concentration on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: temperature (80 °C), PH (2.5), flow rate (350 cm³/min), oxygen: flow rate (700 cm³/min), temperature (80 °C), and current density (0.2 A/cm²) for the both system.

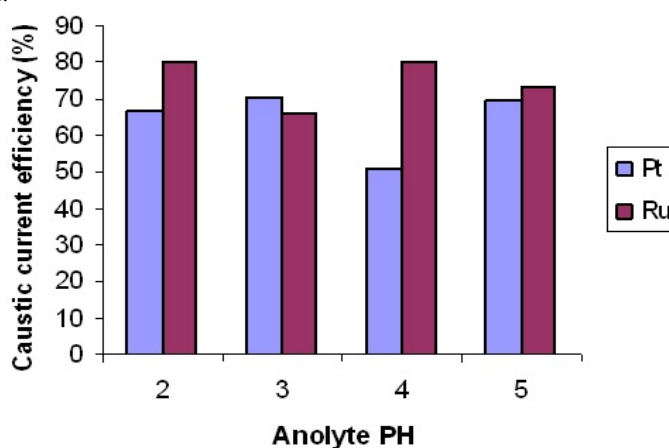


Fig. 5: The effect of anolyte pH on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (210 g/L) temperature (75 °C), flow rate (350 cm³/min), oxygen: flow rate (500 cm³/min), Temperature (75 °C), and current density (0.2 A/cm²).

As seen in figure-6, 7 the gas diffusion layer with Ru electro-catalyst in the reaction layer have the best average performance in comparison with ESNS cathode.

Effects of Anolyte and Oxygen Flow Rates:

As shown in figure-8, 9 the gas diffusion layer with Ru electro-catalyst in the reaction layer has the best average performance in comparison with ESNS cathode. To see the effects of anolyte and oxygen flow rates on performance of ACA cells, we studied each parameter individually. By increasing anolyte flow rate (velocity), CCE increases. This result is in complete agreement with the conventional membrane cells (Jalali and Thesis, 2005). This may be because the amount of attached Cl₂ bubbles on anodic side of the membrane and those remained within anolyte are reduced (Pierre and Wragg, 1993; Xiong *et al.*, 1992). In fact, the bubbles decrease the effective area of the membrane by blinding effects especially at low anolyte flow rates. The effect of oxygen flow rate on CCE was not linear also. The result shows that CCE increases with increasing oxygen flow rate as what observed with ELAT® (Mohammadi *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004). The increase of CCE at higher rates of oxygen flow rate most likely results from the effect of gas flow on the effectiveness of caustic removal from the electrode. High gas velocity in the cathode chamber makes the removal of caustic from the electrode pores easier than low velocities. In very low gas velocities, we had accumulation of viscous caustic in the cathode chamber.

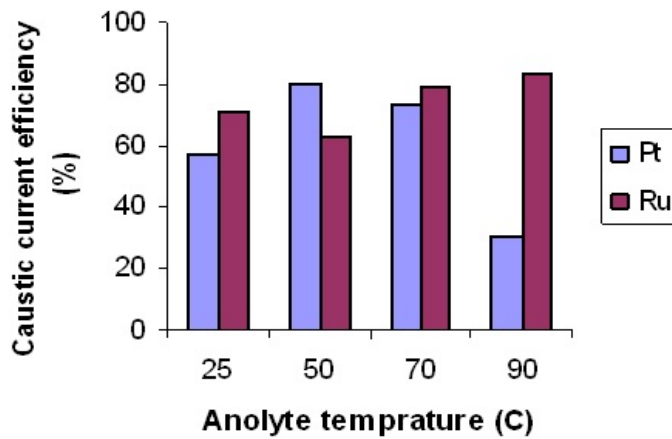


Fig. 6: The effect of anolyte temperature on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (230 g/L), pH (2.5), flow rate (350 cm³/min), and oxygen: flow rate (900 cm³/min), Temperature (75 oC), and current density (0.2 A/cm²).

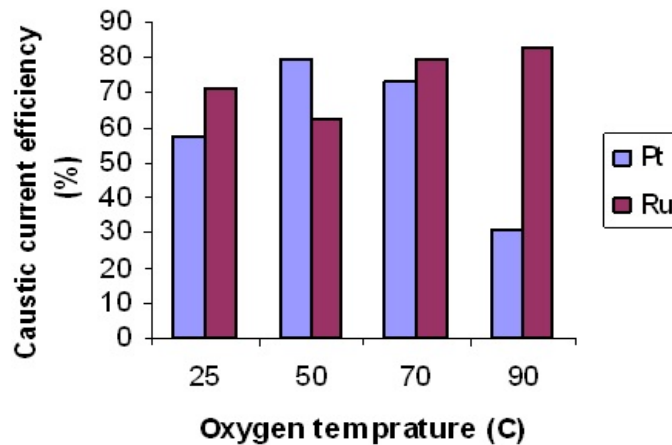


Fig. 7: The effect of oxygen temperature on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (230 g/L), pH (2.5), flow rate (250 cm³/min), temperature (70 oC), and oxygen: flow Rate (500 cm³/min), and current density (0.2 A/cm²).

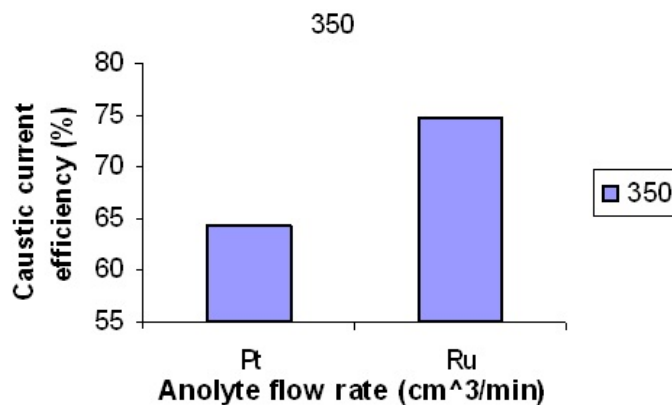


Fig. 8: The effect of anolyte flow rate on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (280 g/L), pH (2.5), temperature (75 oC), oxygen: flow rate (700 cm³/min), Temperature (75 oC), and current density (0.3 A/cm²).

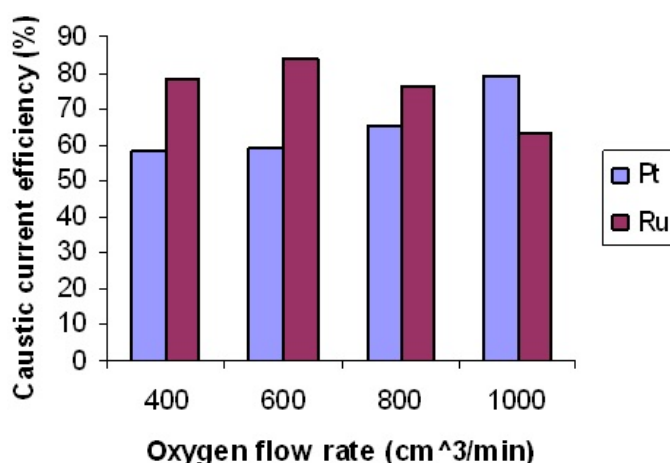


Fig. 9: The effect of oxygen flow rate on CCE and a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (250 g/L), pH (2.5), flow rate (400 cm³/min), temperature (70°C), and oxygen: Temperature (70 °C), and current density (0.15 A/cm²).

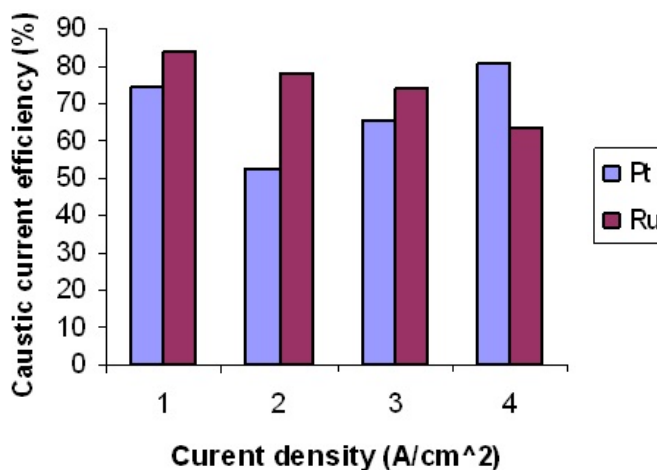
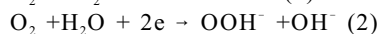
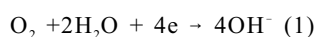


Fig. 10: The effect of current density on CCE a typically comparison between the performance of Ru carbon support and the ESNS cathode at anolyte: concentration (270 g/L), pH (3), flow rate (450 cm³/min), temperature (80 °C), oxygen: temperature (80 °C), flow rate (800 cm³/min).

Effect of Current Density:

The cell was operated at six current densities between 0.1 and 0.4 A/cm² as industrial membrane cells. As shown in fig-10, decrease in CCE with increasing current density is similar to ELAT® results especially at low current density (Mohammadi *et al.*, 2008; Lipp *et al.*, 2005; Chlistunoff, 2004). Effect of current density on CCE is believed to originate from the different kinetics of desirable complete 4- electron reduction and unwanted partial 2-electron reduction of oxygen:



In fact, the increase of current density shifts the cathode potential towards the more negative values and this phenomenon affects the relative rates of the two reactions. Higher current densities are likely to decrease CCE by increasing membrane swelling and permeability (Keating and Gerner, 1997), by more significant contribution of the oxygen evolution reaction as well as by membrane blinding by chlorine gas in anode side.

As seen in this figure the gas diffusion layer with Ru electro-catalyst in the reaction layer have the best average performance in comparison with ESNS cathode.

Conclusion:

The Ru/C electro-catalyst was synthesized by a modified organic colloid method in an ethylene glycol solution. The addition of Ru could improve the dispersion of active components significantly. The particle size of active components of Ru/C catalyst could be as small as 1.5 nm as determined by XRD and SEM. The catalyst showed good activity for oxygen reduction similar to that of Pt/C in advanced Chloro alkali process; In this research we studied the effects of seven process parameters individually also. The experimental results revealed that CCE increases by increasing in brine concentration and anolyte and oxygen temperatures and flow rates and decreases by increasing in current density within the experimental range studied. It implied that Ru/C catalyst exhibited a better performance in comparison with the Pt/C catalyst. Besides, the addition of Ru could prevent the aggregation and growth of platinum nano-particles in the thermal heating process effectively. On the basis of electrochemical experiment data, a multi-electron charge transfer process ($n=4e$) for the ORR on Ru/C catalyst was determined. The higher activity, good stability and the better caustic current efficiency in the most of experiments make the Ru/C catalyst a potentially suitable cathode catalyst for application in advanced Chloro alkali process. At finally, alloy Pt-Ru/C electro-catalyst is the best selection for advanced Chloro alkali process.

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