RESEARCH NOTES

Studies Relating To Cathodic Reactions In Neutral Chloride Solutions Used In Chlorate Processes

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The present work has been conducted to elucidate on the cathodic reactions in neutral alkali and alkaline-earth metal chloride solutions. The experiments were carried out on platinum anode in neutral chloride solutions of sodium, potassium, magnesium, strontium, and barium (electrolyte for chlorate process) by means of steady-state $E-\log i$ curves. The results indicate that the cathodic hydrogen evolutions in sodium and potassium chloride electrolyte yield similar curves. The cathodic hydrogen evolution reaction in magnesium, strontium, and barium chloride electrolytes takes place at more negative potentials (about 120−150 mv) than that in sodium and potassium chloride. This is due to the difference in local pH and hydroxide precipitation near the cathode surface. The hydroxide precipitation on the cathode surface in the case of alkaline earth metal salts was overcome by the rotation of cathode at 1.38 m s^{-1}.

1. Introduction

Both the cathodic hydrogen and anodic chlorine evolution reactions, from neutral chloride media, are important reactions in the technology of chlorate production, and it is in this context that the present study addresses the cathodic hydrogen evolution reactions. The hydrogen evolution reaction has been studied little in neutral chloride solutions,[1] because the pH at the cathode surface often is determined by the reaction itself, rather than by the bulk pH, and, thus, is generally unknown. Bockris and Watson[2] and Lukovzer et al.[3] studied the pH dependence of the hydrogen evolution reaction on mercury and nickel electrodes, respectively.

The preparation of alkali metal chlorates by electrolysis of the corresponding chlorides has been studied extensively by different authors.[4] However, studies on the electrochemical oxidation of alkaline earth-metal chloride and chlorate are scarce. It is well-known that, in the electrolysis of solutions of alkali and alkaline earth-metal chlorides for the preparation of chlorates, the primary anode process is the discharge of chloride ions and the liberation of free chlorine. At the cathode, the discharge of hydrogen ions is accompanied with the liberation of OH$^-$ ions. If the OH$^-$ ions and chlorine formed react in equivalent amounts, the product finally leads to 100% efficiency, which depends on the formation and solubility of metal hydroxides. In general, while the solubility of hydroxides of alkali metals is high, the solubility of alkaline earth-metal hydroxides is low.[5−11]

Since the literature reveals that no such type of study has been reported, the present work has been undertaken to explain further the relative effects of cation and pH on cathodic reactions in neutral chloride solutions of sodium, potassium, magnesium, strontium, and barium (used as starting solution for corresponding chlorate preparation).

2. Experimental Section

A Princeton Applied Research (PAR) model 371 Potentiostat-Galvanostat and a Wenking Scan Generator (VSG 83), in combination with a Kontron digital multimeter for potential indicating and HIL 2103 multimeter for current indication, were used. The curves were recorded using a X-Y/t recorder (Rikadenki, Japan).

A two-compartment cell that has an external jacket for water circulation, to maintain electrolyte temperature, was used. The cathode and anode compartments of the cell, each of which has a volumetric capacity of 100 mL, were separated by a glass frit (Grade-3). The experiments were conducted on a platinum-working electrode (with a working area of 0.2 cm^2) embedded in Teflon, with a standard calomel electrode (SCE) as the reference electrode and a platinum foil counterelectrode. The cathode was connected to a rotating assembly for cathode rotation.

The working electrode was polished with alumina polish on microcloth for 2 min and cleaned with distilled water. This was then followed by ultrasonic cleaning for 5 min to remove any residual alumina particles from the surface and finally rinsing with acetone. The temperature was maintained at 301 K. The experiments were carried out in varied concentrations (1.0 to 3.0 M) of sodium, potassium, magnesium, strontium, and barium chloride solutions, using a scan rate of 100 mV·s^{-1}. The salt solution (100 cm^3) was taken in the cell and deaerated with pure nitrogen. The pretreated electrode was allowed to attain a steady potential value for 5 min. Polarization experiments were conducted between the potential range of −0.6 to −1.6 V (vs SCE), and the E vs log i plots were recorded. The local pH at the interface was measured by an advanced pH meter (TOA-DKK, Japan).

3. Results and Discussion

During the electrolytic oxidation of chloride solution to obtain chlorate, the primary products of the anode and cathode reactions are chlorine and alkali, respectively, which react in the bulk electrolyte between the electrodes to form hypochlorous acid and hypochlorite. These are subsequently reacting chemically to form chlorate.[4] The main reactions in the chlorate electrolysis process can, thus, be written as follows.
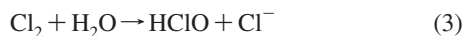
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At the anode, chlorine is formed:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$

At the cathode, hydroxyl ions and hydrogen are formed:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (2)$$
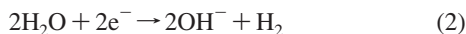
At the bulk, chlorine ions formed at the anode react rapidly with water to form hypochlorous acid:
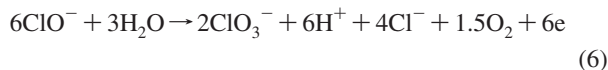
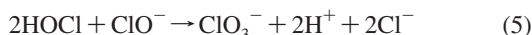$$Cl_2 + H_2O \rightarrow HClO + Cl^- \qquad (3)$$

Since the electrodes are close together and have no diaphragm, the chlorine can react with hydroxyl ions formed at the cathode to produce hypochlorite ions,

$$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O \qquad (4)$$

As a result, the solution around the anode becomes strongly acidic and the solution in contact with the cathode is alkaline. In addition to this pH gradient, the concentration of hypochlorous acid also establishes a gradient that is relatively high around the anode and relatively low around the cathode.

It is usually assumed that chlorate is formed by the reaction of hypochlorite ion by free hypochlorous acid (eq 5) when pH is 6.0–6.5. However, when pH is slightly alkaline, the electrochemical formation of chlorate through discharge of the hypochlorite

$$2HOCl + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (5)$$

$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 6H^+ + 4Cl^- + 1.5O_2 + 6e \qquad (6)$$

ion at a potential equal to that for discharge of the chloride ion (reaction 6).

According to reactions 5 and 6, chlorate may be formed in two ways, either by a purely chemical reaction of the hypochlorite ion with hypochlorous acid in the bulk solution (chemical chlorate formation) or by electrochemical oxidation of the hypochlorite at the anode under simultaneous oxygen evolution (anodic chlorate formation). If all chlorate is formed by chemical reaction 5, 6 and 12 faradays are consumed in the oxidation of 1 mol of chloride to chlorate in the case of alkali and alkaline earth metal, respectively. This is said to correspond to a maximum current efficiency of 100%. If all chlorate is formed by reaction 6, the current efficiency cannot be higher than 66.5%, since one-third of the current is used for the evolution of oxygen. In other words, reaction 6 can be considered as an anodic loss reaction. It has been established that reaction 5 is more plausible than reaction 6.[4] The most favorable operating conditions for reaction 5 are a temperature of 333–348 K with a pH of 6.0–6.5. Under these conditions, apart from reaction 2, in the case of alkaline earth-metal cations, an additional cathodic loss reaction, viz., precipitation of metal hydroxide, will be encountered because of their low solubility. According to M–H₂O Pourbaix diagram,[12] hydroxide formation is predicted by the following reaction

$$M^{2+} + 2OH^- \rightarrow M(OH)_2$$
$$\log[M^{2+}] = \log K - 2pH \qquad (7)$$
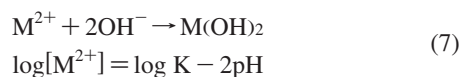
where M is magnesium, strontium, or barium.

The magnesium, strontium, and barium hydroxide forms an adherent coating over the cathode in the range of pH 8.5–12.0, 12.0–13.0, and 12.5–13.0, respectively. Magnesium, strontium, and barium ions as hydroxides can protect the cathode surface and hinder further cathodic reactions. The above cathodic loss
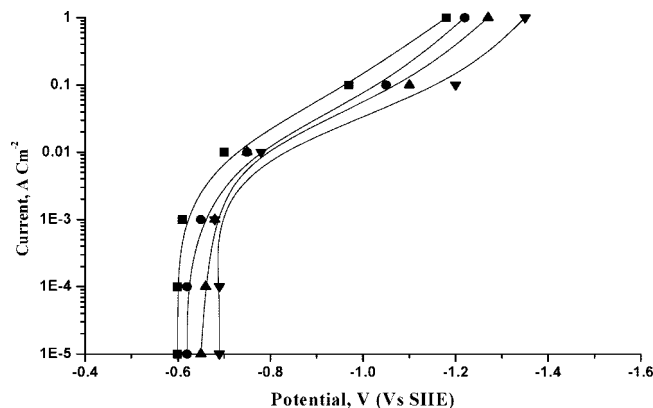

Figure 1. Polarization curves for hydrogen evolution reaction at 303 K in sodium chloride solutions: ▼, 1.0 M; ▲, 1.5 M; ●, 2.0 M; ■, 2.5M.
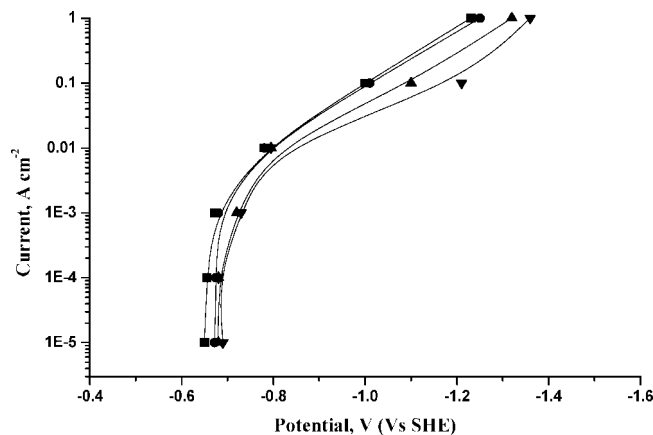

Figure 2. Polarization curves for hydrogen evolution reaction at 303 K in magnesium chloride solution: ▼, 1.0 M. ▲, 1.5 M; ●, 2.0 M; ■, 2.5 M.

reaction (eq 7) was not encountered in the case of alkali metals because of their higher solubility. To study and overcome the precipitation and to increase the current efficiency for alkaline earth-metal chlorate formation, the cathodic hydrogen evolution reaction study has been carried out in electrolytes like magnesium, strontium, and barium chlorides at 303 K and compared with sodium and potassium chloride electrolytes. Figures 1 and 2 are typical examples for E vs log i curves for hydrogen evolution reaction on platinum in deaerated solutions of sodium and magnesium chloride, respectively, in the concentration range of 1.0–2.5 M. The solutions were maintained at 303 K, and initially the pH was adjusted to 6.0. Potentials were recorded after each current was passed for 5 s. All the curves are nearly parallel, and the potential changes very little in the current density range of 10^{-5} to 10^{-3} A·cm^{-2}; then the potential change is marked having a large value of Tafel slope with the increase in current density up to 0.1 A·cm^{-2}, and beyond this current density, the Tafel slope decreases. The region of the curves above 10^{-3} A·cm^{-2} may be linked to two short Tafel regions at the extreme current ranges with a smooth potential "step" in between. Sodium and potassium chlorides show similar curves, whereas the curves for magnesium, strontium, and barium chlorides lie at negative side to those of sodium and potassium. This potential difference, which is between 130–200 mV, is due to the differences in pH increased both in the bulk electrolyte and adjacent to the electrode surface as the experiment proceeded.[13,14]

In the case of measurements of local pH, it is reported[13] that the local pH for 1.0 M ammonium sulfate in platinum electrode is the same in bulk pH when the current density is increased
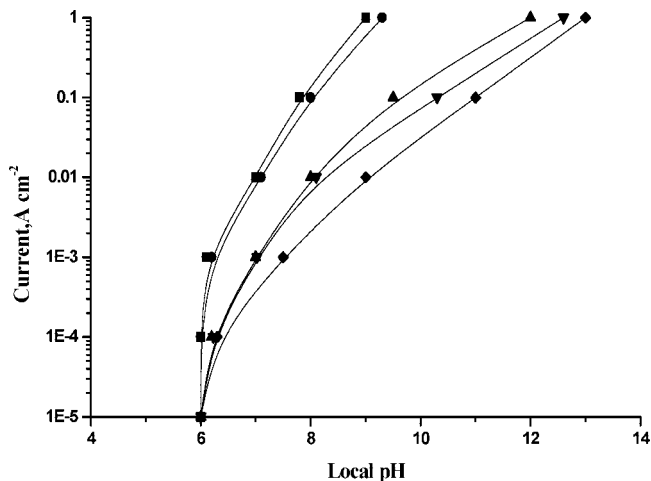
Figure 3. Variation of local pH with current density at a bulk pH of 6.0: ■, KCl; ●, NaCl; ▲, MgCl$_2$; ▼, SrCl$_2$; ◆, BaCl$_2$.

from 10^{-5} to 10^{-2} and deviates significantly from the bulk pH value of 8.1 only above 0.1–0.2 A·cm^{-2}. This is because ammonium salt solutions act as self-buffered solutions. However, the local pH for sodium sulfate deviates significantly from bulk at a current density of 0.01 A·cm^{-2}. A similar trend has been obtained in the present instance also, i.e., in the case of sodium and potassium chloride solutions, the local pH deviates slowly from the current density of 10^{-2} A·cm^{-2} onward. However, in the case of magnesium, strontium, and barium chloride solutions, the local pH changes gradually even from the current density of 10^{-4} A·cm^{-2}. Figure 3 shows the variation of local pH with current density at an initial pH value of 6.0. Since pH 6.0 is used as the starting pH in all chlorate cells, it is now taken as a typical example for explanation. It is clear from the figure that the sodium and potassium chloride show an increase of local pH to 9.5 and 9.0, respectively, at the current density of 1 A·cm^{-2}. These results are in conformity with earlier results,[15] where local pH increased with increasing current density in KCl electrolyte on platinum electrode. However, in the case of magnesium, strontium, and barium chlorides, the local pH raises to 12.0, 12.5, and 13.0, respectively, at the same value of current density (1 A·cm^{-2}). In all the cases, the deviation between local pH and bulk pH is due to the generation of OH$^-$ ions and accumulation of the same adjacent to the cathode surface. Particularly in the case of alkaline earth metals, the solubilities of their hydroxides are very low, resulting in the formation of a film on the cathode.

The polarization was carried out for sodium, potassium, magnesium, strontium, and barium chloride solutions at a constant temperature of 303 K at different pH values. Figures 4 and 5 represents the typical examples for sodium and strontium chloride electrolytes. The electrode was pretreated, cycling anodically and then cathodically 10 times at 0.01 A·cm^{-2}. Then the electrode was polarized galvanostatically starting from the lowest current density to the higher current densities, keeping the current constant for 5 s before recording the potential. In general, all the curves are in a similar way except the initial and final potentials, which are varying depending on the type of chloride used. At a current density of about 10^{-2} A·cm^{-2}, the curves are merging into the common Tafel region. Similar types of curves are also obtained by Vetter[16] and Andersen et al.[11] It is reported[11,16] that hydrogen is evolved from water irrespective of the salt solution used.

It is reported[16] that the increase of cathode rotation decreases the local pH of the electrode. From the results, it is found that
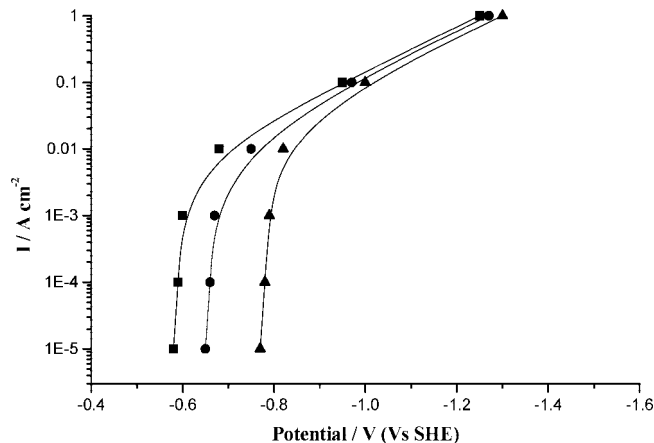

Figure 4. E vs log i curves in 1.0 M sodium chloride at different pH's at 303 K: ▲, 5.0; ●, 6.0; ■, 7.0.
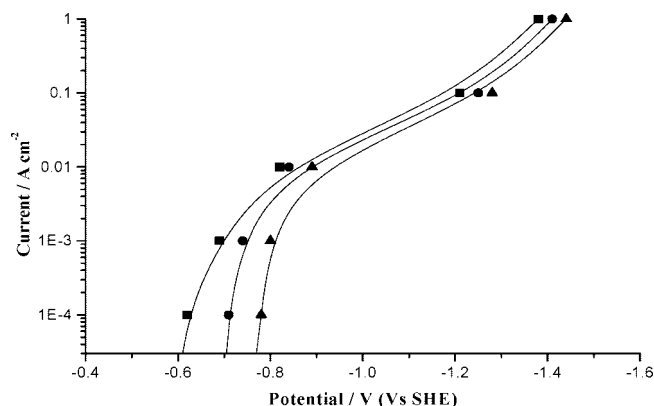

Figure 5. E vs log i curves in 1.0 M strontium chloride at different pH's at 303 K: ▲, 5.0; ●, 6.0; ■, 7.0.

the local pH value has decreased from 9.5 and 9.0 (under stationary condition) to 6.2 and 6.1 for sodium and potassium chlorides, respectively, with the increase of cathode rotation to 1.38 m s^{-1}. This deviation between local pH and bulk pH is due to the generation of OH$^-$ ions and the accumulation of the same adjacent to the electrode (cathode) surface under stationary conditions.[16] In the case of alkaline earth-metal chlorides, the decrease in local pH with rotation is well-pronounced, i.e., the local pH decreases from 12.0, 12.5, and 13.0 (under stationary condition) to 6.0, 6.2, and 6.4 for magnesium, strontium, and barium chlorides, respectively. Figures 6 and 7 are typical examples that show the effect of cathode rotation on the local pH for sodium and barium chloride. This is because, at very low cathode rotations, the accumulation of OH$^-$ ions adjacent to the cathode surface is high due to poor solubility of alkaline earth-metal hydroxides. These results are in conformity with earlier results.[16]

4. Conclusion

From the results, it is concluded that the cathodic hydrogen evolutions in sodium and potassium chloride electrolyte yield similar curves. The cathodic hydrogen evolution reaction in magnesium, strontium, and barium chloride electrolytes takes place at more negative potentials (about 120–150 mv) than that in sodium and potassium chloride. This is due to the difference in local pH and hydroxide precipitation near the cathode surface. The hydroxide precipitation on the cathode surface in the case of alkaline earth-metal salts was overcome by the rotation of the cathode at 1.38 m s^{-1}. These studies are very useful in the
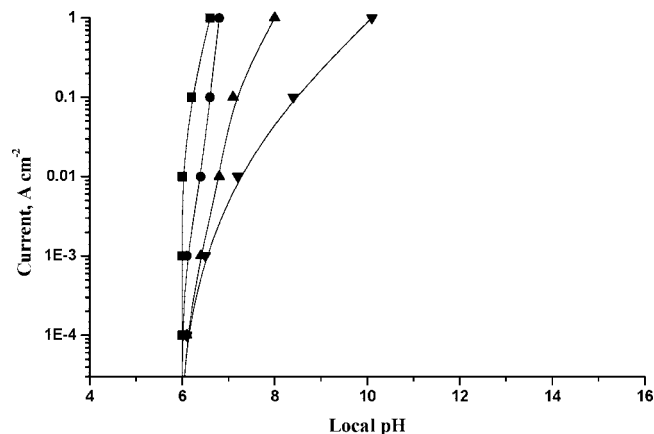
Figure 6. Variation of local pH with current density of sodium chloride electrolyte at different rotations at 303 K: ▼, 0.0 m·s^{-1}; ▲, 0.67 m·s^{-1}; ●, 1.103 m·s^{-1}; ■, 1.38 m·s^{-1}.

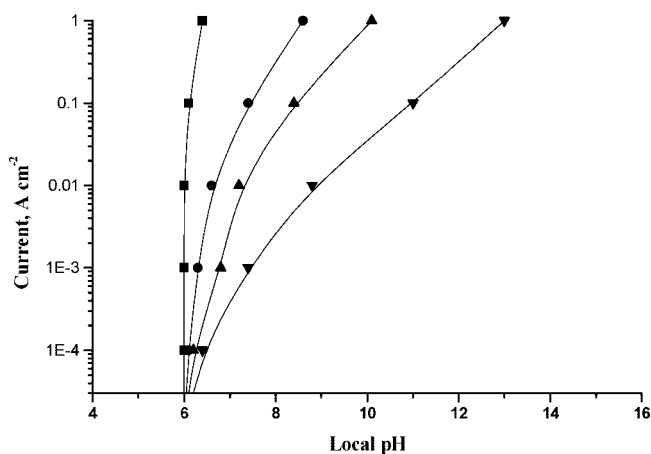**Figure 7.** Variation of local pH with current density of barium chloride at different rotations at 303 K: ▼, 0.0 m·s^{-1}; ▲, 0.67 m·s^{-1}; ●, 1.130 m·s^{-1}; ■, 1.38 m·s^{-1}.

case of oxidation of chloride to chlorate and further oxidation to perchlorate of alkaline earth-metal cations.

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