

Effect of Cations of Alkali and Alkaline-Earth Metal Chlorides for Chlorine Evolution Reaction

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The chlorine evolution reaction was conducted on a metal-oxide-coated titanium anode (RuO₂/TiO₂/SnO₂) in neutral chloride solutions of sodium, magnesium, strontium, and barium, using steady-state $E-(\log i)$ curves. From the results, it is concluded that the chlorine evolution reaction has no dependence on the cations in alkali and alkaline-earth metal chlorides.

Introduction

The production of chlorates is one of the major electrochemical technology industries in the world. Because the evolution of chlorine is a primary electrochemical reaction in the production of chlorates, this reaction has spurred considerable interest in the understanding of mechanistic and kinetic aspects of the same, as is evident from the large amount of work done in this field for alkali metal chlorides.^{1–4} However, the effect of cations of alkali and alkaline-earth metal chlorides on the evolution of chlorine has not been studied.

Hence, polarization studies have been undertaken using alkaline-earth metal chlorides. The literature data available^{1,3–6} on the Tafel slope for mixed-oxide-coated anodes are listed in Table 1.

Materials and Methods

A Princeton Applied Research (PAR) Model 371 Potentiostat-Galvanostat and a Wenking scan generator (Model VSG 83), in combination with a Kontron digital multimeter for potential indicating and a Model 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 (G3). The experiments were conducted on a noble mixed-oxide-coated titanium plate (RuO₂/TiO₂/SnO₂) working electrode (with a working area of 1.0 cm²), with a standard calomel electrode (SCE) as the reference electrode and a platinum foil counter-electrode. The temperature was maintained at 301 K. The experiments were conducted in various concentrations (1.0–3.0 M) of sodium, magnesium, strontium, and barium chloride solutions, using a scan rate of 100 mV/s. The salt solution (100 cm³) was taken in the cell and deaerated with pure nitrogen. The electrode was allowed to attain a steady potential value for 5 min. Polarization experiments were conducted between the potential range of +1.0 V to +1.2 V (vs SCE), and the E vs $\log i$ plots were recorded.

Preparation of Noble Metal-Oxide-Coated Electrodes

The coating solution for the preparation of the anodes was prepared from the chlorides of three metals (viz., RuCl₃·xH₂O (38.4% Ru) (Johnson Matthey, U.K.), TiCl₄ (25.1% Ti) (Riedel

De Haan AG, Germany) and SnCl₄·5H₂O (33.9% Sn) (J.T. Baker Chemical Co., USA). The salts of the aforementioned three metals were taken in the ratio of 30 RuO₂/50 TiO₂/20 SnO₂, dissolved in isopropanol (Johnson Matthey, U.K.), and then painted over the pretreated titanium mesh (which was polished, degreased, and etched in a 10% oxalic acid (Johnson Matthey, U.K.) solution at 363 K for 30 min) to produce a uniformly spread layer. The paint layer was dried at 353 K in an air oven for 10 min, to evaporate the solvent. The samples were then transferred to a muffle furnace that was maintained at 673 K for 10 min. During this period, the heating zone of the furnace was maintained with a good supply of air from a compressor. The electrode was then removed from the furnace and cooled. The process of brushing the coating solution, drying at 353 K, and then heating in the presence of air at 673 K was repeated 6–8 times. After the final coating, the electrode was heated at 723 K for 1 h and allowed to cool in the oven, by itself, over a period of 8 h.

Results and Discussion

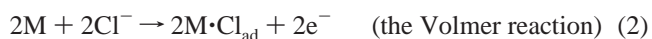
Chlorine evolution reactions at the mixed-oxide-coated anode in various concentrations of sodium, magnesium, strontium, and barium chlorides at 303 K were performed. The typical polarization curves are presented in Figures 1–4.

The overall reaction that describes the evolution of chlorine, via the oxidation of the Cl[–] ion, is given as



The steps involved in the anodic evolution of chlorine are analogous to those in the cathodic evolution of hydrogen, except that the ion discharge step(s) is(are) anodic. Also, the reactant ion (Cl[–]) may be more strongly chemisorbed than H₃O⁺, under certain conditions at noble-metal oxide surfaces. The following are obvious steps and mechanisms considered by various workers^{2–4} at metal surfaces or surface oxide sites (M).

Mechanism I.

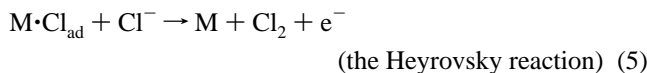
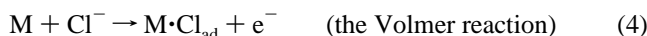


In this mechanism, which is known as the Volmer–Tafel mechanism, the first step corresponds to the discharge of chlorine at the free sites on the electrode surface to form adsorbed Cl atoms. Subsequently, the adsorbed Cl atoms collide with each other and combine to form a chlorine molecule. Thus the second step is a chemical step and does not involve charge transfer.

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Table 1. Tafel Slopes for Chlorine Evolution Reaction on Mixed-Oxide-Coated Electrodes

sample	electrode	electrolyte	concentration (M)	temperature (K)	Tafel slope (mV)	ref
1	RuO ₂	NaCl	3	303	38	7
2	RuO ₂	NaCl	5	303	40	8
3	RuO ₂	NaCl	5	353	30	9
4	RuO ₂	HCl + NaCl + Cl ₂	1.5 + 2.5	303	33	10
5	RuO ₂ /IrO ₂ /SnO ₂	NaCl	4	293	32	11
6	RuO ₂ /TiO ₂	HCl	1	298	38	12
7	RuO ₂ /TiO ₂	NaCl	5	293	46	13
8	Pt/SnO ₂ /SbO _x	NaCl	3	303	31	7
9	SnO ₂ /SbO _x /RuO ₂	NaCl	3	303	31	7
10	RuO ₂ /TiO ₂ /SnO ₂	NaCl	5	293	40	13

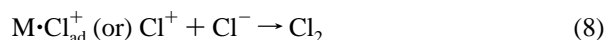
Mechanism II.

In this mechanism, which is known as the Volmer–Heyrovsky mechanism, the first step is the same as that in mechanism I (i.e., Cl atoms are discharged at the free sites on the electrode surface to form adsorbed Cl atoms). In the second step, another Cl atom comes into contact with the adsorbed Cl atom and gets discharged to form a chlorine molecule (Cl₂), as shown in eq 4. The second step is the charge-transfer step, thereby suggesting a consecutive charge-transfer scheme for the reaction mechanism.

Mechanism III. A third type of mechanism was considered by Krishtalik et al.,^{14–16} based on the possible formation of the chloronium ion (Cl⁺):



or



According to this mechanism, the reaction proceeds first through a fast discharge of the Cl[−] ion on the surface with the formation of adsorbed atomic chlorine, followed by oxidation to the Cl⁺ ion, which reacts rapidly to form Cl₂. The reaction order, stoichiometric number, and Tafel slope data supported this mechanism; however, the involvement of the Cl⁺ ion in aqueous solution is questionable, because of its great instability as a strong Lewis acid in water.

Because the proposed mechanisms and also the values of the experimentally obtained Tafel slopes differed with various workers, the mechanism of the chlorine evolution reaction on RuO₂–TiO₂ electrodes, as well as on the RuO₂ electrode itself, was re-examined by Janssen et al.^{5,17} They compared the theoretical Tafel slopes and reaction orders, with respect to Cl[−] and Cl₂, with the experimental values. Because only a high Tafel slope (viz., 118.4 mV) is observed when the Volmer reaction is the rate-determining step, this was omitted from consideration. For both the Volmer–Tafel and Volmer–Heyrovsky mechanisms, the same minimum Tafel slope was observed (viz., 29.6

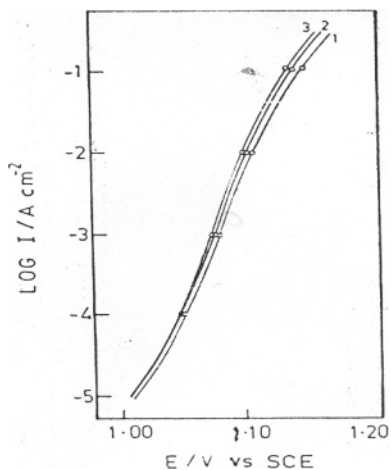


Figure 1. *E* vs log *i* curves for chlorine evolution reaction at 303 K in a sodium chloride solution at a scan rate of 100 mV/s: curve 1, 1.0 M (as Cl[−]); curve 2, 2.0 M (as Cl[−]); and curve 3, 3.0 M (as Cl[−]).

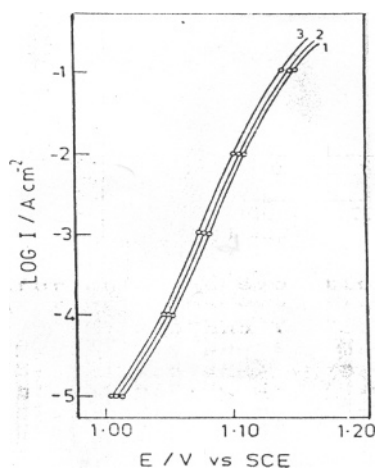


Figure 2. *E* vs log *i* curves for chlorine evolution reaction at 303 K in a magnesium chloride solution at a scan rate of 100 mV/s: curve 1, 1.0 M (as Cl[−]); curve 2, 2.0 M (as Cl[−]); and curve 3, 3.0 M (as Cl[−]).

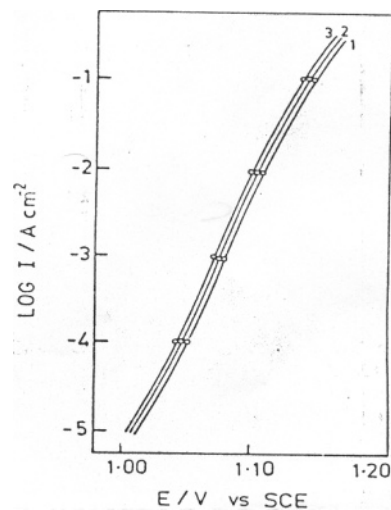


Figure 3. *E* vs log *i* curves for chlorine evolution reaction at 303 K in a strontium chloride solution at a scan rate of 100 mV/s: curve 1, 1.0 M (as Cl[−]); curve 2, 2.0 M (as Cl[−]); and curve 3, 3.0 M (as Cl[−]).

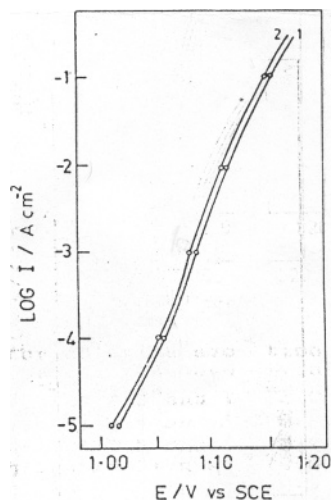


Figure 4. E vs $\log i$ curves for chlorine evolution reaction at 303 K in barium chloride solution at a scan rate of 100 mV/s: curve 1, 1.0 M (as Cl^-); curve 2, 2.0 M (as Cl^-); and curve 3, 3.0 M (as Cl^-).

mV). For the Volmer–Tafel mechanism, this slope has been found when the rate-determining step is either the Tafel reaction or the chlorine diffusion. The slope is determined either by the Tafel reaction or by chlorine diffusion. A slope of 29.6 mV has also been observed for the Volmer–Heyrovsky mechanism when the chlorine diffusion is the rate-determining step. When no limitation of chlorine diffusion occurs, a minimum Tafel slope of 39.5 mV has been obtained for the Volmer–Heyrovsky mechanism where the Heyrovsky reaction is the rate-determining step. Subsequently, for the Volmer–Heyrovsky mechanism, the Tafel slope can be used to decide whether the Heyrovsky reaction (slope of 40 mV) or chlorine diffusion reaction (slope of 30 mV) is the rate-determining step. On RuO_2 and $\text{RuO}_2\text{--TiO}_2$ anodes, experimental Tafel slopes of 30 and 40 mV, respectively, have been observed. Both slopes can be explained by the Volmer–Heyrovsky mechanism where the Volmer reaction is in quasi-equilibrium.

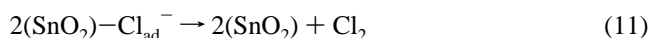
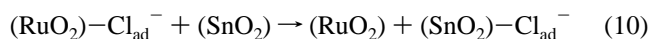
Apart from the aforementioned general mechanism, later investigators of RuO_2 -based electrodes proposed various reaction schemes, taking into account other parameters, such as participation of the oxide surface and pH effects.⁴ Although the usual Tafel slopes of 30–40 mV could be explained with any of the mechanisms indicated above, Tafel slopes of <30 mV have been attributed to the different compositions of the electrodes or to recombination control (the Volmer–Tafel mechanism).

An alternative explanation for the lower Tafel slopes has been offered by Losev.¹⁸ According to this author, the E vs $\log i$ curve for chlorine evolution can have three sections, depending on what controls the reaction: (a) concentration overpotential, (b) the saturation (or supersaturation) of chlorine, and (c) activation overpotential. Because of the large exchange current density value for chlorine evolution, region c (that which is determined by the activation overpotential) may not be attained within the acceptable experimental range of currents, and the average Tafel slope between regions a and b (defined by the concentration overpotential and the saturation/supersaturation of chlorine, respectively), as described previously, may be mistaken as the true Tafel slope. Under these conditions, the experimental Tafel slope can be <30 mV. When the solubility of chlorine is less (at high temperature), the slope value may be much lower. The solubility of the gaseous chlorine determines the current density of transition from region a to region b. The

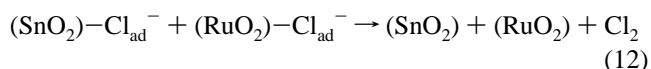
current density of transition from region b to region c is determined by the exchange current density.

The observed Tafel slopes in the mixed-oxide catalysts ($\text{RuO}_2/\text{TiO}_2/\text{SnO}_2$) used in this work are in the range of 30 mV, which is consistent with the reported value for the evolution of chlorine.

In the case of mixed-oxide electrodes with SnO_2 , the mechanism, as reported by Iwakura et al.⁷ and Chertykovtseva et al.,¹⁹ is given as follows:



(or)



Conclusion

Based on the observed Tafel slope value in chloride solutions of sodium, magnesium, strontium, and barium, one can conclude that the chlorine evolution reaction has no dependence on cations (for example, alkali and alkaline-earth metals).

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