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ORIGINAL PAPER

A simplified model to predict the current–voltage relationship of an electro-chlorination cell

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Abstract A simplified model is described to predict the Current–Voltage (*I*–*V*) relationship of a parallel plate electro-chlorination cell containing aqueous NaCl solution as electrolyte. The simplifications allowed obtaining an analytical solution without recourse to computationally intensive numerical solutions like finite element method. The anodic and cathodic exchange current densities and symmetry factors for the model were obtained using linear sweep voltammetry experiments for two different electrodes, viz. graphite and mixed metal oxide coated titanium. Using them, anodic and cathodic overpotential values (for a particular device current *I*) were predicted using the Butler–Volmer equation. The solution potential drop for the same device current was determined using a modified Nernst–Plank equation. The predicted device voltage (for the device current *I*), which is the sum of equilibrium electrode potentials, electrode overpotentials and solution potential drop, was compared with experimental (*I*–*V*) data for the two electrochemical cells as mentioned above. Results showed that the simplified model could predict the *I*–*V* data well, when the electrode surface area was assumed to be twice the superficial area.

Keywords Electro-chlorination · Voltammetry · Exchange current density · Overpotential · Butler–Volmer equation · Nernst–Plank equation

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1 Introduction

Chlorine and hypochlorite are extensively used for chemical oxidation, bleaching, disinfecting water etc. Due to hazards of storing and transporting chlorine and various hypochlorite species (HOCl, OCl^-), On Site Generation (OSG) through electrochemical route provides a simple and safe alternative [1, 2].

The generation of chlorine, from the electrolysis of aqueous NaCl solution is a known electrochemical process [1], which involves application of voltage/current across the electrodes, leading to generation of chlorine at the anode. The chlorine generated reacts in solution to produce hypochlorite. The current paper focuses on prediction of the current–voltage relationship for two electrochemical cells, one consisting of a pair of graphite electrodes and another consisting of a pair of mixed metal oxide (MMO) coated titanium electrodes.

Various attempts to model the electrochemical process as well as design equipments have been made through rigorous pseudo two-dimensional FEM (Finite Element Method) solutions and one-dimensional steady state solutions [3, 4]. Byrne et al. [5] presented a numerical model to calculate the current density distribution and concentration profiles of ionic species in an electrochemical cell. Their model accounts for diffusion, migration and convection and establishes that migration contributes significantly to species transport.

In the current paper, a simplified analysis is adopted, neglecting convective and diffusive ion transport and their effect. It is shown that this simplification allows for an analytical solution of the problem, while effectively predicting the voltage requirement for an electro-chlorination cell as described above. The validation of the model with experimental results testifies this.

2 Experimental methods

An electro-chlorination cell, consisting of two parallel rectangular electrodes—either a pair of hard graphite electrodes (Graphite India Ltd.) or a pair of MMO coated titanium electrodes (Titanium Tantalum Products Ltd. Chennai, India) of superficial area (A) 2.0×10^{-4} m^2 each and separated by a gap (L) 1.0×10^{-2} m was fabricated in acrylic. The cell was filled with NaCl solution of concentration 2.5×10^{-1} M, prepared using NaCl crystals (Merck, GR) and de-ionized water (Scientific Distillery Works, Bangalore, India). Current–Voltage characteristics of the cell were studied using a regulated DC power supply, with in-built voltage and current meters (Dot Tech, 0–30.0 V, 0–5.0 A). The power supply was used to apply current/voltage and measure voltage/current.

The current–overpotential relationship for the electrode were experimentally obtained using an electrochemical workstation (Princeton Applied Research, 263 A), using a graphite or MMO coated Titanium working electrode, Ag/AgCl reference electrode (2.2×10^{-1} V with respect to Standard Hydrogen Electrode, SHE) and Pt counter electrode, dipped in 2.5×10^{-1} M NaCl solution.

3 Model development

Application of adequate voltages across electrodes immersed in aqueous NaCl solution results in the generation of chlorine and hydrogen gases at the electrode surfaces as given by the reactions below.

$$Cl_2(g) + 2e^- \rightarrow 2Cl^- \quad (E_{0a} = +1.36\,V) \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (E_{0c} = -0.83\,V) \tag{2}$$

Chlorine which is generated at anode reacts in solution with hydroxyl ions to form hypochlorous acid. The hypochlorous acid dissociates to give hypochlorite ions (OCl^-) in solution ($pK_a = 7.5$).

$$Cl_2 + OH^- \rightarrow Cl^- + HOCl \tag{3}$$

The amount of Cl_2 generated at anode is directly proportional to the current, as given by Faraday's law [6].

$$w = \frac{Ite}{96500} \tag{4}$$

Where w is the amount of Cl_2 produced (g), e is the equivalent weight of chlorine (35.5) and I (A) is the current passed for time t (s). The relationship between the current passed and the amount of chlorine produced in solution is given by (4). However, the voltage applied to drive the required current through the cell requires a deeper understanding of electrodic and ionic processes.

The current–voltage (I–V) relationship for the electrolytic cell was predicted using the approach described below. The applied potential drops across the anode–solution interface, cathode–solution interface and in the bulk solution. The potential drop across an electrode–solution interface is a sum of the equilibrium electrode potential and the electrode overpotential. Thus, the applied device voltage can be written as follows

$$V = E_{0a} + \eta_a + \eta_c + E_{0c} + \varphi_s \tag{5}$$

Where, η_a and η_c are the overpotentials applied to the anode and the cathode respectively. φ_s is the bulk solution potential drop. E_{0a} and E_{0c} are the values of equilibrium electrode potentials for anode and cathode (with respect to SHE) respectively.

The solution potential drop φ_s is predicted from (7) considering the Cl^- ion transport in the bulk NaCl solution (and is arrived from the Nernst–Plank equation), where F is the Faraday constant, u_{Cl^-} is the ionic mobility, C_{Cl^-} is the concentration, D_{Cl^-} is the diffusion constant and Z_{Cl^-} is the valency of the Cl^- ion.

$$I = A\left[FZ_{Cl^-}D_{Cl^-}\,\mathrm{grad}(C_{Cl^-}) + F^2Z_{Cl^-}^2u_{Cl^-}C_{Cl^-}\,\mathrm{grad}(\varphi_s)\right]; \quad \mathrm{grad}(\varphi_s) = \left(\frac{\varphi_s}{L}\right) \tag{6}$$

In Nernst–Plank equation (6), the first term is the diffusion term and the second one is the electromigration term. A calculation of the magnitude of the two terms (values of constants are given in Table 1), assuming that the gradients of both solution potential and concentration are constants and are equal to the solution potential drop (5.0 V) and the maximum allowable accumulation/depletion concentration (2.5×10^{-1} M) across the considered electrode gap (1.0×10^{-2} m) respectively, led us to the two terms being 9.5×10^{-1} A m^{-2} (electromigration) and 4.8×10^{-3} A m^{-2} (diffusion) respectively, with the electromigration flux largely dominant over the diffusion flux. The diffusion flux term was hence dropped from further analysis. Thus, simplifying (6), the expression for the device current is given as,

Table 1 Values of constants (at 298 K) used for calculating diffusion and electromigration flux [7–9]

Constant	Value	Unit
F	96500	C mol^{-1}
Z_{Cl^-}	1	–
D_{Cl^-}	2.0×10^{-9}	$m^2\ s^{-1}$
C_{Cl^-}	2.5×10^{-1}	M
u_{Cl^-}	8.2×10^{-13}	$m^2\ mol\ s^{-1}\ J^{-1}$

$$I = AF^2 Z_{\mathrm{Cl}^-}^2 u_{\mathrm{Cl}^-} C_{\mathrm{Cl}^-} \left(\frac{\varphi_s}{L}\right) \tag{7}$$

Using this approach, for a given I, the potential drop (φ_s), across the bulk solution was predicted.

The current–overpotential relationship across an electrode–solution interface is given by the Butler–Volmer equation (8), where, J is the current density, J_0 is the exchange current density, α is the symmetry factor, n is the number of electrons transferred, R is the gas constant (8.3 J mol^{-1} K^{-1}) and T is absolute temperature. The exchange current density is dependent on the reaction at the electrode, the electrode material and concentration of electrolyte. The current density is the current through the electrode per unit surface area.

$$J = J_0\left[e^{\frac{-(1-\alpha)nF\eta}{RT}} - e^{\frac{\alpha nF\eta}{RT}}\right];\ I = J \times A \tag{8}$$

$$I_c = I_a = I \tag{9}$$

Equation 9 is the continuity equation for the electrochlorination cell, where I_c, I_a, I are the cathode anode and the device current respectively. In this case, η_a and η_c (as a function of current), can be predicted by knowing J_0 and α, for both anodic and cathodic reactions respectively for the electrode–NaCl solution interface.

4 Results and discussion

In order to determine the overpotentials, it is important to know the J_0 and α, which were determined using an electrochemical workstation, with graphite as working electrode (area 2.6×10^{-4} m^2). All the experiments were conducted at an ambient temperature (T) of 298 K. The linear sweep voltammogram (LSV, working electrode potential-E, vs. current-I plot) was obtained at 2.0×10^{-2} V s^{-1} scan rate (Fig. 1a) and the current density versus overpotential data was plotted (for overpotentials above 5.0×10^{-2} V) using the Tafel equation as given below.

$$\ln[J] = \left(\frac{\alpha nF}{RT}\right)\eta + \ln[J_0] \tag{10}$$

J_{0a}, J_{0c}, α_a and α_c were computed at $T = 298$ K and were found to be 9.1 A m^{-2}, 6.0 A m^{-2}, 1.5×10^{-1} and 5.0×10^{-2} from the cathodic (Fig. 1b) and anodic (Fig. 1c) Tafel Plots. Using these values in Butler–Volmer equation (8) the overpotentials for both anode and cathode, for the particular device current (I) were solved.

Finally, the solution potential drop (φ_s), η_a, η_c, and the equilibrium electrode potential values for cathode and anode were added to predict the total device voltage using Eq. 5 for the device current I.

Significant difference between the superficial surface area (A) and the actual area (A_T), can contribute to error in predicting the device voltage. It has been reported that the actual area can be at least twice that of the superficial area [10]. A surface area correction factor $f_{sa} = (A_T/A)$ was hence introduced. Device voltage was calculated using this actual surface area (A_T) and the best fit between theory and experiment is obtained for $f_{sa} = 2.0$ (Fig. 1d).

It is to be noted here that the fit, though reasonable, does show departures from the experimental measurement. This

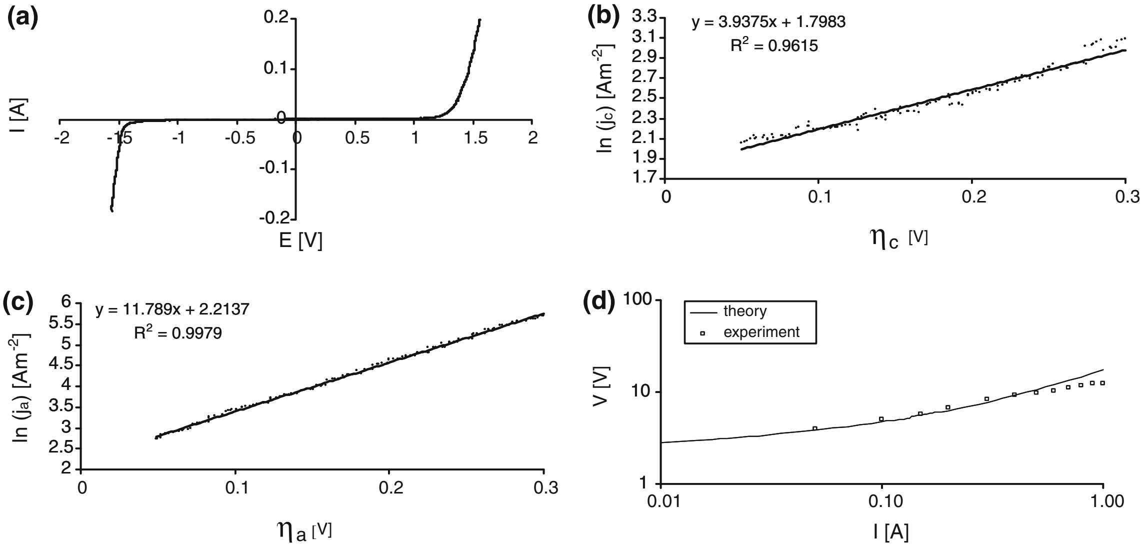

Fig. 1 **a** Linear sweep voltammetry trace for high density graphite working electrode in 2.5×10^{-1} M aqueous NaCl solution. **b** Plot of current density and cathodic overpotential, extracted from experimental LSV (cathodic Tafel plot). *Dots* represent experimental data and solid line represents the linear fit. **c** Plot of current density and anodic overpotential, extracted from experimental LSV (anodic Tafel plot). *Dots* represent experimental data and solid line represents the linear fit. **d** Comparison of experimental *I*–*V* data and theoretical fit for graphite electrolytic cell

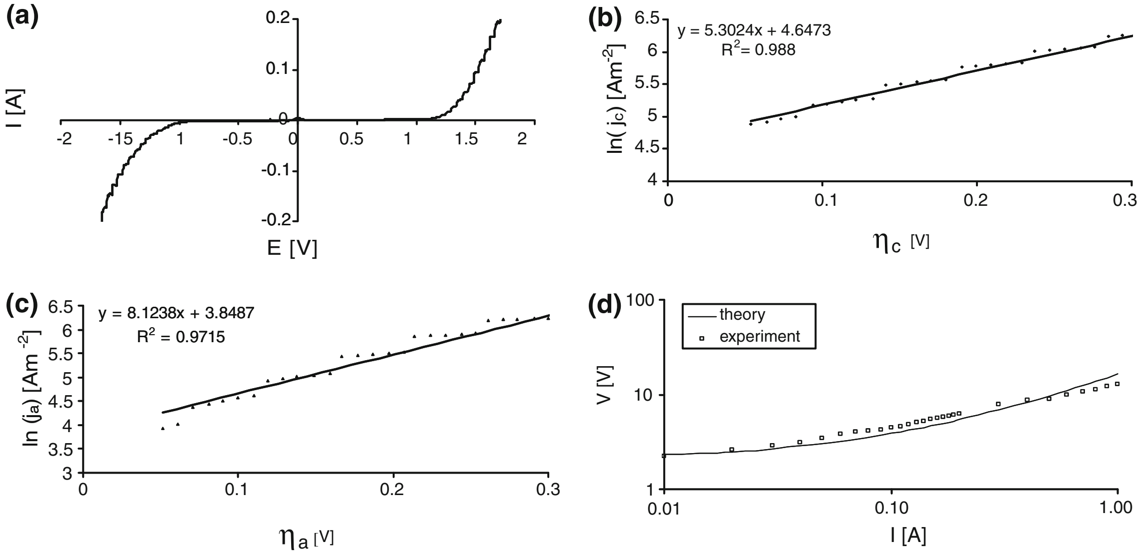

Fig. 2 **a** Linear sweep voltammetry trace for MMO coated titanium working electrode in 2.5×10^{-1} M aqueous NaCl solution. **b** Plot of current density and cathodic overpotential, extracted from experimental LSV (cathodic Tafel plot). *Dots* represent experimental data and *solid line* represents the linear fit. **c** Plot of current density and anodic overpotential, extracted from experimental LSV (anodic Tafel plot). *Dots* represent experimental data and *solid line* represents the linear fit. **d** Comparison of experimental *I–V* data and theoretical fit for MMO coated titanium electrolytic cell

could be on account of various factors, which include the basic assumptions made, such as, dilute regime, the independence as well as dominance of the electromigration term over the diffusion term, the discarding of convection contributions in the model (which may be present due to the bubbling at the electrodes) experimental and deduction errors from the voltammetry measurement and the inability to estimate the actual electrode surface area. The use of "surface area correction factor", while arising from experimental reports of similar surfaces as those used in the experiment, does provide a good fit. The factor might also compensate for the other sources of deviation as discussed above.

The theoretical model was validated for another electrochlorination cell, having two MMO coated Ti electrodes with the same geometry dipped in 2.5×10^{-1} M NaCl solution. The values of J_{0a}, J_{0c}, α_a, α_c were computed at 298 K from the Tafel Plots (Fig. 2b, c) obtained from the LSV experiments (Fig. 2a) done with MMO coated Ti working electrode at an ambient temperature of 298 K. The voltage scan rate used was 1.0×10^{-2} V s^{-1} in this case. The values are given by 46.9 A m^{-2}, 104.3 A m^{-2}, 1.0×10^{-1}, 6.8×10^{-2} respectively. Using these values, the best fit is again obtained with $f_{sa} = 2.0$ which is shown in Fig. 2d.

The paper provides significant insights through predicting the *I–V* relationships of a bench-scale electrochlorination cell, a problem of practical applicability. Simplifications used in this model (decoupling the diffusion and electromigration term in Nernst–Plank equation) leads to deriving design rules for electrochemical cells, which is practically quite difficult. Parameters used in the model are also obtained through simple experiments. The model with only one fitting parameter f_{sa} provides an effective tool to an experimentalist that is simple and still capable of producing reasonable results for electrochemical cells with various electrode geometries. While the current effort does not replace the need for very rigorous solution (using FEM etc.), this approach is conceptually simpler and needs considerable lesser computational resources.

5 Conclusions

I–V relationship for an electro-chlorination cell consisting two parallel rectangular graphite electrodes (dipped in 2.5×10^{-1} M NaCl aqueous solution) is predicted from a simple first principle approach. The values of J_{0a}, J_{0c}, α_a, α_c for graphite were obtained experimentally using an electrochemical workstation. These values were used to predict the anodic and cathodic overpotential values by solving the Butler–Volmer equation and the solution potential drop (φ_s) was obtained using a modified Nernst–Plank equation. The overpotentials and the solution potential drop were added to predict the device voltage for a particular device current. In the above model, the actual electrode surface area used was 2.0 times than the superficial area, which provided the best agreement between theory and experiment. The model was also validated in another similar electro-chlorination cell but, with MMO coated Ti electrodes. The analytical model successfully predicted the device *I*–*V* relationship for both cases.

The model is simple and avoids rigorous solution techniques like Finite Element Method, albeit giving accurate results. The exercise also proves that the diffusive transport is relatively small as compared to the electromigration flux and neglecting the contribution of the diffusive transport can result in significantly easing out the solution without compromising on the predictive capability of the model. The model considers a surface area factor f_{sa}, which appears logical considering the various assumptions made while developing the model.

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