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Modelling current efficiency in an electrochemical hypochlorite reactor

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ABSTRACT

A mathematical model was set up for anodic, cathodic and overall current efficiencies of an electrochemical cell for hypochlorite production acting as an ideal stirred reactor. A 0.06–0.20 mol dm⁻³ NaClO hypochlorite solution was obtained in the cell by the electrolysis of 0.25–0.50 mol dm⁻³ sodium chloride solution at a temperature of 20 °C, at a current density of 100 mA cm⁻² and at 8.3 < pH < 8.7. Anodic current losses occur through hypochlorite and water oxidation at the DSA anode, and cathodic current losses result from hypochlorite reduction at the titanium cathode.

Theoretical dependences of the anodic current efficiency on the overall anodic current density, hypochlorite concentration and partial current density for water oxidation were established. Theoretically derived relations and the corresponding experimental results showed that oxygen evolution due to water and hypochlorite oxidation leads to reduced thickness of the anodic diffusion layer and increases the limiting diffusion current for hypochlorite oxidation. Mathematical models for the dependence of the cathodic current efficiency on the cathodic current density and hypochlorite concentration in the bulk solution were also established. The expression for the overall current efficiency of the electrochemical cell for hypochlorite production was derived on the basis of both the anodic and the cathodic current efficiency. The good agreement between experimental results and the values provided by the mathematical models has confirmed the correctness of the proposed models, suggesting that the model can be used to optimise electrolysis parameters. (The term hypochlorite is used to include both hypochlorite and undissociated hypochlorous acid.)

The concentration of dissolved elementary chlorine in the slightly alkaline environment is negligible compared to hypochlorite concentration.

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Keywords: Hypochlorite; Limiting diffusion current; Current efficiency; Mathematical model

1. Introduction

Gaseous chlorine is used to disinfect drinking waters and waters used in food industry facilities and in wastewater treatment. The electrochemical mineralisation of organic pollutants as a wastewater treatment method has been developed recently. It is particularly suitable for the treatment of highly toxic organic pollutants present in industrial wastewater (Comninellis and Chen, 2010; Polcaro et al., 2004; Brillas et al., 2004; Haenni et al., 2004; Martinez-Huitle et al., 2004; Polcaro et al., 2005; Chen et al., 2005; Boye et al., 2004, 2006). The method employs anodes with high oxygen

evolution overpotential and high chemical reactivity for organic oxidation (Comninellis and Chen, 2010; Polcaro et al., 2004; Brillas et al., 2004; Haenni et al., 2004; Martinez-Huitle et al., 2004; Polcaro et al., 2005; Chen et al., 2005; Boye et al., 2004, 2006; Fóti and Comninellis, 2004).

The interest in local hypochlorite electrogeneration has increased in recent years because of the potential hazards of transporting, storing and handling large volumes of liquid chlorine (Timofeev and Yu Yogud, 1996; Spasojević et al., 2013; Byrne et al., 2001). Different types of cells are commercially used today, the most common being undivided cells which use dilute brine or sea water electrolyte and divided chlor-alkali

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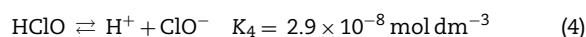
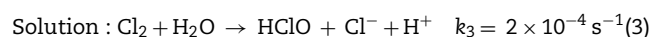
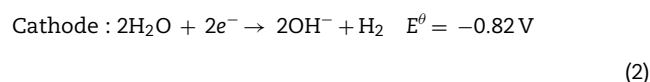
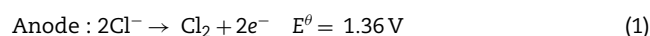
Nomenclature

c_1	concentration of chlorine (mol dm^{-3})
\bar{c}_1	mean concentration of chlorine (mol dm^{-3})
c_2	concentration of hypochlorite (mol dm^{-3})
\bar{c}_2	mean concentration of hypochlorite (mol dm^{-3})
c_0	concentration of hypochlorite in the bulk solution (mol dm^{-3})
D_1	diffusion coefficient of chlorine ($D_1 = 1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)
D_2	diffusion coefficient of hypochlorite ($D_2 = 1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)
j_a	anodic current density (mA cm^{-2})
j_1	partial current density for the oxidation of chloride ions (mA cm^{-2})
$j_{1,5}$	partial current density for the oxidation of chloride ions and hypochlorite (mA cm^{-2})
$j_{5,7}$	partial current density for the oxidation of hypochlorite and water (mA cm^{-2})
j_5	partial current density for hypochlorite oxidation (mA cm^{-2})
j_7	partial current density for water oxidation (mA cm^{-2})
j_c	cathodic current density (mA cm^{-2})
j_2	partial current density for the hydrogen evolution reaction
j_8	partial current density for hypochlorite reduction (mA cm^{-2})
l_a	height of the anode (cm)
l_c	height of the cathode (cm)
F	Faraday constant (C mol^{-1})
k_3	the rate constant of chlorine hydrolysis ($k_3 = 2 \times 10^{-4} \text{ s}^{-1}$),
K_4	the dissociation constant of hypochlorous acid ($K_4 = 2.9 \times 10^{-8} \text{ mol dm}^{-3}$)
S	part of the anode surface where old elements of the solution are replaced by new ones per unit of time
t_1	part of current density $j_{1,5}$, corresponding to chlorine generation
I	current in the electrolyser (mA)
I_a	anodic current (mA),
I_c	cathodic current (mA)
x	distance from the anode (cm)
τ	time (s)
δ_a	thickness of the anode diffusion layer (cm)
δ_c	thickness of the cathode diffusion layer (cm)
η	total current efficiency for hypochlorite generation
η_a	total anodic current efficiency for hypochlorite generation
$\eta_{1,5}$	current efficiency of partial current density $j_{1,5}$, for hypochlorite generation
η_c	current efficiency for the hydrogen evolution reaction

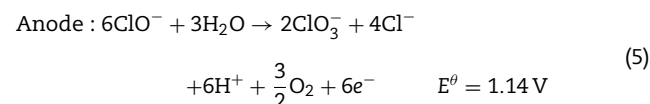
cells which incorporate a membrane and use purified brine anolyte (Timofeev and Yu Yogud, 1996; Spasojević et al., 2013; Byrne et al., 2001; Krstajić et al., 1991; Ferrigino et al., 1999; Yu Bashtan et al., 2001; Krstajić et al., 1986; Spasojević et al., 2012; Thangappan and Sampathkumaran, 2008; Ou et al., 1995;

Belyakova et al., 1998; Grinberg et al., 2001; Chem et al., 2007; Li et al., 2001; Kraft et al., 1999; Bergmann and Koparal, 2005; Bergmann et al., 2001; Jeong et al., 2002; Rajkumar and Kim, 2006). In a divided cell, gaseous chlorine and NaOH solution are continually fed to a water cooled reactor, where the two combine to produce up to 15 wt.% sodium hypochlorite solution which can be used to disinfect drinking water or prevent heat exchanger fouling (Belyakova et al., 1998). In an undivided cell, the electrolyte is pumped between parallel plate electrodes at high velocity to give a large volume of low strength NaClO, due to the fact that the maximum attainable hypochlorite concentration is limited by loss reactions (Grinberg et al., 2001). Undivided cells are more commonly used due to their more economical and easier operation compared to that of divided cells (Spasojević et al., 2013; Chem et al., 2007; Li et al., 2001; Kraft et al., 1999; Bergmann and Koparal, 2005; Bergmann et al., 2001; Jeong et al., 2002; Rajkumar and Kim, 2006).

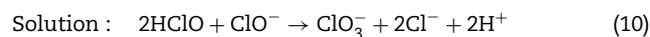
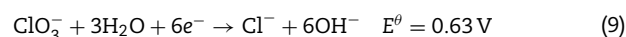
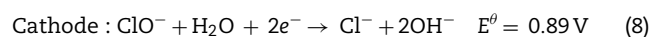
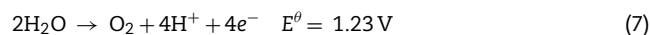
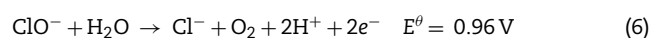
During the electrolysis of diluted NaCl solutions, the following primary reactions take place:



The loss reactions include:



Reactions of such high orders are highly improbable and must certainly proceed in several steps.



The primary reactions (1) and (2) are charge transfer controlled, and the chlorine evolved diffuses through the diffusion layer towards the bulk solution where it is subject to hydrolysis (reaction (3)). The hydrolysis reaction is very fast; therefore, at pH values above 6.5, almost all the chlorine dissolved hydrolyses within the anode diffusion layer, δ_a (Spasojević et al., 1984, 2012, 2013; Krstajić et al., 1986, 1991; Foerster, 1924; Jakšić, 1974; Rudolf et al., 1995a; Ibl and Vogt, 1981; Jakšić, 1976; Despić et al., 1972; Jakšić et al., 1975). Reactions (5) and (8) are usually

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