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# An Overview of How to Measure the Kinetic Properties of an Anode Material for the Chlorine Evolution Reaction

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## Abstract

The process of generating chlorine gas using electrolysis in aqueous systems is well established. However, a new process requires chlorine to be generated at high temperatures using molten salt. This harsh environment requires a new study of anode materials for the chlorine evolution reaction. Anode materials can be compared by their kinetic parameters, the transfer coefficient  $\alpha$  and the exchange current  $i_0$ . The basic theory of these properties as they relate to the chlorine evolution reaction has been detailed and an analysis method for finding these effective parameters has been shown and demonstrated.

**Keywords:** chlorine evolution, exchange current, transfer coefficient

## 1 Introduction

Electrolysis is the main method of chlorine generation. This is typically done in aqueous solutions, and the method and anode material are well established in industry. However, a new process has been proposed that generates chlorine gas *in-situ* in a high temperature application [1] to reduce the hazards of storing and plumbing  $\text{Cl}_2$  gas. This proposed process includes chlorine generation from a molten chloride salt. This high temperature, corrosive environment calls for a new study of the anode material used for chlorine generation in this application.

Anode materials can be compared through their compatibility with the chlorine evolution reaction (CER) and their kinetic properties of the CER in the process environment. Compatibility can be shown as the electrode material has an oxidation potential higher than that of chlorine, is solid at operating conditions, and is resistant to corrosion from the molten chloride and the generated chlorine gas. The focus of this paper, however, is on the kinetic properties of the CER on the anode material, assuming compatibility.

The kinetic properties of focus are the transfer coefficient  $\alpha$  and the exchange current  $i_0$ . Their significance and applicability are defined below in Section 2.

This paper details the method for measuring the kinetic properties of the CER for a given anode material using electroanalytical techniques. The method is then applied to example theoretical data to show an example plot and data analysis to find the relevant kinetic properties.

## 2 Theory

This section details the significance of the kinetic properties  $\alpha$  and  $i_0$  and the applicable equations used to find them from the chlorine evolution reaction. Unless otherwise specified, all equations are drawn from the text *Electrochemical Methods* by Bard et al. [2].

### 2.1 Significance of Kinetic Properties

The transfer coefficient  $\alpha$  and the exchange current  $i_0$  are defined.

#### 2.1.1 Transfer Coefficient $\alpha$

The transfer coefficient  $\alpha$  “is a measure of the symmetry of the energy barrier for a single electron-transfer step” [2] and is dependent on the chemical makeup of the system. In other words, it is the fraction of electrode potential promoting the forward reduction reaction, varying from 0 to 1. If the electrode potential promotes reduction and oxidation reactions equally,  $\alpha=0.5$ . If the forward/cathodic reaction is promoted more,  $\alpha>0.5$ , and if the reverse/anodic reaction is promoted more,  $\alpha<0.5$ . Depending on the model and potential range used,  $\alpha$

can be constant or potential dependent. In our case, a smaller value of  $\alpha$  is preferred (i.e., oxidation promoted more).

### 2.1.2 Exchange Current $i_0$

The exchange current  $i_0$  is a measure of magnitude of the anodic and cathodic currents when no net current is flowing and is directly proportional to the standard rate constant  $k^0$ , which is a measure of reaction kinetics. In the Butler-Volmer model for a one-step, one-electron process:

$$i_0 = F A k^0 C_O^{*(1-\alpha)} C_R^{*\alpha} \quad (1)$$

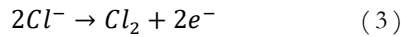
where  $F$  is Faraday's constant,  $C_O^*$  is the bulk oxidized species concentration, and  $C_R^*$  is the bulk reduced species concentration.  $i_0$  can be normalized with area to become the exchange current density:

$$j_0 = i_0/A \quad (2)$$

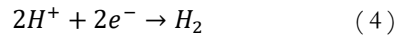
where  $j_0$  is the exchange current density and  $A$  is the electrode area. The exchange current density is best when directly comparing anode materials, as it removes the correlation with area from  $i_0$ . In our case, a larger exchange current density is preferred as it indicates a faster reaction.

## 2.2 Chlorine Evolution Reaction

The CER is a multi-electron transfer reaction:



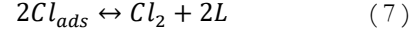
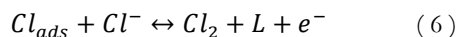
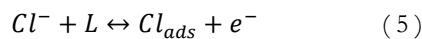
As such, the reaction can be represented by elementary steps. The CER is analogous to the cathodic hydrogen evolution reaction (HER):



The HER and its reaction mechanism has been studied in-depth and can be directly related to the CER. The relations used for the kinetics of the CER have been taken from the relations derived for the HER.

### 2.2.1 Reaction Mechanisms

The reaction mechanisms of the CER are as follows [3]:



where  $L$  is a surface site and  $Cl_{ads}$  is an adsorbed chlorine. Eq. (5) is the Volmer reaction, Eq. (6) is the Heyrovský reaction, and Eq. (7) is the Tafel reaction, all analogous to the reactions of the HER.

### 2.2.2 Reaction Kinetics

As this is not a one-electron, one-step reaction, it is impossible to define  $\alpha$  and  $i_0$  exactly as explained above as each step has its own properties. However, we can define an overall  $\alpha$  and  $i_0$  that act as effective properties for the CER and allow for comparison between different anode materials by assuming one of the above reaction steps is rate-limiting. We define these properties by fitting the anodic Tafel equation to the mass transfer limited region of the oxidation side of the Tafel plot. This equation is:

$$\ln i = \ln i_0 + \frac{(1-\alpha)F}{RT} \eta \quad (8)$$

where  $\eta$  is the overpotential,  $R$  is the gas constant,  $T$  is the temperature, and  $i$  is the response current. While this method will not give a true exchange current, it will give an effective parameter that can be used to compare anode materials. The transfer coefficient will be the  $\alpha$  of the rate-limiting step.

The rate-limiting step and potential will determine the fractional surface coverage of the adsorbed chlorine. Which step is rate-limiting could be potential dependent and/or material dependent, but in this case the exact step does not matter. The effective  $\alpha$  and  $i_0$  used for comparison represent whatever is happening for a specific material at the operating conditions and do not need to be completely understood mechanistically for comparison. In this treatment,  $\alpha$  is simply an alternative expression of the Tafel slope and can be greater than unity, and  $i_0$  captures many terms, such as the number of electrons exchanged and the formal potential. For further discussion of the rate-limiting step and the limitations of this approximation, see section 15.2 in Bard et al. [2].

## 3 Methods

This section details how to collect and analyze data used to fit Eq. (8) and find effective values of  $\alpha$  and  $i_0$ . We will use Tafel analysis to find these values.

Typically, this analysis is done on both the anodic and cathodic reactions, but in our case, the oxidized species  $\text{Cl}_2$  is gaseous and will form bubbles around the electrode that will disperse from the electrode surface. This increases the difficulty of measuring the cathodic reaction without bubbling  $\text{Cl}_2$  around the electrode. To simplify the analysis, we will focus only on the anodic reaction using Eq. (8). Current versus overpotential data is collected using linear sweep voltammetry, and then plotted on a Tafel plot to extract the effective values of  $\alpha$  and  $i_0$ .

### 3.1 Linear Sweep Voltammetry

Linear sweep voltammetry is a potentiostatic method where the potential  $E$  is varied with time as shown in Eq. (9), and the current response is recorded.

$$E = E_0 + vt \quad (9)$$

Where  $E_0$  is the starting potential,  $v$  is the scan rate, and  $t$  is the time.

Data can be collected by choosing an  $E_0$  lower than the equilibrium potential of the reaction  $E_{eq}$  and scanning past  $E_{eq}$  to at least where the anodic reaction accounts for more than 90% of the current. This corresponds to a value of at least 4.6 for  $\eta F/RT$  using Butler-Volmer kinetics [2]. This process can also be done in reverse, starting at the highest potential and scanning down to below  $E_{eq}$ , or cyclically and then choosing the direction that gives the cleanest data.

The equilibrium potential is defined using the Nernst equation as follows:

$$E_{eq} = E^{0'} - \frac{RT}{2F} \ln\left(\frac{C_{\text{Cl}^-}^*}{C^0}\right) \quad (10)$$

where  $E^{0'}$  is the formal potential,  $C_{\text{Cl}^-}^*$  is the bulk concentration of  $\text{Cl}^-$  ions,  $C^0$  is a standard concentration (typically 1 M), and the activity of  $\text{Cl}_2$  is assumed to be unity. If the formal potential and/or chloride concentration is not available, the beginning of the peak can be assumed to be  $E_{eq}$ . Overpotential is defined as:

$$\eta = E - E_{eq} \quad (11)$$

### 3.2 Tafel Plot and Analysis

The Tafel plot is made by graphing the natural log of the current versus the overpotential. The graph

should have a section of the data that is linear, as shown in the example below in Section 4. The slope of this region, known as the Tafel slope, can be used to directly calculate the effective  $\alpha$  through Eq. (8). This gives:

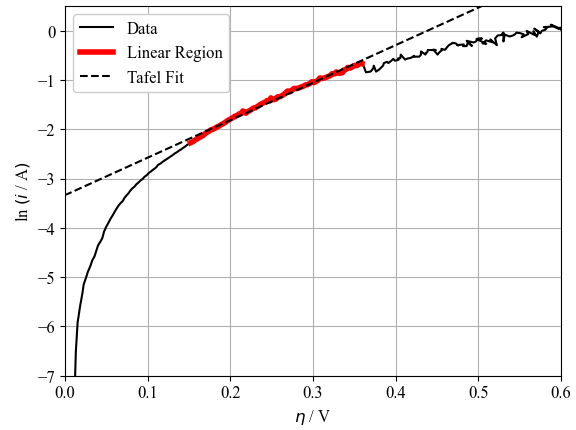
$$\alpha = 1 - (\text{slope}) \frac{RT}{F} \quad (12)$$

We can use the intercept of this region to calculate  $i_0$  through Eq. (8) as well:

$$\ln i_0 = \text{intercept} \quad (13)$$

## 4 Example Results

Figure 1 shows example data that can be used to calculate the kinetic parameters  $\alpha$  and  $i_0$ . The linear region was selected, and a linear Tafel fit was regressed using the data from that region to find the slope and intercept. These values were then used to calculate the transfer coefficient and the exchange current with Eqs. (12) and (13). The resulting values are shown in Table 1.



**Figure 1:** Natural log of current vs overpotential for the CER on a platinum anode ( $A \sim 30 \text{ mm}^2$ ) in molten  $\text{CaCl}_2$  at  $900^\circ\text{C}$ . The linear region is highlighted in red, and the Tafel Fit is shown with a dashed line. This analysis assumes all current is from the CER, while platinum has been shown to oxidize as well [4].

**Table 1:** Fitted Kinetic Parameters from Figure 1

Transfer Coefficient $\alpha$	Exchange Current $i_0 / \text{mA}$
0.231	35.6

To compare exchange currents between materials, use Eq. 2 to find the exchange current density  $j_0$ .

## 5 Conclusions

The basic theory of CER kinetics has been detailed, and an analysis method for finding the effective values of the transfer coefficient  $\alpha$  and the exchange current  $i_0$  for a given anode material for comparison has been shown, along with the limitations of these values. This analysis method was demonstrated using example data.

Future work will involve applying this analysis method to different anode materials and comparing the kinetic parameters to find the most energy efficient anode material.

## 6 Acknowledgements

The author would like to acknowledge the work done by Bard, Faulkner, and White in the text *Electrochemical Methods* for being the basis of the work in this paper.

## 7 References

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