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On the influence of hydronium and hydroxide ion diffusion on the hydrogen and oxygen evolution reactions in aqueous media

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ABSTRACT

We present a study concerning the influence of the diffusion of H^+ and OH^- ions on the hydrogen and oxygen evolution reactions (HER and OER) in aqueous electrolyte solutions. Using a rotating disk electrode (RDE), it is shown that at certain conditions the observed current, i.e., the reaction rate, does not depend on the kinetics but on diffusion properties; In fact we demonstrate how studying these reactions in 0.1 M non-buffered aqueous electrolytes with pH-values ranging between pH 1 to pH 13, the diffusion coefficients of H^+ and OH^- ions can be determined. Within the experimental error limits, we found no pH dependency on the diffusion coefficients for any of the investigated ions.

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1. Introduction

The aim of this work is to demonstrate the influence of hydronium and hydroxide ion diffusion on the hydrogen and oxygen evolution reactions (HER and OER) in aqueous electrolytes. In general it is assumed that under conditions established in rotating disk electrode (RDE) measurements these reactions are only influenced by the kinetics, i.e. the catalytic properties of the working electrode, and convective properties [1]. In our work we show that under certain conditions, i.e. in 0.1 M non-buffered aqueous electrolytes with pH-values ranging between pH 1 to pH 13, this is no longer the case. In fact RDE measurements can even be used to determine the diffusion coefficients of hydronium and hydroxide ions. Understanding how and under which conditions ion diffusion influences the HER and OER is important both from a fundamental point of view and for applications. More specifically, devices such as fuel cells and electrolysers are based on electrochemical processes involving these ions. Understanding their behaviour is helpful to optimize these processes and devices, respectively. In particular we examined if the diffusion coefficients are concentration (pH) dependent.

Diffusion coefficients of ions in an electrolyte are commonly calculated from experimental data obtained by using a conductivity cell [2] or a diaphragm-cell [3] setup. In a conductivity cell setup, the total current driven by a voltage applied between two electrodes is measured as function of the current channel geometry and the total ion concentration. As a consequence the diffusion of one specific ion cannot be measured directly, but must be calculated comparing measurements with different ion pairs and concentrations. A diaphragm cell relies on the controlled flux of a specific ion through a porous diaphragm between two adjoined chambers filled with supporting electrolyte. The first chamber contains a known concentration of the specific ion of interest, while at the beginning of the measurement the second chamber is free of this ion. As the ion of interest diffuses through the membrane, its concentration in the second chamber is measured as a function of time. The specific ion diffusion coefficient can be calculated given the diaphragm parameters, which have to be meticulously determined. Measurements using a diaphragm cell can be very time demanding [4] and as in the case of the conductivity cell, the diffusion of the ion of interest depends on the diffusion of a respective counter-ion.

An RDE setup in a three electrode configuration combines electrochemistry with well-defined mass transport conditions. In this respect, the RDE-setup has several advantages for studying the HER/OER and measuring specific diffusion coefficients as the ion specific flux of hydronium and hydroxide can be measured directly. Tuning the electrode potential allows the selection of a specific electrode process. At high over potentials the rate of an electrochemical reaction does not depend on the kinetics of the process, but solely on mass transport [1]. The mass transport is provided by the well-defined convection control of the rotating disk. The relation between flux of reactants and rotation rate of the disk (ω) is described by the Levich Eq. (1). The flux observed via the

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diffusion limited current density (J_{dl}) of the respective electrochemical reaction is proportional to the diffusion coefficient (D) and the concentration (C) of the reactant:

$$J_{dl} = \underbrace{n(0.620)F\nu^{-1/6}}_{B} D^{2/3}\omega^{1/2}C \tag{1}$$

where n is the number of transferred electrons per molecule, ν the kinetic viscosity of the electrolyte, and F the Faraday constant [5].

In the presented study, we focus on two electrochemical reactions: the HER and OER, since their reaction paths change depending on the surface concentration of H^+ and OH^- ions, respectively. In the case of the HER in an acidic environment, protons are combined to form hydrogen (2). This reaction is reversible and the back reaction is called hydrogen oxidation reaction (HOR).

$$H^+ + 2e^- \leftrightarrows H_2(g) \quad E_0 = -0.000 V_{SHE} \tag{2}$$

The HOR/HER couple at standard conditions defines the standard hydrogen electrode (SHE) to which electrochemical potentials are typically referred. For clarity reasons, we therefore use the subscript SHE to the unit Voltage (V) when describing electrochemical voltages.

In contrast, the hydrogen source of the HER in alkaline solution is water. The water splits to form hydrogen and hydroxide:

$$2H_2O + 2e^- \leftrightarrows H_2(g) + 2OH^- \quad E_0 = -0.828 V_{SHE} \tag{3}$$
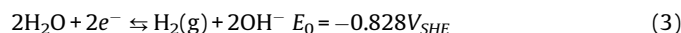
The OER is often related to the HER, for example in an electrolyser [6,7]. In alkaline solution, the OER consumes hydroxide to form oxygen and water. This reaction is reversible as well and the back reaction is called oxygen reduction reaction (ORR). The reactions are expressed as

$$O_2 + 2H_2O + 4e^- \leftrightarrows 4OH^- \quad E_0 = 0.401 V_{SHE} \tag{4}$$
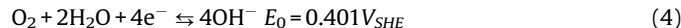
In acidic electrolyte, oxygen and protons form water (ORR) or water is consumed to form oxygen and protons (OER):

$$O_2 + 4H^+ + 4e^- \leftrightarrows 2H_2O \quad E_0 = 1.229 V_{SHE} \tag{5}$$
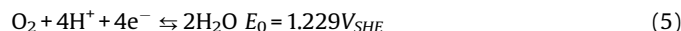
In the following we study we study the HER and OER at moderate acidic/alkaline pH in aqueous electrolyte solution.

2. Experimental

The electrochemical setup consisted of a one-compartment electrochemical cell out of Teflon [8]. An RDE setup was used with a polished polycrystalline platinum disk (PC Pt) as working electrode (WE). The WE had a surface area of 0.196 cm^2. The counter electrode (CE) was a platinum mesh and the reference electrode a saturated calomel electrode (SCE) or an Hg/HgO electrode, respectively. The SHE was experimentally determined to −0.245 V versus the used SCE RE and –0.311 V versus the used Hg/HgO. All measurements are presented versus the Standard Hydrogen Electrode (SHE).

Two base stock electrolytes, 0.1 M NaOH and 0.1 M HClO$_4$, were prepared from NaOH salt (suprapure Merck) and HClO$_4$ (70% Suprapure^{TM} Merck), and diluted with ultrapure water (MilliQ, 18.2 MΩ cm^{-1}). These electrolyte solutions were then mixed in different ratios to create new electrolytes of various pH, but with a constant total ion concentration of 0.1 M. The pH of these mixtures was determined by comparing the potential of the reversible hydrogen reactions (E_{RH}) Reaction (2) and (3) to the SHE using the Nernst equation. As a double check the pH value was verified by an electronic pH-meter. The relative uncertainty of the determined ion concentration of H^+ and OH^- was estimated to be 3%. The electrolytes were constantly purged by either H$_2$ or Ar, both 99,999% pure (Air Liquid).

The electrochemical experiments were conducted using an in-house developed potentiostat and software. The solution resistance was online recorded (AC: 5 kHz, 5 mV) and compensated for by an analogue positive feedback scheme [9]. The compensation was tuned so that the resulting effective solution was about 15 Ω in order to obtain stable measurements at all current ranges. Cyclic voltammograms (CV) and polarization curves were recorded between −1.5 V$_{SHE}$ and 2.2 V$_{SHE}$ at a rate of 0.1 Vs^{-1}. The voltage ranges were in some cases truncated due the current and voltage compliance limitation of the potentiostat. All measurements were conducted at room temperature (20 °C).

3. Results and Discussion

In the following we present our results of studying the HER and OER in aqueous electrolyte solutions at moderate acidic/alkaline pH. For this purpose, cyclic voltammetry of a PC Pt electrode was performed in four different argon purged electrolytes: 0.1 M NaOH (pH 13.0), 0.1 M HClO$_4$ (pH 1.0) and two mixtures of these electrolytes resulting in pH values of 2.55 and 11.49. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} and a disk rotation velocity of 4900 rpm. As at the positive voltage limit a hysteresis between the positive and negative scan exists, for simplicity reasons we have chosen only to show and discuss the negative going scans throughout the manuscript. The interpretation and discussion of the results is not affected by this choice. The resulting polarization curves are presented in Fig. 1. Fig. 1A displays measurements obtained at high and low pH values, respectively; whereas in Fig. 1B, measurements from intermediate pH values are plotted. We start our discussion with the measurements obtained at low and high pH, i.e., pH 1 and pH 13. The main reactions taking place at the electrode are the HER at low potentials and the OER at
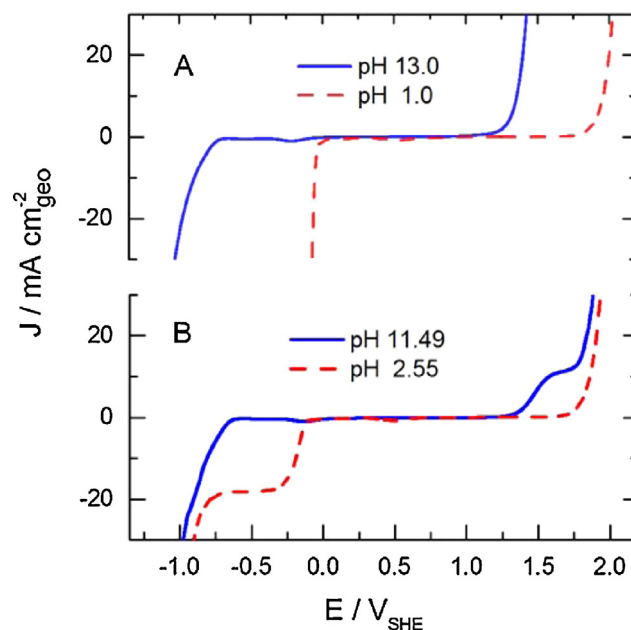

Fig. 1. Polarization curves (negative scan direction) of PC Pt recorded in four different electrolytes at a constant total ion concentration of 0.1 M, but different pH values. The curves were recorded in Ar saturated electrolytes at 0.1 V s^{-1} and 4900 rpm. (A) shows measurements obtained at high and low pH values, respectively; whereas in (B), measurements from intermediate pH values are plotted.