



Solution Resistivity, Ohmic Drop and Oxygen Reduction Rate at High Temperature Pressurized Water



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ABSTRACT

The solution resistivity (R_{sol}) and ohmic drop (ΔE_{Ω}) of a three electrode high temperature electrochemical autoclave system containing a water + 11550 ppb NH_4OH ($\text{pH}_{(25^\circ\text{C})}$ 10) solution were analyzed in the temperature range of 25°C to 285°C using electrochemical impedance spectroscopy (EIS) and galvanostatic potentiometry combined with automatic current interrupt *iR* compensation technique. The determined values were compared with the conductivity values calculated by a pH & Conductivity Calculator software. The results showed that when the temperature of the solution is increased the magnitude of the R_{sol} and therefore ohmic drop of the system decrease and after a defined temperature (150°C for EIS and 180°C for current interrupt) increase. The variations in the conductivity of the solution versus temperature calculated by the pH & Conductivity Calculator software were in more agreement with the impedance based R_{sol} values determined in this study. While investigation of the oxygen reduction reaction on platinum versus temperature showed that exactly at 180°C (the temperature corresponding to minimum R_{sol} and ohmic drop values determined using the current interrupt technique) the oxygen reduction reaction reached its maximum rate and by further increasing the temperature the oxygen reduction rate decreased and the reaction mechanism switched from a mixed mass–charge transfer controlled process to a charge transfer controlled process. The experiment results revealed that the R_{sol} values determined by the current interrupt technique are more accurate than the values obtained by EIS.

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1. Introduction

1.1. Background on the role of ohmic resistance (R_{Ω})

In electrochemistry ohmic drop (ΔE_{Ω}) is a well-known phenomenon which occurs in almost most of the electrochemical measurements. In an electrochemical system the R_{Ω} followed by the ohmic drop ($\Delta E_{\Omega} = i \times R_{\Omega}$) is expressed by the potential drop between the working electrode and the reference electrode (also counter electrode) when current is flowing between the working and counter electrodes. Therefore, considering the ohmic ΔE_{Ω} , the actual effective potential (E_{eff}) at the surface of the electrode will be the difference between the potential applied by the potentiostat (E_{app}) and ΔE_{Ω} [1]:

$$E_{\text{eff}} = E_{\text{app}} - (i \times R_{\Omega}) \quad (1)$$

Consequently, the absolute value of the corrected potential is always smaller than the uncorrected potential.

The conductivity of the electrolyte, the distance between the working electrode and the reference/counter electrode and the magnitude of the applied current are three significant factors affecting the value of ΔE_{Ω} [2].

Depending on the electrochemical system the amount of ΔE_{Ω} can become out of a negligible range especially in presence of large current densities in low conductivity solutions. This means even a small value of the R_{Ω} can cause a large ΔE_{Ω} if a large current is passed through the system, for example in a fuel cell [3].

To minimize this ΔE_{Ω} normally some technical modifications of the electrochemical system are suggested such as increasing the conductivity of the electrolyte, decreasing the size of the working electrode, decreasing the distance between the working and reference/counter electrodes and application of lower scan rates when techniques such as cyclic voltammetry are used.

However, in practice usually zero ΔE_{Ω} cannot be achieved even by carefully placement and designing the electrochemical setup.

These experimental works plus several theoretical studies on the ΔE_{Ω} and its effect on the electrochemical measurements

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have been reported in the literature by many authors, especially in the field of electroanalytical chemistry and energy storage [3–19].

1.2. Solution resistivity (R_{sol}) and conductivity in aqueous solutions

The conductivity of a solution is a measure which shows its ability to transport current and is inversely proportional to the resistivity of that solution. The resistivity and conductivity of liquids are temperature dependent. Increasing the temperature of aqueous solutions increases the number of ions in solution due to dissociation of water molecules and simultaneously decreases the viscosity and therefore increases the mobility of ions in the solution. As the conductivity of a solution is dependent on these factors any increase in the solution temperature will increase its conductivity [20–24].

It is also known that 1 °C rise of the temperature will increase the conductivity of pure water around 2% [23]. Increasing the conductivity and decreasing the viscosity of a solution will increase the mass transportation rate of ions and therefore, reaction rate at metal–solution interface will be increased. Low conductivity (high R_{sol}) in an aqueous solution therefore, results in high R_{Ω} . While lower R_{sol} permits easier current flow during the electrochemical reaction [23,24].

Moreover, the ionic product of pure water (H_3O^+/OH^-) increases as the temperature increases to a defined temperature and after decreases. pH of water is another parameter which decreases with increasing the temperature due to the change in the water dissociation constant. A 1 unit decrease in pH indicates that the hydronium ion concentration has been increased by 10 times [24]. These parameters may vary if water chemistry changes by addition of chemicals.

1.3. Research motivation

Although, the problem of ΔE_{Ω} is not a new issue and has been discussed in the literature, still in some electrochemical systems especially in corrosion research is ignored and assumed negligible. While, practical observations show that large errors may occur if iR correction is overlooked, especially in electrolytes with low conductivity [2,3]. For example, strangely there is no clear data regarding the ΔE_{Ω} and its effect on the electrochemical measurements in aqueous high temperature electrochemical systems.

In the literature there are different theoretical and experimental methods for measuring and correction of $R_{sol}/\Delta E_{\Omega}$ such as AC resistance method, high frequency resistance method, iR compensation by positive feedback, iR compensation by negative resistance, iR compensation by alternating current methods, distance variation method and iR compensation by numerical post-measurement method [4,5,7–14,25–33].

This article does not discuss the technical modifications or theoretical methods of studying the ΔE_{Ω} mentioned above. This study investigates the R_{Ω} of a high temperature autoclave system containing low conductivity, pressurized water. Here we analyzed the effect of the applied temperature on the amount of the ΔE_{Ω} in an autoclaved aqueous system and on the rate of the oxygen reduction reaction on platinum (Pt) and Alloy 690. The ΔE_{Ω} and R_{sol} of the electrochemical system were analyzed in the temperature range of 25 °C to 285 °C using electrochemical impedance spectroscopy (EIS) and galvanostatic potentiometry combined with current interrupt iR compensation techniques and the obtained results were compared with the conductivity values calculated by a pH & Conductivity calculator software.

We believe that this study can be highly useful for researchers who work in the field of aqueous electrochemical measurements,

in particular corrosion engineers who use high temperature aqueous electrochemical systems.

2. Experimental

2.1. Specimens and sample preparation

All experiments in this study were performed on Pt and Alloy 690 working electrodes. The Alloy 690 coupon had the following chemical composition (in wt. %): Ni bal., Cr 27.520, Fe 9.360, C 0.083, Si 0.239, Mn 0.741, Ti 0.247, Co 0.017, Cu 0.012, P 0.007, S 0.012, Nb 0.005, and B 0.006.

The Alloy 690 coupon used in this study was 1 × 1.4 cm in diameter, 0.25 cm thick and 2.80 cm² surface area. The Pt plate was 2 × 1 cm in diameter and 4 cm² surface area.

The Alloy 690 coupon was ground with 400, 800, 1200, 2000, 4000 grit silicon carbide papers respectively and then polished with a polishing cloth (MicroCloth, Buehler) using a 0.50 μm water based diamond paste. The Pt plate was polished carefully by a 4000 grit silicon carbide paper. Finally, the Alloy 690 coupon and the Pt plate were washed with distilled water and acetone and rinsed ultrasonically in ethanol for five minutes.

2.2. Electrochemical setup and solution

The electrochemical experiments were carried out in double distilled water containing NH₄OH using an autoclave with a circulating water system. A schematic drawing of the setup is shown in Fig. 1. The inlet and outlet dissolved oxygen (DO) concentration, $pH_{(25\text{ }^{\circ}\text{C})}$, and conductivity_(25 °C) were controlled and monitored online. The fluctuations in temperature were controlled to within ±0.50 °C. $pH_{(25\text{ }^{\circ}\text{C})}$ was adjusted at 10 to an accuracy of ±0.05 by the automatic injection of NH₄OH into the water. At 25 °C, pH 10, achieved by addition of 11550 ppb NH₄OH, corresponds to the conductivity of 26.82 μS/cm. During the electrochemical measurements at different temperatures, the actual pH and conductivity inside the autoclave were calculated. The DO concentration was controlled at 100 ppb by continuous bubbling of a mixture of high-purity argon (99.99%) and/or a mixture of pure argon and oxygen (5% by volume) into a glass water tube with a capacity of 6 L. Multi-Digital MFC—CS200 (Vol. 1) software was used to control the injection procedure. The pressure of the autoclave was controlled by a high-pressure metering pump and a high precision back pressure regulator and was maintained at a constant value of 8.0 ± 0.1 MPa with a flow rate of approximately 4.0 ± 0.1 L/h, corresponding to a volumetric refresh rate of approximately 2 times/h.

A Gamry Reference 600 potentiostat/galvanostat/ZRA in a three electrode setup with an internal Ag/AgCl/KCl (0.1 M KCl) reference electrode and a Pt plate as counter electrode in an autoclave made of 316 L stainless steel (UNS S31603) was used to record the electrochemical plots. The working electrode was either a Pt plate or an Alloy 690 coupon welded to a Ni wire with a diameter of 0.5 mm. In all the electrochemical measurements the distance between the electrodes was constant. The working electrode was positioned in the distance of 1 cm from the counter electrode inside the autoclave, both with the same distance from the reference electrode.

The lead wires of the working and counter electrodes were double shielded with polytetrafluoroethylene heat shrinkable tubes. All of the measured potentials in this work were converted to the standard hydrogen electrode (SHE) according to the following equation [34]:

$$E_{SHE} = E_{obs} + 0.2866 - 0.001 \times (T_1 - T_2) + 1.745 \times 10^{-7} \times (T_1 - T_2)^2 - 3.03 \times 10^{-9} \times (T_1 - T_2)^3 \quad (2)$$

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