Short Communication

Temperature dependence of hydrogen evolution reaction on nickel oxide electrode in sealed nickel/cadmium cells

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Abstract

The impedance of sealed nickel/cadmium cells around a cell e.m.f. of 0.0 V was measured at five different temperatures between -10 and $+30$ °C. The results show that the behaviour is similar at all temperatures. Based on the experimental results, the relation between charge-transfer resistance (R_{ct}) and temperature (T) has been established for the Volmer reaction. Further, the value of cathodic transfer coefficient (α) has been estimated.

Introduction

It is well known that the impedance of sealed nickel/cadmium cells provides information about the reactions and their kinetics at the electrodes. It has been shown that the impedance of sealed nickel/cadmium cells at low states-of-charge ($<0.1\%$) is mainly due to the nickel oxide electrode. It has also been found that around a cell e.m.f. (V^r) of 0.0 V, the cell impedance is due to the occurrence of the hydrogen evolution reaction (HER) at the nickel oxide electrode [1].

The impedance associated with a faradaic reaction is a function of temperature. Furthermore, the variation of impedance with temperature, generally, gives information about the kinetics of the faradaic reaction. Hence, the impedance of sealed nickel/cadmium cells was measured at five different temperatures from -10 to $+30$ °C. These span the normal temperature range experienced by such cells. The charge-transfer resistance (R_{ct}) for the HER at different temperatures, the value of the cathodic transfer coefficient, and the dependence of these two parameters on temperature are usually the parameters of most interest.

In this paper, the variation of impedance of a 12 Ah sealed nickel/cadmium cell with temperature at a low state-of-charge around a cell e.m.f. (V^r) of 0.0 V has been investigated.

Experimental

The impedance of a 12 Ah nickel/cadmium cell was measured using a Solartron frequency response analyser (FRA) in conjunction with an electrochemical interface (ECI). The impedance was measured in series equivalent form $(R_s \pm jX_s)$ by applying a signal of 1 mV (rms). The cells were kept in an environmental chamber whose temperature was controlled to within ± 0.5 °C of the required value. Cells were soaked at the set temperature for at least 4 h before measurements were commenced.

In order to obtain a near-zero state-of-charge ($<0.1\%$), an initially charged cell was discharged at the 2 h rate to 1.0 V, followed by a discharge across a 0.5 Ω resistor for 16 h. The cell was subsequently dead-shorted for 24 h to remove all the charge and then left open for 24 h, during which time the cell voltage recovered to about 1.2 V.

Before starting the test, the cell was shorted across a 0.5 Ω resistor for 10 min; the cell voltage fell to below 10 mV. The cell was then potentiostatically polarized to 0.0 V and the excitation signal was applied 20 min later. At each frequency, the impedance measurement was commenced after a delay of 20 s. Measurements were performed in the frequency range of 0.01 to 10 Hz at temperatures of -10, 0, $+10$, $+20$ and $+30$ °C and in voltage steps of 25 mV.

Results and discussion

The impedance of a 12 Ah sealed nickel/cadmium cell at different temperatures in the complex plane $(R_s \pm jX_s)$ is shown in Fig. 1. The measurements were made at a cell e.m.f. of 0.0 V; this corresponds to the HER on the nickel oxide electrode. The impedance spectrum shows a semicircular region followed by a linear region. The slope of the linear part does not change with temperature, but the radius of the semicircle decreases as the temperature is raised.

The impedance of the HER at a nickel oxide electrode in a sealed nickel/cadmium cell can be modelled by the equivalent circuit shown in Fig. 2 [1]. This equivalent circuit represents a two-step HER, i.e., an electron-transfer reaction (Volmer reaction) and an adsorption/desorption reaction (Tafel reaction) [2]. The values of the circuit elements in the equivalent circuit (shown in Fig. 3) were calculated by fitting to the experimental results at 20 °C. From the values of the resistive parts, it may be seen that the adsorption/desorption step is the rate-limiting step. Similarly, the value of the charge-transfer resistance for the Volmer reaction (R_{ct}) at different temperatures and $V^\tau = 0$ V was estimated. The variation of R_{ct} with temperature is plotted in Fig. 4. The value of R_{ct} varies from 0.68 Ω at -10 °C to 0.062 Ω at $+30$ °C.

It is interesting to investigate the relationship between R_{ct} and temperature at an impregnated nickel oxide electrode. As stated earlier, it is reasonable to assume that the HER occurs via the Volmer–Tafel route, with the Tafel reaction limiting the reaction rate. Further, it may be assumed that the HER occurs near equilibrium and all bulk activities can be calculated from equilibrium conditions. Based on these assumptions, it can be shown that for the Volmer reaction:

$$R_{ct} = \frac{RT}{AF^2 K_V^0} \frac{1}{(a_{OH^-})^\alpha (a_{H_2O})^{1-\alpha} K_T^{\alpha/2}} \exp\left(\frac{\alpha}{RT} F(E_H^i - E_H^r)\right) \tag{1}$$
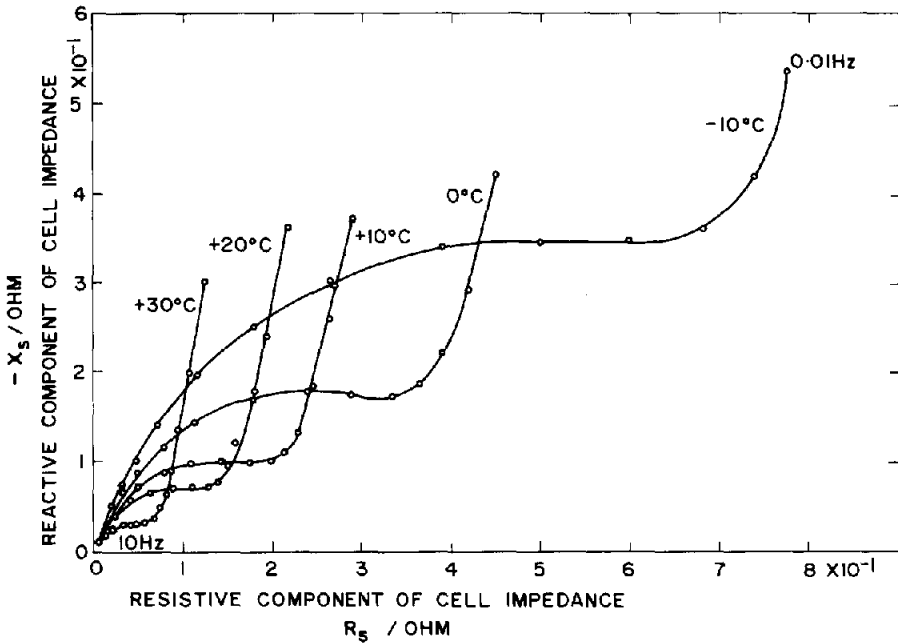
Fig. 1. Complex plane plot of the impedance of a cell at $V^r=0.0$ V for different temperatures in the frequency range 0.01 to 10 Hz for a 12 Ah sealed nickel/cadmium cell.
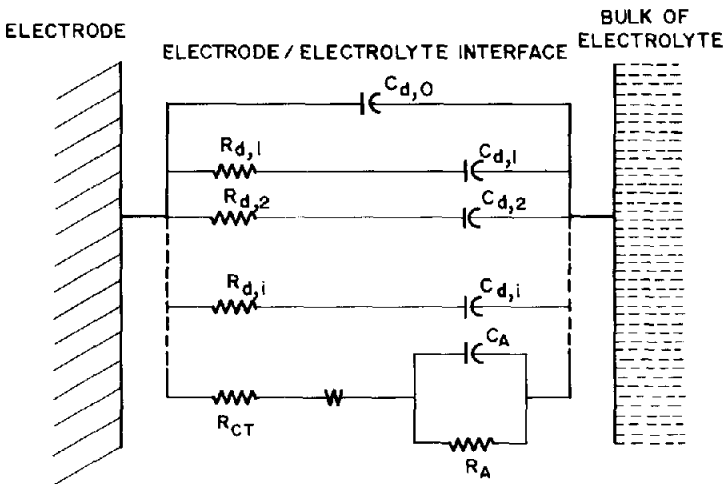

Fig. 2. Equivalent circuit that represents the processes occurring at the nickel oxide electrode of a sealed nickel/cadmium cell around cell e.m.f. (V^r) of 0.0 V. $R_{d,1}$, $R_{d,2}$, $R_{d,i}$ and $C_{d,0}$, $C_{d,1}$, $C_{d,2}$, $C_{d,i}$ represent the components of the non-faradaic impedance. R_{ct}, W, C_A and R_A represent the components of the faradaic impedance.
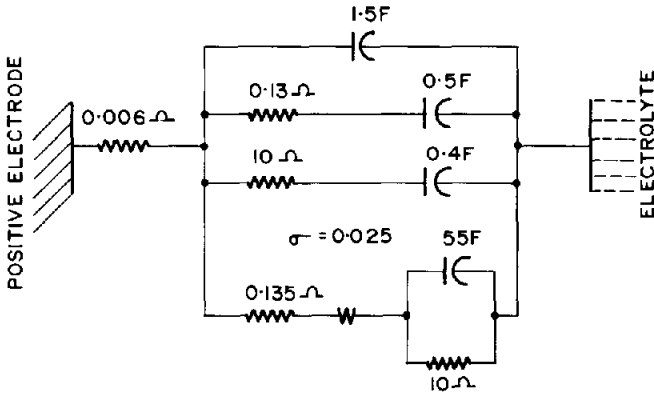
Fig. 3. Equivalent circuit that fits the experimental results at $V^r=0.0$ V in the frequency range 0.01 to 10 Hz at 20 °C for a 12 Ah sealed nickel/cadmium cell.
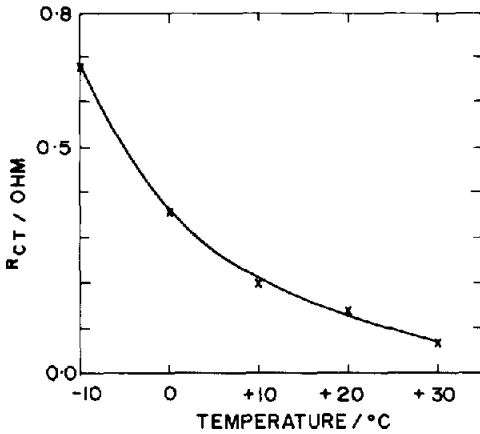

Fig. 4. Variation of charge-transfer resistance (R_{ct}) with temperature for hydrogen electrode reaction at nickel oxide electrode at $V^r=0.0$ V for a 12 Ah sealed nickel/cadmium cell.

where $R_{ct}=$ charge-transfer resistance of Volmer reaction, $R=$ universal gas constant, $A=$ area of electrode, $F=$ Faraday constant, $a_i=$ activity of species 'i', $\alpha=$ cathodic transfer coefficient for Volmer reaction, $K_V^0=$ standard rate constant for Volmer reaction, $k_T=$ equilibrium constant for Tafel reaction, $E_H'=$ formal potential for the HER, $E_H^r=$ reversible potential of the HER, and $T=$ temperature.

The above equation can be written as:

$$R_{ct}=K_{ct}T \exp\left(\frac{\alpha}{RT} F(E_H'-E_H^r)\right) \tag{2}$$

where $K_{ct}=R/AF^2K_V^0(a_{OH^-})^{\alpha}(a_{H_2O})^{1-\alpha}K_T^{\alpha/2}$ or:

$$\ln \frac{R_{ct}}{T} = \ln K_{ct} + \frac{\alpha F}{R}(E_H'-E_H^r)\frac{1}{T} \tag{3}$$

Thus, a plot of $\ln(R_{ct}/T)$ versus $1/T$ should be a straight line. This is confirmed by the data given in Fig. 5. This also indicates that K_{ct} is a constant over the temperature range of interest.

Equation (2) suggests that, if the value of R_{ct} is known experimentally at different values of E_H^I, then it is possible to estimate the value of α. If the reference electrode is Cd/Cd(OH)$_2$, then $E_H^I = V^r$ (i.e., the cell e.m.f.). At each of the temperatures, the impedance of the cell was measured at cell e.m.f.s up to 0.125 V from 0.0 V in steps
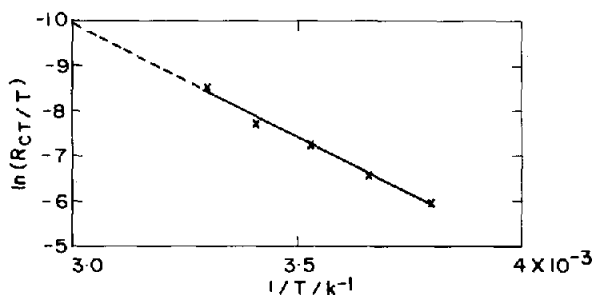

Fig. 5. Plot of ln R_{ct}/T vs. $1/T$ at $V^r = 0.0$ V for a sealed nickel/cadmium cell in the temperature range -10 to $+30$ °C.
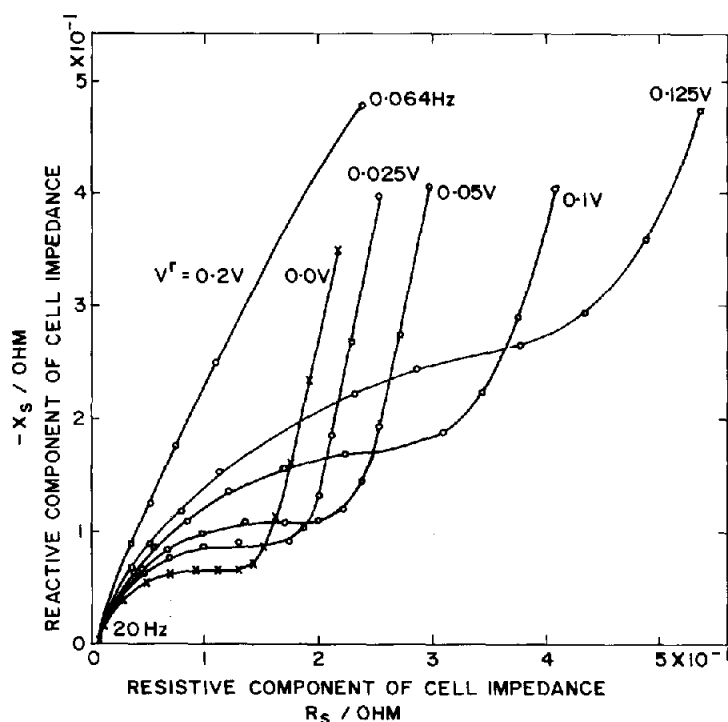

Fig. 6. Complex plane plot of cell impedance around $V^r = 0.0$ V in frequency range 20 to 0.01 Hz at 20 °C. Cell e.m.f. is shown on the curves. Except at $V^r = 0.2$ V, lowest frequency is 0.01 Hz.
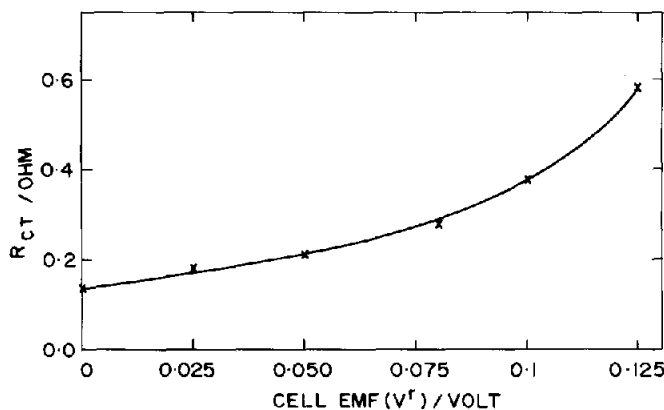
Fig. 7. Variation of charge-transfer resistance (R_{ct}) for hydrogen electrode reaction with cell e.m.f. (V^r) at nickel oxide electrode of a 12 Ah sealed nickel/cadmium cell at 20 °C.

of 25 mV. The impedance at only 20 °C is shown in Fig. 6. From the measured impedance spectrum, R_{ct} was evaluated for different cell e.m.f.s at different temperatures. Figure 7 shows the variation of R_{ct} with cell e.m.f. V^r at 20 °C. By substituting the measured value of R_{ct} at $E_H^R = V^r = 0$ V and 0.1 V, R_{ct} is 0.135 and 0.38 Ω at $V^r = 0.0$ and 0.1 V, respectively.

Substituting in eqn. (2) gives:

$$0.135 = K_{ct}T \exp\left(\frac{\alpha E_H'}{0.0252}\right) \tag{4}$$

$$0.38 = K_{ct}T \exp\left(\frac{\alpha(0.1 + E_H')}{0.0252}\right) \tag{5}$$

Solving these two eqns. yields:

$\alpha = 0.26$

From similar calculations, the value of α was found to be 0.26, 0.34 and 0.32 at 20 and 30, 10 and −10 °C, respectively.

Conclusions

In this paper, the variation of impedance of sealed nickel/cadmium cells at a cell e.m.f. of 0.0 V as a function of temperature has been presented. The variation of charge-transfer resistance (R_{ct}) with temperature for the Volmer reaction has been calculated and the relationship between R_{ct} and T has been established. Further, the value of the cathodic transfer coefficient, α, for the Volmer reaction at a nickel oxide electrode has been estimated.

References

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2 S. U. Falk and A. J. Salkind (eds.), *Alkaline Storage Batteries,* Wiley–Interscience, New York, 1969, pp. 42–55, 516–559, 577–633.