TECHNICAL NOTE

A method of *IR* drop measurements using a current interruption technique: an application to half cell studies with porous gas diffusion electrodes

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1. Introduction

In performance studies of fuel cell and electrolyser electrodes, it is necessary to separate any ohmic potential drop from the measured potential difference between the working and reference electrodes. This is essential for the identification of the mass transfer limitations and activation overpotential behaviour of the electrodes. The ohmic overpotential should also be included in the design and operation of electrochemical energy converters and electrochemical producers.

In PTFE-bonded, Raney metal type, gas diffusion electrodes, which are widely used for alkaline fuel cells, *IR* drop is extremely sensitive to current densities, electrolyte temperature, electrolyte concentration, material and physical structure of the electrode and back pressure on the gas side. In a half cell, which is the widely used setup for electrode screening and modelling, accurate measurement of the ohmic resistance between the working electrode and reference electrode is very important for establishing the components of overvoltage.

In a review by Hayes *et al.* [1] the main characteristics of different techniques for measuring ohmic drops in electrochemical cells were discussed. Britz [2] presented another review where the effects of uncompensated resistance and instrumental and non-instrumental methods of *IR* elimination were discussed, together with a stability analysis.

Kordesch and Marko [3] developed a circuit which measured the voltage of a cell during discharge by eliminating its ohmic component. This interrupter bridge, although very applicable for the low frequency range (60 Hz), gave inaccurate results when polarizations having short time constants relative to the bridge frequency are involved. Niedrach and Tochner [4] measured polarization curves with a modified Kordesch–Marko bridge and with a d.c. interruption technique. Even higher frequency interrupter bridges require constant monitoring while the d.c. method seems to be the most reliable since the voltage transient is examined and measured directly with an oscilloscope [4]. A mercury-wetted relay is used as the interrupter by most investigators, the operation of which is strongly dependent on the surface tension of mercury which could be affected by a variety of factors. For efficient routine use, a solid state relay

that can electronically interrupt the circuit would be more suitable [5].

In the present work, a d.c. interruption method using a noise-free solid state relay is described. The method is applied to H_2 gas diffusion electrodes in a half cell assembly in alkaline electrolyte. The convenience of the method for half cell measurements is shown.

2. Principle of the method

Figure 1 shows the circuit and equipment used for *IR* drop measurement. A potentiostat was used as a galvanostat by using an external resistor (R_1). This resistor was inserted between the working electrode and its potentiostat cable connection. The reference electrode leading from the potentiostat was connected to the point where the external resistor is linked to the working electrode. In this manner, the potentiostat controlled the voltage drop across the external resistor, and, therefore, the circuit current. The potentiostat had separate leads for the circuit current and potential of the working electrode. It also had connections for the counter electrode and grounding. A solid state relay in series with a milliammeter was connected to the working electrode of the half cell. The potential difference between the working and reference electrode was measured by a high impedance voltmeter.

A dual channel digital storage oscilloscope was used to monitor the working electrode potential and cell current through channels A and B, respectively. The cell current transient was recorded as a voltage drop across an accurately known resistor, R_3. A mechanical switch, S_2, when opened, activated the batteries in series which then de-energized the relay thus breaking the circuit current. Without using a pulse generator, switch S_2 was simultaneously used for pretriggering the oscilloscope by connecting the terminals to the external triggering input of an oscilloscope with shielded concentric cables.

The initial instantaneous jump of the voltage recovery upon going from an operating load to open circuit was recorded as the *IR* drop in the half cell. The reproducible delay in the opening of the solid state relay and the adjustment of the level of the signal provided a ready synchronization with the
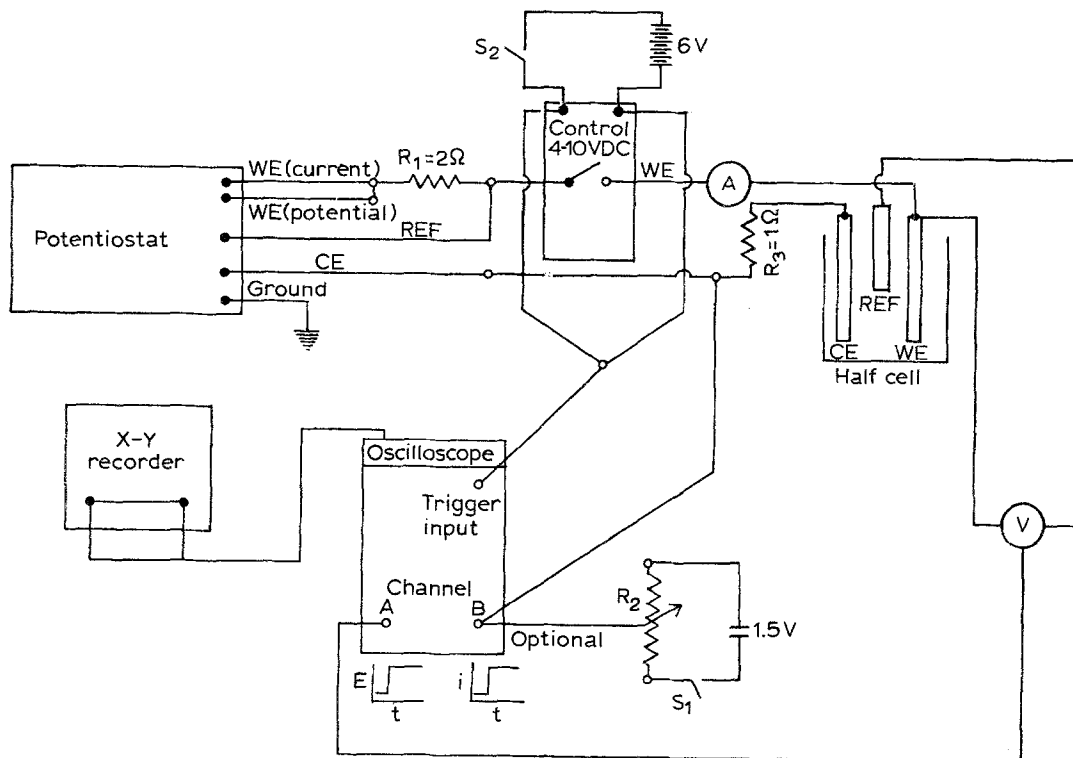

Fig. 1. Circuit for measuring the *IR* potential drop.

oscilloscope sweep at a preset trigger level. The signal was digitally recorded in the memory of the oscilloscope and then plotted on an *X-Y* recorder. The optional connection to channel B was used to adjust the vertical level of signal when high sensitivities were required.

3. Experimental details

To demonstrate the applicability of this method, a PTFE-bonded, Raney nickel, porous, gas diffusion electrode, which was prepared by a reactive mixing technique, was polarized in a half cell assembly in
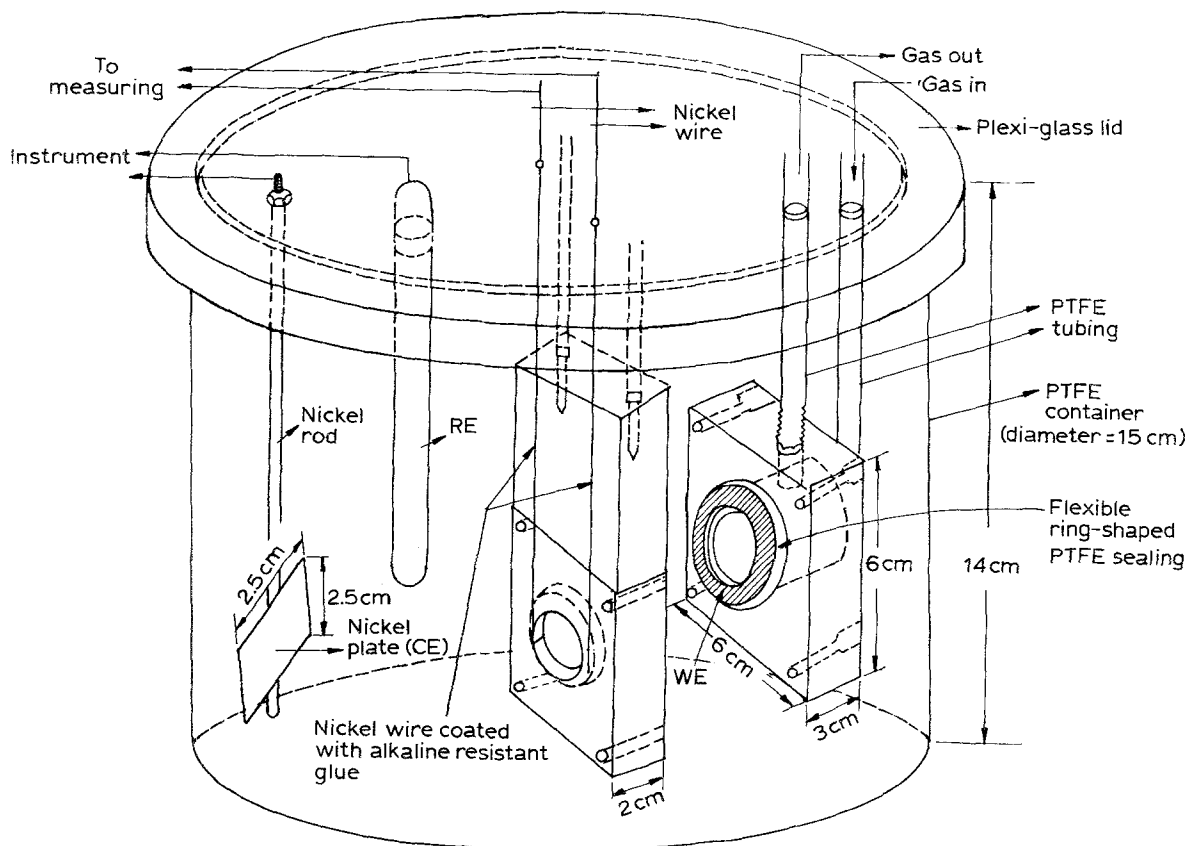

Fig. 2. Half cell setup.

KOH electrolyte. High-purity hydrogen gas was used as the fuel. A schematic diagram of the half cell is shown in Fig. 2. The geometric surface area of the electrodes was $6\,cm^2$. The electrolyte concentration was 25 wt % KOH. The half cell was placed in a thermostated water bath and measurements were taken at 25° C and 55° C. A Wenking type POS 73 potentioscan was used to apply the desired load of current to the electrodes. The oscilloscope was equipped with two memories, plot mode and 2 K bytes pretrigger view on screen. It had a sensitivity of 5 mV division^{-1} at 20 MHz. The solid state relay was a Teledyne SSP p/N 603-3 type with a control of 4–10 V d.c.

The half cell used was fabricated from Plexiglass and consisted of a gas chamber and a rectangular piece which housed the gas diffusion electrode, PTFE sealing and the nickel-wire current collectors. It was mounted into a PTFE container filled with the electrolyte. The counter electrode was a nickel plate welded onto a nickel rod which was attached onto the lid of the PTFE container. The reference electrode was a Hg/HgO electrode filled with 25% KOH solution and was fixed in space in the electrolyte through an opening in the lid of the PTFE container.

In the second phase of experiments, the accuracy of the method was tested by replacing the half cell with a dummy cell containing two resistances in series, one resistance being fixed at $1.6\,\Omega$ which was suitably chosen to simulate the zero-current resistance of the half cell. This was obtained from a plot of experimental data given in Fig. 3. The potential difference at zero current and the slope indicated the existence of a
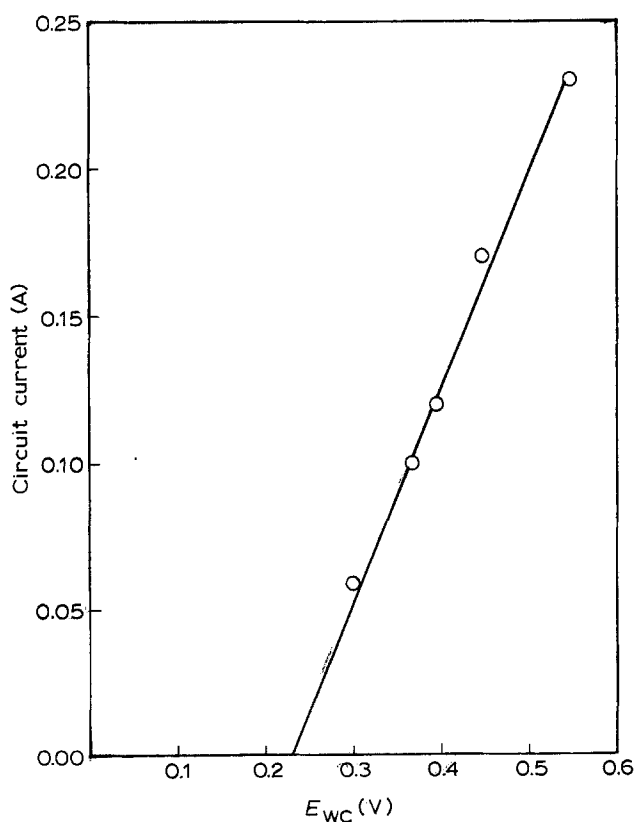
potential 0.25 V to be overcome before any current flowed through the cell and a corresponding resistance of $1.6\,\Omega$. On the other hand, the second resistance was chosen as $0.45\,\Omega$ which was representative of the resistance between the working and reference electrodes.

4. Results and discussion

The potential drop, IR, in a half cell was determined by measuring the voltage drop between two non-current-carrying locations which were the reference electrode dipped in the bare electrolyte and the working electrode.

The IR-drop-corrected and non-corrected polarization curves for the hydrogen electrode at 25° C and 55° C are given in Fig. 4. Ohmic resistances were also calculated from the IR drop and are shown in Fig. 5.

The resistance of the solution between the tip of the reference electrode and the metal mesh support of the electrode was found to be $0.50–0.52\,\Omega$ at 25° C and $0.30–0.32\,\Omega$ at 55° C. In Fig. 4, at both 25° C and 55° C, the IR drop including overpotential was observed to be 3–4 times larger than the IR-drop-corrected overpotentials at all current densities. This showed the importance of accurate determination of ohmic resistances in half cell studies.

The magnitudes of the IR drop obtained by this method was checked against the predictions of the electrolyte resistance based on the known resistivity of the electrolyte and the geometry of the sample. Ohmic resistance was calculated from

$$R_e = \frac{\rho_{electrolyte}\,\gamma}{A}$$

where $\rho_{electrolyte}$ is the resistivity, γ is the distance between the tip of the reference and working elec-

Fig. 3. Plot of circuit current against potential difference between WE and CE.
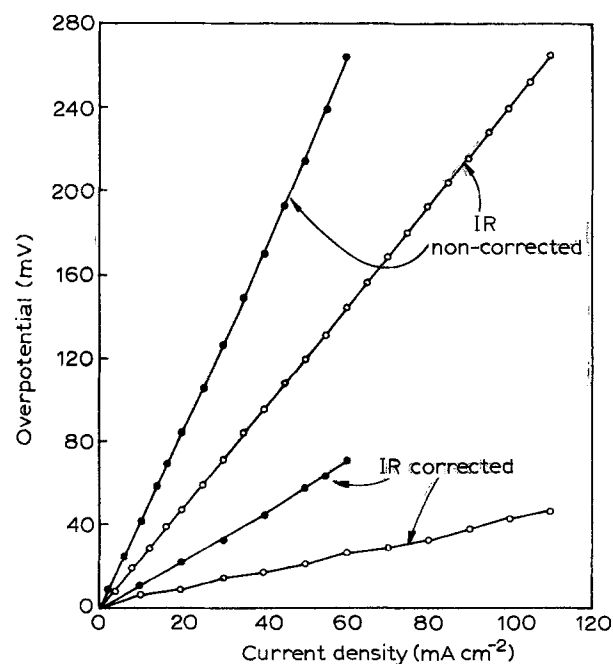

Fig. 4. Polarization curves for H_2 gas electrode at (O) 55° C and (●) 25° C.
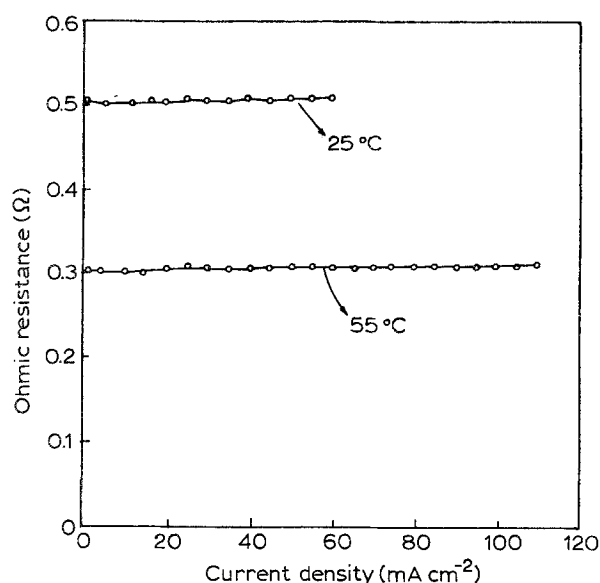
Fig. 5. Ohmic resistances as calculated from IR potential drops at 25° C and 55° C.

trodes, which was 3.7 cm, and A is the area of the working electrode. Resistivities at 25° C and 55° C for 25% KOH solution were 1.6 and 0.95 Ω cm, respectively [6]. These values gave ohmic resistances as 0.59 and 0.35 Ω. Experimental values were 0.52 and 0.32 Ω, showing a reasonably good agreement.

Results of experiments with the dummy cell of known resistance are shown in Table 1. The error in the measurements was always below 1%.

5. Conclusion

A simple and efficient method of the IR drop measurement is demonstrated for a half cell assembly with gas diffusion electrodes. The circuit involved is based on interrupting the current and recording the instantaneous change in the potential on a dual-channel digital storage oscilloscope. A solid state relay is used to break the circuit as a switching device with input terminals isolated from the output switch path. This has high noise immunity and it is free from false actuation. The circuit used is especially suitable for a half cell study with porous electrodes and does not require the presence of an electrolyte bridge and a luggin capillary. Measurements with a dummy cell of precisely known resistances have verified the accuracy of the method. Although this method is time consuming, it is more reliable than the bridge methods because of the necessity that the voltage transients are to be monitored and recorded directly with an oscilloscope. Sweep rates of 20–50 μ s/division have been found adequate for the measurement of the ohmic drops in the half cell used in this study. Linearity of the IR drop against current density data was another proof of the accuracy of this method.

It is also observed from the experiments that the current establishment and current interruption oscillograms display exactly the same ohmic resistance, showing the absence of heating effects.

Table 1. Ohmic drop measurement with known resistance of 0.45 Ω

Circuit current (mA)	Potential drop across 0.45 Ω (mV)	Theoretical potential drop (mV)	Error (%)
100	45.1	45	0.22
200	90.2	90	0.22
300	135.2	135	0.15
400	180.2	180	0.11
500	225.5	225	0.22

References

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