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An in situ *method for determination of internal resistances in fuel cells*

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An *in situ* method has been demonstrated for the determination of internal resistances in electrochemical energy converters without disturbing the test conditions or interrupting the cell operation. While operating the cell at a desired current, the apparent internal resistance and cell voltage are measured following a standardized procedure. A mathematical equation has been derived to calculate the true internal resistance from the observed resistance, cell voltage and operating current. A typical example is given to show the excellent agreement of the *in situ* measured internal resistances with those obtained by a current interruption technique.

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1. Introduction

In the development of electrochemical energy converters such as fuel cells, batteries and electrolysers, it is essential to determine empirically the internal resistances so that the electrochemical behaviours of electrodes can be accurately and effectively described. In the 'engineered' phase or production, internal resistances and the resulting resistive overpotentials should be included in the key parameters for quality control.

The presence of gas bubbles in the electrolyte and local acidification near the electrode surfaces have substantial impact on the cell internal resistance. In phosphoric acid fuel cells (containing less than 0.1 cm^3 electrolyte per cm^2) for example, acid concentration is extremely sensitive to the variation of operational parameter such as current density, temperature, pressure and process gas flow rate [1]. Since the cell internal resistance is highly dependent on acid concentration, an *in situ* resistance measurement technique is needed to avoid the erros arising from the change of operation conditions.

In a recent review by Hayes *et al.* [2], the main features of various techniques for measuring ohmic drops in electrochemical cells have been exhaustively described. In the present work, an a.c. bridge method utilizing a 1 kHz signal was used to minimize measurement errors due to electrolytic polarization and thermal e.m.f.s. Through a series of theoretical considerations, the effect of the external load on the resistance measurements was essentially eliminated. The main purpose of this study is to demonstrate a convenient *in situ* method for precise determination of cell internal resistance without disturbing the operation conditions.

2. Principle of method

Fig. 1 shows the schematic arrangement of a subscale fuel cell. The current leads of a milliohmmeter are connected to the current collectors at both ends of the single cell, and the voltage terminals to both the anodic and cathodic end plates of the cell. Note that if the voltage terminals of the milliohmmeter are also connected to the two current collectors, the measured cell internal resistance will include the contact resistance between each current collector and its adjacent end plate. Conversely, if the current and voltage terminals of the milliohmmeter are all connected to the voltage leads of both end plates, the milliohmmeter will erroneously pick

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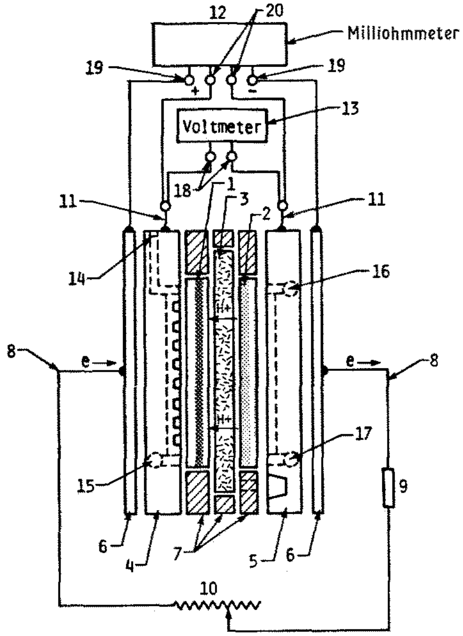

Fig. 1. The schematic of a phosphoric acid fuel cell and its test facilities. 1. Cathode 2. Anode 3. Matrix 4. Cathodic end plate 5. Anodic end plate 6. Current collector 7. Gaskets 8. External circuit 9. Shunt 10. Load 11. Voltage leads 12. Milliohmmeter 13. Voltmeter 14. Oxidant gas inlet 15. Oxidant gas outlet 16. Fuel gas inlet 17. Fuel gas outlet 18. Voltage terminals 19. Current terminals 20. Voltage terminals.

up the electric resistances of the lead wires and contact resistances in the junction of each voltage lead to the end plate.

During the measurement, the milliohmmeter passes an a.c. through the test cell and its external load as shown in the simplified electric circuit in Fig. 2. At the time t, the total current $i(t)$ from the milliohmmeter is divided into an external circuit $i(t)_{\mathrm{ex}}$ (passing through the external circuit, shunt and load) and an internal current $i(t)_{\mathrm{in}}$ (passing through the cell and the interface between each current collector and its adjacent end plate). It is noted that, in Fig. 2, R_{ex} represents the summation of resistances in the external circuit, including shunt and load, and R_{in} denotes the cell internal resistance. The contact resistances between the cathodic end plate and its adjacent current collector, and between the anodic end plate and its adjacent current collector are designated as $R_{\mathrm{cont,c}}$ and $R_{\mathrm{cont,a}}$, respectively. Ohm's law gives

$$i(t)_{\mathrm{in}}\,(R_{\mathrm{cont,c}} + R_{\mathrm{in}} + R_{\mathrm{cont,a}}) = i(t)_{\mathrm{ex}} R_{\mathrm{ex}} \tag{1}$$

Rearranging Equation 1 yields

$$i(t)_{\mathrm{ex}} = \frac{i(t)_{\mathrm{in}}}{R_{\mathrm{ex}}}\,(R_{\mathrm{cont,c}} + R_{\mathrm{in}} + R_{\mathrm{cont,a}}) \tag{2}$$

Since the voltage terminals of the millohmmeter are connected to the electric leads on both end plates, the potential drop monitored by the milliohmmeter is $i(t)_{\mathrm{in}} R_{\mathrm{in}}$. However, the total current passing through the millohmeter is $i(t)$ rather than $i(t)_{\mathrm{in}}$. Thus, the observed resistance R_{obs} in the milliohmmeter is expressed as follows

$$R_{\mathrm{obs}} = \frac{i(t)_{\mathrm{in}} R_{\mathrm{in}}}{i(t)} \tag{3}$$

Because $i(t)$ is the summation of $i(t)_{\mathrm{in}}$ and $i(t)_{\mathrm{ex}}$, Equation 3 becomes

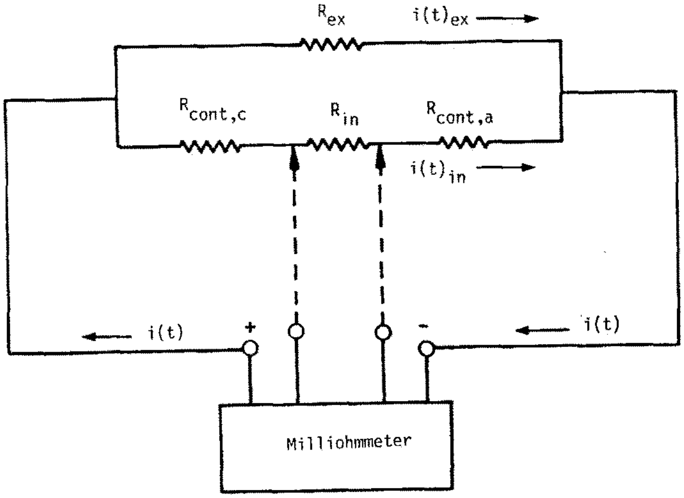

Fig. 2. A simplified circuit for the measurement of cell internal resistances.

$$R_{\mathrm{obs}} = \frac{i(t)_{\mathrm{in}}R_{\mathrm{in}}}{i(t)_{\mathrm{in}} + i(t)_{\mathrm{ex}}} \qquad (4)$$

By substituting Equation 2 into Equation 4 and rearranging, we have

$$R_{\mathrm{in}} = R_{\mathrm{obs}}\,(R_{\mathrm{ex}} + R_{\mathrm{cont,c}} + R_{\mathrm{cont,a}})/(R_{\mathrm{ex}} - R_{\mathrm{obs}}) \qquad (5)$$

While operating the cell at a constant d.c. I, the cell voltage E_{cell} is measured between two potential leads connecting to both end plates (see Fig. 1). From the standpoint of the cell, the overall external resistance is composed of $R_{\mathrm{cont,c}}$, R_{ex} and $R_{\mathrm{cont,a}}$. Thus, the cell voltage is given by

$$E_{\mathrm{cell}} = I(R_{\mathrm{ex}} + R_{\mathrm{cont,c}} + R_{\mathrm{cont,a}}) \qquad (6)$$

The combination of Equations 5 and 6 yields

$$R_{\mathrm{in}} = R_{\mathrm{obs}}E_{\mathrm{cell}}/\,[E_{\mathrm{cell}} - I(R_{\mathrm{cont,c}} + R_{\mathrm{cont,a}}) - IR_{\mathrm{obs}}] \qquad (7)$$

If the terminal voltage $E_{\mathrm{c\text{-}c}}$ between the two current collectors is also measured, the overall external resistance is only R_{ex} in this case. Thus, we have

$$E_{\mathrm{c\text{-}c}} = IR_{\mathrm{ex}} \qquad (8)$$

From Equations 6 and 8, the summation of both contact resistances is obtained through the following equation

$$R_{\mathrm{cont,c}} + R_{\mathrm{cont,a}} = (E_{\mathrm{cell}} - E_{\mathrm{c\text{-}c}})/I \qquad (9)$$

By substituting Equation 9 into Equation 7, the cell internal resistance R_{in} can be calculated from an equation as follows:

$$R_{\mathrm{in}} = \frac{R_{\mathrm{obs}}E_{\mathrm{cell}}}{E_{\mathrm{c\text{-}c}} - IR_{\mathrm{obs}}} \qquad (10)$$

3. Experimental details

To demonstrate the validity of Equation 10 for the precise determination of cell internal resistances, experimental work was performed at 190° C in a phosphoric acid fuel cell. Carbon-supported platinum of loadings ~ 0.50 and ~ 0.30 mg cm^{-2} were used to prepare the Teflon-bonded catalyst layer of the cathode and anode, respectively. The matrix was made of uncatalysed carbon powder using Teflon binder. The geometric (active) electrode area was approximately 25 cm^2. During the cell assembly, 100 wt % phosphoric acid was applied to the cathode and matrix. At various flow rates, air and hydrogen were used as the oxidant and fuel gas, respectively.

Under the desired conditions, the (copper) current collectors were connected to the external circuit, which comprises a shunt for the current measurement and a variable resistor (load) for the adjustment of current density. Digital multimeters (Fluke Model 8600A) were used to measure the cell voltage and load current. The current and voltage terminals of a milliohmmeter (Hewlett-Packard Model 4328A) were connected to the current collectors and end plates, respectively, of the test cell. The milliohmmeter had an input impedance of at least 1 MΩ, thus resulting in no impact on the cell performance. With this instrument, the a.c. voltage across the sample is less than 200 μV peak. In addition, it was able to withstand a d.c. voltage up to 150 V without causing any measuring errors. After equilibration at the desired current density and process gas flow rates for at least 10 min, the cell internal resistance was obtained from the measured resistance, current density, cell voltage and terminal voltage using Equation 10.

In the verification test, an electronic interruptor, capable of interrupting the current in a few milliseconds, was incorporated (in series) into the test circuit. The analog output of the milliohmmeter was monitored by a time-base X–Y recorder (Soltec Model 6432S). The load current was instantaneously interrupted after being stabilized at the desired conditions for ~ 30 min, and the cell internal resistance was monitored as a function of the elapsed time using the X–Y recorder (at a sweep rate of 2 cm s^{-1}). After the current interruption, the interference of external load was completely eliminated, and thus the observed resistance on the milliohmmeter was the true internal resistance of the test cell at the disconnected condition.

4. Results and discussion

Fig. 3 shows the variation of the observed cell resistance with time. Prior to the current interruption, a stable resistance of ~ 4.8 mΩ was observed on the milliohmmeter. Due to the use of the a.c. bridge method, spikes appeared in the first second of the elapsed time. Past this period, the measured internal resistance started to increase

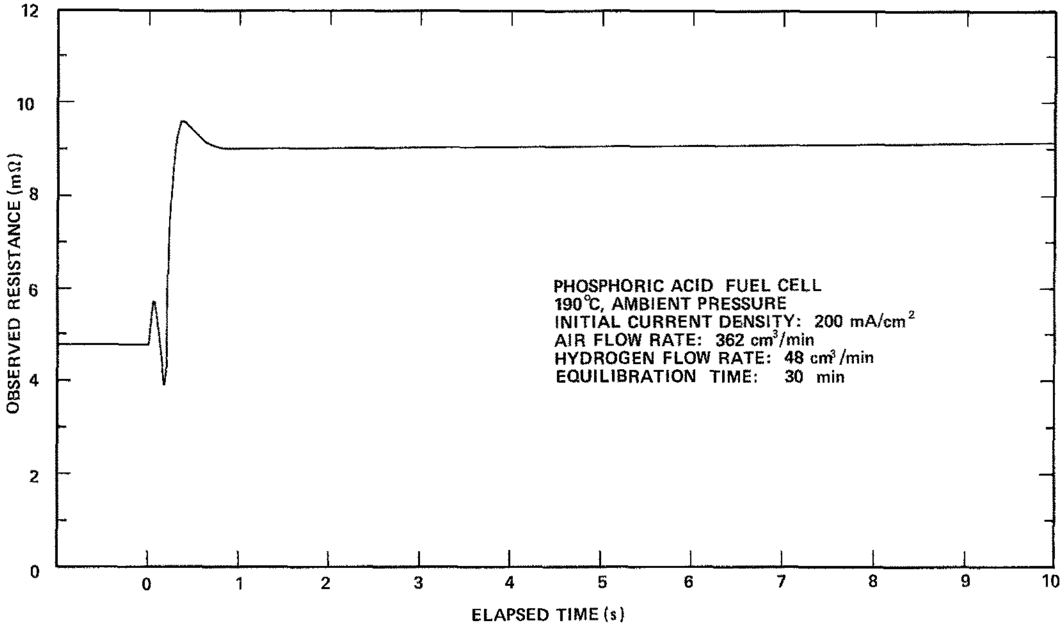

Fig. 3. Transient response of the observed resistance after the interruption of load current, 200 mA cm^{-2}.

constantly with time. This is essentially due to the continuous increase of acid concentration in the test cell, arising from the gradual evaporation of water from the electrolyte at 190° C. [1]. Note that, at any load current density, water generated in the electrochemical reactions normally compensates for the evaporation loss, thus reaching an equilibrium state of less concentrated electrolyte than at the disconnected condition. Since the water evaporation is a relatively slow process, the resistance measured within a few seconds after the current interruption should be very close to the true internal resistance at that particular current density.

At 80% H_2 utilization and various air flow rates, the cell internal resistances obtained by the *in situ* technique and by the current interruption method are given for comparison in Table 1. It should be noted that the subscale fuel cell in this study was galvanostatically pretested at 200 mA cm^{-2} for approximately 2300 h. The formation of oxide layer on the current collectors increased substantially the contact resistance between each end plate and its adjacent current collector. As a result, the measured terminal voltages between two current collectors (i.e. $E_{c\text{-}c}$ in Table 1) were much lower than the observed cell voltages E_{cell}.

At a desired current density, the true internal resistance was obtained from the measured E_{cell}, $E_{c\text{-}c}$ and R_{obs} through the use of Equation 10. Each calculated internal resistance was rounded to the nearest 0.05 mΩ, which was the smallest distinguishable reading on the millohmmeter at 10 mΩ full scale used in this study. By using the interruption method, the data presented in Table 1 are the cell internal resistances measured at 2 s after the current interruption. At 200 mA cm^{-2} and air flow rate of 362 cm^3 min^{-1}, for example, the calculated internal resistance using the *in situ* method is 8.85 mΩ. This *in situ* measured resistance is in good agreement with the observed value of 9.05 mΩ (see Fig. 1) from the current interruption method, if the accuracy (i.e. ± 0.2 mΩ at 10 mΩ full scale) of the milliohmmeter is taken into consideration.

As seen in Table 1, the cell internal resistances at a constant current density were increased slightly with increasing air flow rate no matter which method was used for the resistance measurement. Apparently, the air flow through the test cell expedited the water evaporation, resulting in an increased acid concentration and a decreased electrolyte conductivity.

At an identical current density and air flow rate, the internal resistances obtained from the

Table 1. Comparison of cell internal resistances measured by an in situ *technique and by a current interruption method**

Current density $(mA\ cm^{-1})$	*Air flow rate $(ml\ min^{-1})$*	E_{cell} *(mV)*	E_{c-c} *(mV)*	R_{obs} *(mV)*	*Internal resistance $(m\Omega)$ obtained from*		*Percentage difference*
					in situ *method*†	*Interruption method*‡	
200	181	607	353	4.70	8.65	8.85	2.3
	272	611	357	4.80	8.80	8.95	1.7
	362	612	358	4.85	8.85	9.05	1.7
	453	612	359	4.85	8.90	9.10	2.2
100	91	675	546	7.05	9.00	9.05	0.6
	136	678	548	7.15	9.15	9.20	0.5
	181	679	548	7.20	9.25	9.30	0.5
	227	680	548	7.25	9.30	9.35	0.5

* At 190° C, ambient pressure and 80% H_2 utilization

† Calculated internal resistance from an equation of the form: $R_{in} = R_{obs}/E_{cell}/(E_{c-c} - IR_{obs})$, where I is the load current in amperes.

‡ Measured internal resistance after interrupting the load current for 2 s.

in situ method are slightly lower than those taken at 2 s after interrupting the load current (see Table 1). At 200 and 100 mA cm^{-2}, however, the differences between the cell internal resistances measured by the two methods are normally below 2.4 and 0.7%, respectively. These results indicate that the *in situ* method of this study is capable of measuring the cell internal resistance very accurately.

5. Conclusions

An *in situ* technique has been developed for continuous monitoring of internal resistances of electrochemical cells with no interference on the cell operation. Through a series of systematic analyses, a mathematical equation has been derived to correct the effect of the external load on the resistance measurements. The precision of this *in situ* technique has been demonstrated by comparing the calculated internal resistances with those obtained from the current interruption method. An excellent agreement has been shown in the internal resistance data obtained from the two different methods. It is thus concluded that, in addition to the convenience, the *in situ* method of the present work is highly accurate and reliable for the determination of cell internal resistances.

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