A. C. impedance analysis of porous oxygen gas diffusion electrodes for alkaline fuel cells

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The reduction of oxygen on porous hydrophilic gas diffusion electrodes containing different catalysts has been investigated using the FFT impedance method. The double layer capacity, electrochemically active surface area, the true exchange current density values were determined for different electrocatalysts.

Key words: Alkaline fuel cells, porous oxygen gas diffusion electrode, impedance analysis

INTRODUCTION

The application of FFT a.c. impedance study for characterising porous oxygen diffusion electrodes both hydrophilic and hydrophobic, has been described in literature [1,2]. Changes in the performance of the porous electrodes due to flooding, loss of surface area or catalytic activity are reported [3]. A general model of oxygen reduction kinetics in semi hydrophobic gas diffusion electrodes has also been described [4].

EXPERIMENTAL

Two layer and three layer gas diffusion electrodes, containing the catalysts acetylene black and silver, were prepared as per method developed earlier [5] and steady state galvanostatic polarisation studies for oxygen reduction were carried out in 6M KOH using a mercuric oxide reference electrode. The impedance values were measured in the frequency range 10 kHz to 0.001 Hz with an a.c. signal amplitude of 10 mV using PAR a.c. impedance system. The experiments were carried out at different gas pressures 0.3, 0.5, 0.7, 1.0 kg.cm^{-2} at different temperatures. The values were processed further by using an Apple Computer for different parameters [6].

RESULTS AND DISCUSSION

Figure 1 represents the Nyquist plot for oxygen reduction on porous nickel electrodes at different polarisation values. The frequency dispersion gradually approaches a semicircle with increase in cathodic overvoltage. At low overpotentials there is a phase shift of 45° between current and potential indicating that the charge transfer is controlled by diffusion.

From the admittance plots, the double layer capacity values determined were same at all potentials (2×10^5 μf). The real surface area was calculated to be 1.5×10^4 cm^2
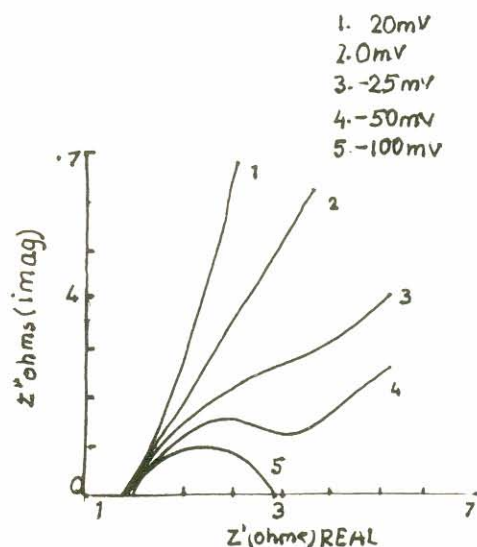

Fig. 1: *Faradaic impedance of a porous nickel electrode for oxygen reduction at different potentials. Oxygen gas pressure: 1.0 kg cm^{-2}; Electrolyte: 6N KOH; Temperature: 303 K*

1. 20mV
2. 0mV
3. -25mV
4. -50mV
5. -100mV

with a roughness factor of 500 and internal surface area 1.43×10^3 cm^2/g.

The effects of gas pressure and temperature are not shown in the figure. It was observed that increase of gas pressure reduced the phase difference between the real and imaginary Z values. But the double layer capacity values were different indicating the shift of the reaction zone and increase in the electrochemically active area inside the electrode. Similarly the temperature had a positive effect in reducing the diffusion contribution to the total impedance at high overpotentials.

The double layer capacity values for electrodes containing acetylene black and silver catalysts showed mixed trends for

different compositions so that the determination of true electrochemical area was difficult. However, the values were higher than pure nickel and the i_0 values were also higher by one order (10^{-4}A cm^{-2}).

REFERENCES

1. P Drossbach, *Electrochim Acta*, **11** (1966) 667

2. D W Wabner, *Metalloberflache-Angew, Electrochem*, **28** (1974) 21

3. R Holze and W Vielstich, *J Electrochem Soc*, **131** (1984) 2298

4. R Holze, I Vogel and W Vielstich, *J Electroanal Chem*, **210** (1986) 277

5. R Pattabiraman, R Chandrasekaran, S Muzhumathi, I Arul Raj, S Dheenadayalan and V K Venkatesan, *Trans SAEST*, **22** (1987) 25

6. R Chandrasekaran, I Arul Raj, S Dheenadayalan, S Muzhumathi and V K Venkatesan, *Bull Electrochem*,, **4** (1988) 723