A Novel Reference Electrode for Application in Alkaline Polymer Electrolyte Membrane Fuel Cells

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Abstract: An in situ fuel cell reference electrode (RE) consisting of a Pd-coated Pt wire exhibits stable potentials in alkaline polymer electrolyte membrane fuel cells (APEMFC). Results indicate that the overpotential and impedance of the anode are higher than those of the cathode in the cells tested (even at low currents); this is contrary to that found in proton-exchange membrane fuel cells (PEMFC) and shows that caution is required when translating prior understating of PEMFC to APEMFC. The working hypothesis is that there is flooding-derived mass transport loss at the anode (where water is electro-generated).

Keywords: alkaline membrane fuel cell; reference electrode; Pd-coated-Pt electrode; anode and cathode potentials; in-situ impedance spectrum

1. Introduction

Fuel cells will play a key role in the delivery of clean energy for a future sustainable society. Alkaline polymer electrolyte membrane fuel cells (APEMFC) are attracting worldwide interest as they offer the potential to utilise cheaper, more abundant, non-platinum catalysts [1,2]; there is increasing evidence of their ability to operate in the presence of carbonate anions [3,4]. To probe the processes occurring at the anode and cathode during fuel cell operation, a suitable reference electrode (RE) is

required. There are reports on the use of a variety of RE types such as dynamic hydrogen electrodes (DHE [5–7]) and reversible hydrogen electrodes (RHE [8–10]) in proton–exchange membrane fuel cells (PEMFC) and solid oxide fuel cells; even carbon filaments can be used as pseudo–REs [11]. Construction of DHEs is complicated due to geometrical restrictions and high contact resistances; power is also needed to generate currents and the potential of DHEs are not stable for long periods of time in the absence of special precautions. For RHEs, pure hydrogen is usually supplied to a separated RE channel, where the potential can be affected by fluctuations in H_2 partial pressures.

Pd is a classical hydrogen storage metal which absorbs hydrogen at ambient temperatures and pressures [12]. Pd(core)/Pt(shell) nanoparticles absorb hydrogen at the Pt–Pd interface [13] and pure Pd and Pd–alloys [14] exhibit high activities towards the adsorption and oxidation of hydrogen in alkaline media. The above indicates that Pd–adsorbed– H_2 is retained for long periods of time, even on exposure to air, and this may be useful for the stabilisation of the potential of a Pt–wire RE. This report demonstrates the successful utilisation of Pd–coated–Pt wire RE in a APEMFC, which exhibits a stable potential that is insensitive to H_2 concentration.

2. Experimental details

Pd was electrodeposited on the surface of Pt wire in aqueous $(NH_4)_2PdCl_4$ (0.04 mol dm^{-3}) containing HCl (1 mol dm^{-3}) and using a current of 30 mA cm^{-2} (geometric). After deposition, the Pt/Pd electrode was charged at 30 mA cm^{-2} for 15 min (cleaning procedure) and then -30 mA cm^{-2} for 15 min (H adsorption) for experiments in both aqueous KOH and H_2SO_4 electrolytes (both 1 mol dm^{-3}). The potentials, currents, and impedance spectra of the alkaline membrane electrode assembly (MEA) electrodes (Pt/C(20%mass), 0.5 mg cm^{-2} Pt loadings) vs. the RE were recorded using a 1470E/1455A

CellTest system (Solartron Analytical, UK). The MEAs, radiation-grafted alkaline anion-exchange membranes (AAEM), alkaline ionomer, and fuel cell test procedures at 50°C were as previously reported [15,16].

3. Results and Discussion

The Pt/Pd wire (pre-treated at -30 mA cm^{-2} for H adsorption) is denoted (Pt)PdH; the RE stability was tested in both aqueous KOH (1 mol dm^{-3}) and H_2SO_4 (1 mol dm^{-3}) without $\text{H}_2(\text{g})$ purge. The (Pt)PdH RE showed two stable potentials with a switch from low to high potential after 10 min. The potentials of the (Pt)PdH RE vs. SHE are summarised in Table 1 and compared with a Pd/ H_2 electrode in the same electrolyte. The low potential plateau of the (Pt)PdH RE is similar to the Pd/ H_2 benchmark and is ascribed to the α - β phase transition of the Pd-H in the Pd layer. In the absence of a $\text{H}_2(\text{g})$ purge, the absorbed H in Pd layer of the (Pt)PdH RE desorbed slowly until the switch to high potential was achieved. When the concentration of the hydrogen absorbed on Pd is $< 2.2 \times 10^{-3} \text{ mol cm}^{-3}$ [18], or concentration ratio of hydrogen to Pd is < 0.03 [19], the α -PdH phase is present. Salvarezza [20] reports that H atoms diffuse into bulk Pd when the cathodised potential (E_s) is more positive than the reversible potential for the H_2 evolution reaction (E_r); when E_s is more negative than E_r the β -phase of PdH is formed. The (Pt)PdH RE showed only one stable potential of 772 mV vs. SHE when a high potential -62 mV vs. Ag/AgCl ($E_s > E_r$ condition) was applied, using aqueous H_2SO_4 (1 mol dm^{-3}) electrolyte, to absorb H_2 into (Pt)Pd RE; this was very close to the high potential plateau (762 mV) of the (Pt)PdH RE after the original -30 mA cm^{-2} H adsorption. This confirms the high potential state of the (Pt)PdH RE was due to the α -PdH at the Pd/Pt interface [13] (provides a constant H environment and yields stable potentials as sensed by the internal Pt wire).

The potential stability of the (Pt)PdH RE was also evaluated under fuel cell conditions. The (Pt)PdH REs were contacted to the surface of the AAEM (inactive area) at both the anode and cathode sides. A narrow channel was used to introduce $H_2(g)$ to the point of contact at anode side; this guaranteed that the low potential of the (Pt)PdH RE is stabilised by preventing desorption of H from the Pd layer (Fig. 1). Both the high potential and low potential states of the (Pt)PdH RE were stable during the test (< 10 mV drift). It is vital that the high potential of the (Pt)PdH RE on the cathode side is stable, as supply of $H_2(g)$ is not possible. The potential in the inactive area is assumed to be uniform as the RE is located at least $3 \times$ AAEM thickness away from the the electrode edge [7, 21]. Fig. 2 shows the $V-I$ curve of a typical alkaline MEA and the recorded anode and cathode potentials. As the performance of the cell deteriorated, the overpotential of cathode increased slowly but the overpotential of anode increased dramatically (in a similar manner to the deterioration of the cell response).

Fig 3 shows the effect of AAEM thickness on performance. The cathode overpotential changed less than that of the anode, which decreased significantly from 550 mV to 280 mV at a current density of 320 mA cm^{-2} when the AAEM thickness decreased from $160 \text{ }\mu\text{m}$ ($2 \times \text{S80}$) to $20 \text{ }\mu\text{m}$ (S20); R_{cell} decreased from $0.46 \text{ }\Omega \text{ cm}^2$ to $0.28 \text{ }\Omega \text{ cm}^2$, equivalent to only 42 mV less at this current density. Hence, the lower anode overpotential contributed more to the superior performance with the thinner AAEM than the ohmic loss. This is consistent with enhanced back diffusion of water from the anode to cathode with the thinner AAEM resulting in less anode flooding; this hypothesis is different to the one previously proposed, which had used the assumption that the anode overpotentials are insignificant compared to the cathode overpotentials (typical with PEMFC) [22]. Typical a.c. impedance spectra are presented in Fig 4. They confirm the d.c. results above in that the anode impedances are larger in magnitude than those of the cathode. The resistance deduced from the medium frequency anode

impedance arc did not decrease in a manner consistent with a charge transfer process (unlike the cathode response) so interferences from mass transport phenomena are suspected.

4. Conclusion

Initial results, obtained using a new concept Pd-coated Pt wire reference electrode, suggest that the significant performance losses in alkaline polymer electrolyte membrane fuel cells (APEMFC) can originate at the anode. This is atypical behaviour when compared to proton-exchange membrane fuel cells (PEMFC) where the cathode is normally the primary source of performance losses. The common assumption that prior knowledge of traditional PEMFC can be directly translated to APEMFC therefore requires caution. The proposed hypothesis is that water generation at the anode of APMFC causes flooding and mass transport impedances; this is alleviated with the use of thinner alkaline membranes, which facilitates back transport of water to the cathode.

Acknowledgement

The authors thank the Engineering and Physical Sciences Research Council (UK, Grant EP/F027524/1) and the Defence Science and Technology Laboratory for funding. Prof. Anthony Kucernak (Imperial College) is thanked for discussions on aspects of reference electrodes.

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Fig. 1. The stability of the (Pt)PdH reference electrode under fuel cell conditions (open circuit): $T_{cell} = 50^{\circ}\text{C}$, flow rates (H_2 and O_2) = $400\text{ cm}^3\text{ min}^{-1}$, RH = 100%, and no back pressurisation.

Fig. 2. The polarization curve and the anode and cathode potentials (vs. (Pt)PdH RE) recorded with a scan rate of 5 mV s^{-1} for a APEMFC containing $2 \times \text{S80}$ ($80\text{ }\mu\text{m}$ thick) alkaline membranes. Test conditions are the same as Figure 2.

Fig. 3. The effect of membrane thickness on the APMFC performance. The RE and other cell and test conditions are the same as Figure 2. Error bars indicate the range of potentials measured in 10 min under constant current discharge.

Fig. 4. The impedance spectra of (a) anode and (b) cathode. The APEMFC and test condition are the same as Figure 2.

Table 1 A comparison of the low and high potential responses of the (Pt)PdH reference electrode with the potentials of the Pd/H₂ system.

Electrolyte	Potential of Pd/H ₂ vs. SHE [17]	Mean low potential (Pt)PdH vs. SHE	Mean high potential (Pt)PdH vs. SHE
H ₂ SO ₄ (aq, 1 mol dm ⁻³)	+ 32 mV*	+36 mV	+761 mV
KOH (aq, 1 mol dm ⁻³)	- 776 mV*	-725 mV	+177 mV

* Corrected for H⁺ concentrations.

Fig. 1

Fig. 2

Fig. 3

Fig. 4