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An oxygen electrode for air-consuming proton exchange membrane fuel cells for transportation applications

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Electrodes for air-driven PEMFCs for transport applications have been developed. The structure of the electrodes has been specifically adapted to run with air as oxidant under near atmospheric pressure; such electrodes can be manufactured using conventional industrial methods and be easily scaled up. The technology has been demonstrated on a $50\,\mathrm{cm}^2$ electrode area, assembled together with a Nafion®117 membrane. Electrodes with different platinum loading, namely 0.4 and 0.2 mg Pt cm^{-2}, have been the subject of long duration tests which show a slow degradation of the cell performance. With air as oxidant at 180 kPa absolute pressure, 80° C as cell temperature and Nafion®117 as membrane, a power density of $350\,\mathrm{mW\,cm}^{-2}$ has been obtained.

1. Background

Proton exchange membrane fuel cells (PEMFCs) have been primarily developed for electric vehicle applications. Energy efficiency and power density need to be as high as possible for such terrestrial transportation applications. The essential criteria for the attainment of high energy efficiency are: (i) low activation overpotentials, which can be achieved by using electrocatalysts with high exchange current densities for the oxygen reduction reaction (ORR) (the exchange current density for the hydrogen oxidation reaction is sufficiently high and thus activation overpotential losses due to this electrode reaction are minimal in all types of fuel cells); (ii) maximizing the electrochemical active surface areas, in other words minimizing platinum requirements; (iii) minimal transport overpotential by optimization of electrode structure to accelerate the transport of reactants to and reaction products away from the active sites; (iv) low ohmic overpotentials, for example, by minimization of the thickness of electrolyte layers and use of membranes with higher proton conductivity; and (v) the attainment of long term stability performance.

2. Structure of oxygen reduction electrodes

One of the challenges in PEM fuel cell R&D is to minimize mass transport overpotentials by using air at low pressures as the cathodic reactant. As generally experienced when using hydrogen/air rather than hydrogen/oxygen as reactants, mass transport limitations have the following effects in PEMFCs: (i) an increased value of the slope in the pseudo-linear region of the cell voltage (V) against current density (I) plot, which decreases with increase in operating pressure and (ii) departure from linearity of the (I/V) plot and a rapid fall-off of V with increasing current density [1].

Now the use of hydrogen/air near atmospheric pressure is necessary for terrestrial transportation applications. An optimization of the structure of the oxygen reduction electrode (ORE) and the membrane electrode assembly (MEA) are essential to overcome mass transport limitations due to poor system water management. Water loss from the membrane can significantly increase its ohmic resistance for proton transport and on the other hand excessive humidification or ineffective removal of water produced at the cathode can cause flooding of the electrode and hence mass transport restrictions. Possible solutions are: (i) altering the PTFE content in the substrate and diffusion layer; (ii) use of electrodes with thinner and better gas diffusion active layers located near the front surface; and (iii) incorporation of a proton conductor during the fabrication of electrodes [1].

Srinivasan and coworkers [1] have estimated that the platinum utilization in the carbon-supported electrodes is only 10%. Much work is still to be done in order to obtain higher electrochemical activity of the platinum and obtain the same, or even higher, performances with lower platinum loading.

3. Technology

The principles of operation of a gas-diffusion electrode are well known. A three-phase interface (gaseous reactant, catalyst, ionomeric material) should be created in which two different kinds of electrical pathways (an ionic path and an electronic path) must be provided.

It is postulated by the present researchers that the low platinum utilization is due to the fact that only the electrocatalyst in direct contact with the ionomeric membrane or via structure incorporated ionomeric material is active. The electrocatalyst particles, which are not at a three-phase interface or not in

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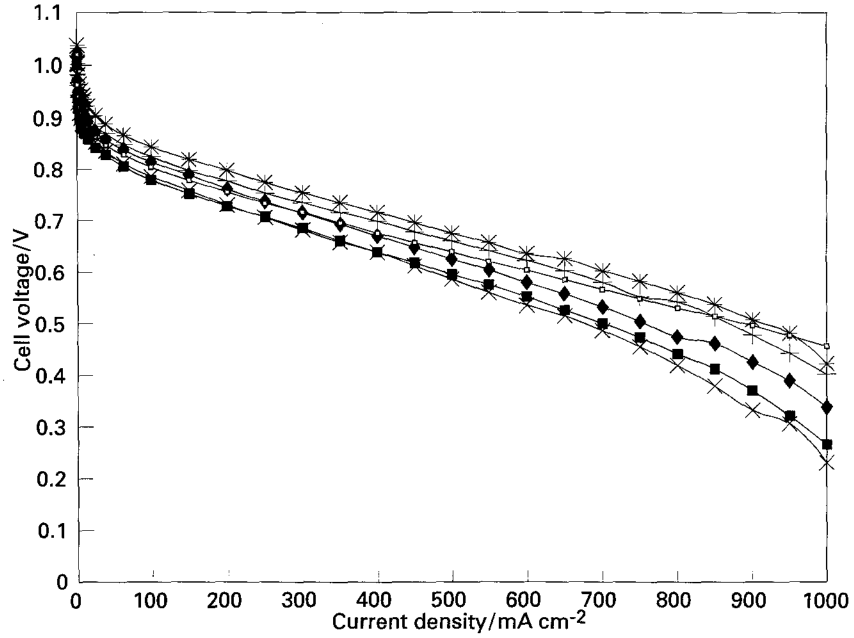

Fig. 1. Influence of gas pressure on the current-voltage curve for a 50 cm^2 single PDN040 cell with 0.43 mg Pt cm^{-2} at the cathode and with Nafion® 117 membrane. Conditions: T(cell) = 80° C; gas stoichiometry = 2.2; (□) H_2/O_2 = 125/125 kPa abs.; (+) H_2/O_2 = 200/210 kPa abs.; (*) H_2/O_2 = 300/310 kPa abs.; (■) H_2/air = 125/180 kPa abs.; (×) H_2/air = 200/220 kPa abs.; (◆) H_2/air = 300/320 kPa abs.

contact with the electrical path-ways, are thus superfluous. Serious attention should also be given to the diffusion properties of the backing (electrode support) in relation to the mass transport of reactants to and products (water) from the active sites.

According to recent publications on single cells based on 'thin-film catalyst' layers with ultralow platinum loading (0.20–0.15 mg Pt cm^{-2}) excellent cell performances have been obtained. Investigators at LANL (Los Alamos National Laboratory) [2–5] have used a contact-printing technique to deposit a thin active layer on a dry ionomeric membrane in the Na^+ form.

CESHR (Centre for Electrochemistry and Hydrogen Research) researchers at Texas A&M University have also fabricated electrodes with ultralow platinum loading using a 'rolling' technique. This method has involved preparation of the 'gas diffusion' and 'active' layers separately and pressing onto these layers a hydrophobic substrate [6].

Taylor *et al.* (PSI-Physical Sciences Incorporated) [7] have deposited platinum catalyst particles into the electrode by an electrochemical catalysation technique.

Based on the 'thin film catalyst'-method where layers with ultralow catalyst loading are cast, using

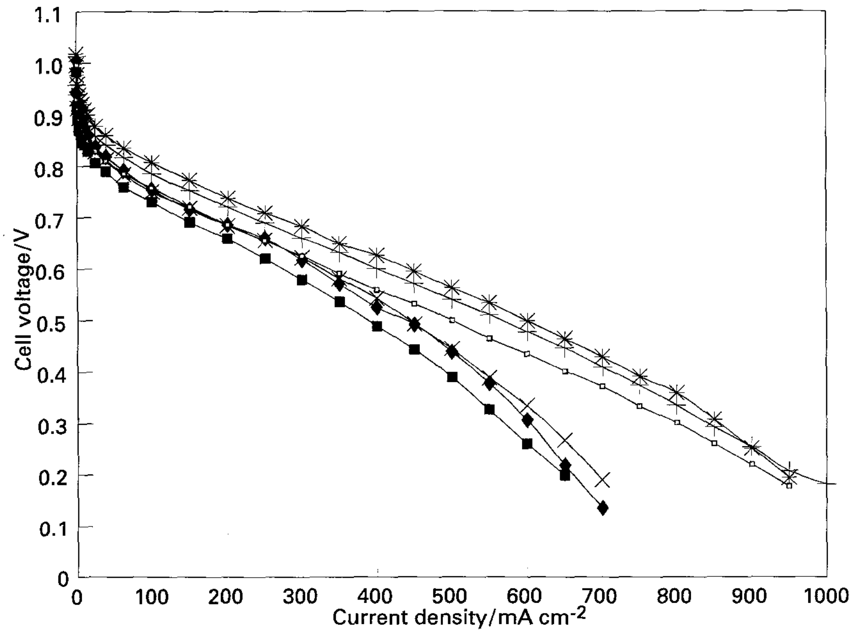

Fig. 2. Influence of gas pressure on the current-voltage curve for a 50 cm^2 single PDN042 cell with 0.21 mg Pt cm^{-2} at the cathode and with Nafion® 117 membrane. Conditions: T(cell) = 80° C; gas stoichiometry = 2.2; (□) H_2/O_2 = 125/125 kPa abs.; (+) H_2/O_2 = 200/210 kPa abs.; (*) H_2/O_2 = 300/310 kPa abs.; (■) H_2/air = 125/180 kPa abs.; (×) H_2/air = 200/220 kPa abs.; (◆) H_2/air = 300/320 kPa abs.

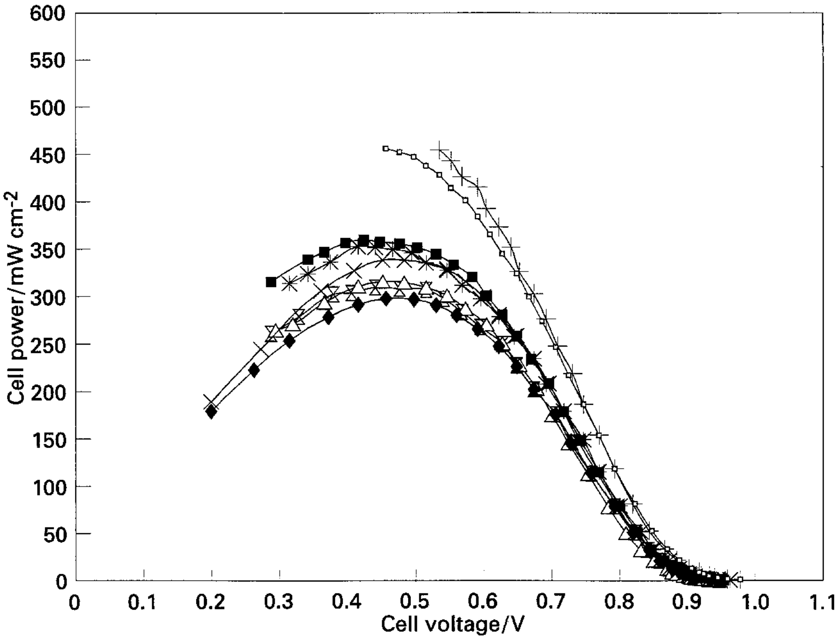

Fig. 3. Power–voltage curves. Durability test of a 50 cm^2 single PDN040 cell with 0.43 mg Pt cm^{-2} at the cathode and with Nafion® 117 membrane. Conditions: T(cell) = 80° C; gas stoichiometry = 2.2; (□) H_2/O_2 = 177 h; (+) H_2/O_2 = 254 h; (∗) H_2/O_2 = 419 h; (■) H_2/O_2 = 1259 h; (×) H_2/air = 252 h; (◆) H_2/air = 490 h; (△) H_2/air = 1261 h; (⊠) H_2/air = 1311 h.

different techniques, directly onto the membrane or onto a gas diffusion hydrophobic substrate, VITO has attempted to simplify the technology without a loss in performance.

The ORE thus developed, especially adapted for running with air as oxidant, can be manufactured using conventional industrial techniques and a production line for this type of electrode can be fully automated. The technique is applicable both for casting a 'thin-film catalyst' onto a membrane and/or a gas diffusion (backing) substrate.

This method of manufacture guarantees a good integration of catalyst-ionomeric material and electrically conducting support material and minimizes the transport limitation when using air as cathodic reactant. The first results obtained with 50 cm^2 cells are promising with air as oxidant under near atmospheric pressures.

4. Experimental details

Two single cells of 50 cm^2 were assembled, using conventional E-TEK Inc. anodes (loading 0.43 mg Pt cm^{-2} of 20% platinum supported on carbon) which were impregnated with Nafion®1100 5% solution (0.8 mg cm^{-2} dry Nafion®) and with home-made electrodes containing different platinum loading, namely 0.43 mg Pt cm^{-2} (code PDN 040, Figs 1 and 3) and 0.21 mg Pt cm^{-2} (code PDN 042, Figs 2 and 4) as cathodes. These electrodes had hydrophobic gas-permeable backings of a proprietary design provided with an electrocatalyst layer. The membrane surface can also be provided with an electrocatalyst layer.

The proton conducting membrane was Nafion® 117 (thickness 175 μm) and was treated in order to remove organic and metallic impurities as described by Srinivasan *et al.* [8]. The electrodes of 50 cm^2 were hot-pressed to the membrane. These membrane electrode assemblies (MEAs) were incorporated in a single cell test fixture and installed in a fuel cell test station (origin GlobeTech Inc.) [9].

The single cells were operated mostly at 80° C on hydrogen/air at 0.6 V cell potential with occasional brief operation on hydrogen/oxygen for the recording of polarization curves. The peak performances were reached after 10 to 20 h of operation.

5. Results

The two single cells PDN 040 and PDN 042 were subjected to prolonged tests lasting about 1300 h, at a cell potential of 0.6 V, with H_2/air as reactants. The fixed cell potential was periodically interrupted to record polarization curves with H_2/air or H_2/O_2 as reactants.

5.1. *Pressure influence*

Figures 1 and 2 depict polarization curves (I/V) of PDN 040 (0.43 mg Pt cm^{-2}) and PDN 042 (0.21 mg Pt cm^{-2}). The curves show the influence of pressure for oxygen and air, respectively, as oxidant. The pressure influence is low for the single cell with electrodes containing 0.43 mg Pt cm^{-2} and gas transport limitation is limited up to more than 1000 mA cm^{-2} current density. The pressure influence is more pronounced for the cell with the lower platinum content of 0.21 mg Pt cm^{-2} starting from a current density of 400 mA cm^{-2} (see Fig. 2).

5.2. *Power generation*

Figures 3 and 4 show power evolution curves of PDN 040 and PDN 042. For the cell with a platinum loading of 0.43 mg Pt cm^{-2} the degradation has stabilized

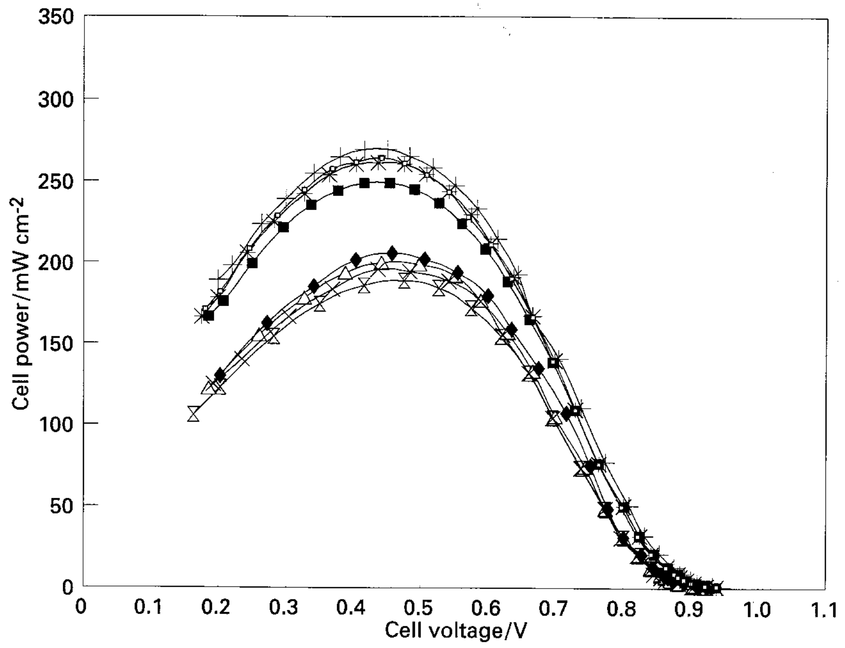

Fig. 4. Power–voltage curves. Durability test of a 50 cm^2 single PDN042 cell with 0.21 mg Pt cm^{-2} at the cathode and with Nafion® 117 membrane. Conditions: T(cell) = 80° C; gas stoichiometry = 2.2; (□) H_2/O_2 = 108 h; (+) H_2/O_2 = 613 h; (∗) H_2/O_2 = 948 h; (■) H_2/O_2 = 1248 h; (×) H_2/air = 110 h; (◆) H_2/air = 614 h; (△) H_2/air = 950 h; (⧖) H_2/air = 1285 h.

after about 1000 h of operation and the cells typically lost 20 to 25% of their original maximum power density over the duration of the life time tests. For the cell with a low platinum loading of 0.21 mg Pt cm^{-2} the decline of power density was found to be limited to a maximum of 10% after 1300 h of operation. This result is surprising because, in general, it is assumed that the degradation should be higher at lower platinum loading due to agglomeration of the catalyst during operation.

6. Conclusion

This limited series of experiments illustrates the potential benefits of cells with low platinum loading manufactured using a conventional industrial technique. The oxygen reduction electrode thus developed has performed well in conditions at near atmospheric pressure with air as the oxidant and had a low pressure influence, a low degradation rate and a low platinum loading.

Acknowledgements

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