

J. Vondrák · B. Klápště · J. Velická
M. Sedlaříková · R. Černý

Hydrogen–oxygen fuel cells

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Abstract Ion exchange non-fluorinated membranes were tested in half-cells used as models for hydrogen–oxygen fuel cells. The lower acidity of the membranes allowed us to reduce the chemical stability requirements for the construction and catalytic materials. The maximum energy yield at room temperature was close to 65% at a current density of 40–60 mA cm⁻².

Keywords Electrocatalysis · Hydrogen electrode Ionex membrane · Membrane fuel cell · Oxygen electrode

Introduction

Electrochemical low-temperature fuel cells have appeared as the focus of interest recently in many institutions [1]. Rapid progress has been made, especially in the development of polymer electrolyte fuel cells (PEFCs). For them to eventually enjoy widespread application, material costs will need to be lowered while the performance and reliability must be maintained [2]. Research activity should lead to the incorporation of low-cost electrodes in the near future [3]. For this reason the decision was made to use a half-cell method, as it is suitable for screening new materials or identifying which specific processes need to be improved in an existing electrode design. We have studied the properties of various catalysts with the aim to perform a possible replacement for platinum catalysts and ion exchange membranes. This work was already partially reported at the ABA-3 conference [4].

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J. Vondrák (✉) · B. Klápště · J. Velická
Institute of Inorganic Chemistry, AV CR, Řež, Czech Republic
E-mail: vondrakj@iic.cas.cz

M. Sedlaříková · R. Černý
Institute of Electro Chemistry, Borno University of Technology,
Borno, Czech Republic

Experimental

Membrane–electrode assemblies

Non-fluorinated heterogeneous membranes of a cationic type were used. The platinum metal, platinized carbon and/or manganese dioxide were deposited on the membrane, thus forming one half of a fuel cell. The assemblies were manufactured by MEGA (Stráž pod Rálskem, Czech Republic) by various procedures and labelled here by the symbols ME-98 to ME-105.

Experimental cell

A simple experimental cell was used (see Fig. 1). It can be used as a complete two-electrode cell or as a half-cell where just a metallic titanium foil serves as the counter electrode. The reservoir and the space between the membrane and the counter electrode were filled with an electrolyte (1 M sulfuric acid). The potential of the working electrode was measured using a saturated calomel electrode situated in the reservoir of the electrolyte. Hence, a small portion of the resistance (the electrolyte between the working electrode and the outlet to the reservoir, 1.5–2 mm approximately, corresponding to a resistance of 2.55 ohm cm⁻²) was included in the total value of the voltage; no compensation for it was performed. The catalytic layer was not in any direct contact with the sulfuric acid solution and oxides of various metals could be used.

All experiments were performed at room temperature (21–23 °C) and atmospheric gas pressure.

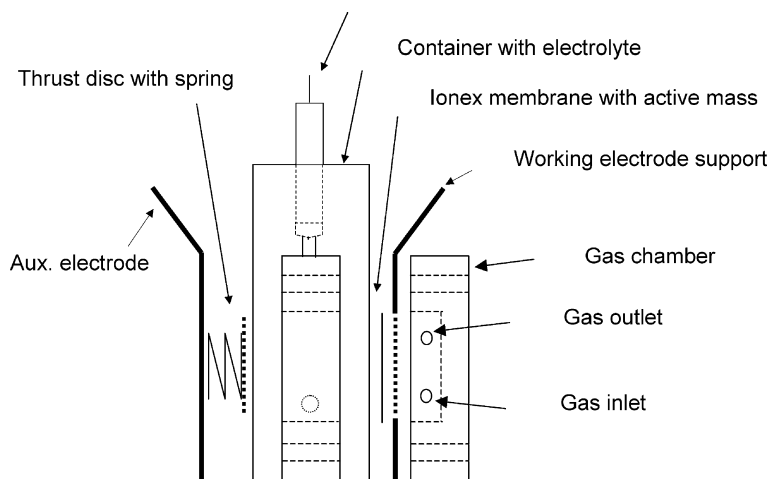
Procedure

In general, the current–potential curves (polarization curves) were recorded using a potentiostat. The electrode was fed with fuel or air, and then with nitrogen. The data obtained when the electrode was fed with nitrogen were considered as a blank run for the half-cell. Therefore, these were subtracted from the former ones (obtained using hydrogen or air) in order to eliminate the current necessary for the change of electrode surface, analogous to our previous work [5]. This was considered to be a net current for the corresponding fuel or oxygen reaction.

On platinum-containing electrodes, slow voltammetry was performed. The area and corresponding charge of hydrogen adsorbed on platinum was then estimated from the hydrogen peak.

Finally, the electrode assembly impedance spectra were measured and evaluated.

Fig. 1 Experimental fuel cell



Results and discussion

Reduction of oxygen

A series of polarization curves for oxygen electrodes with the ion exchange membrane is shown in Fig. 2. A dotted straight line was drawn; it begins at the reversible potential of oxygen and proceeds with the slope of the series resistance of a typical electrode.

Most of the curves exhibit the onset of the reaction at a potential which is considerably lower than the reversible potential of the oxygen reaction. Further, there is a region where the reaction rate is controlled by the kinetics itself and the polarization curve increases rather slowly. The higher the activity of the catalyst, the closer is the polarization curve to the straight line of the resistor (dotted line in Fig. 2). Finally, the end of the polarization curves is more or less parallel to that line,

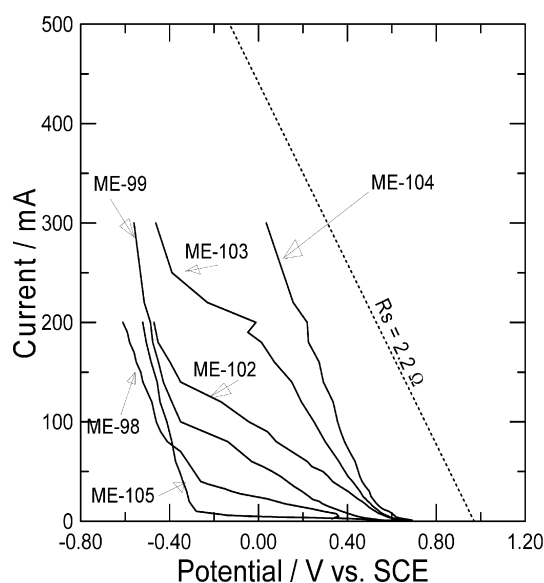


Fig. 2 Polarization curves for selected air-saturated electrodes

thus indicating that the rate-controlling phenomenon is predominately the ohmic resistance of the assembly. The selection of a good catalyst can easily be made in this way. Further, the electrode resistance and residual IR drop play an important role on the shape of the polarization curve.

Oxidation of hydrogen

Analogous curves were obtained for hydrogen electrodes; they are shown in Fig. 3. Apparently, the hydrogen electrodes are much more active than the oxygen ones in our systems. They differ from the former set of curves in several ways. First, the range between the reversible value and the onset is missing entirely on all of them. Second, no significant range governed mainly by the kinetics is apparent (with one exception). Finally, the most active electrodes exhibit control by ohmic resistance only.

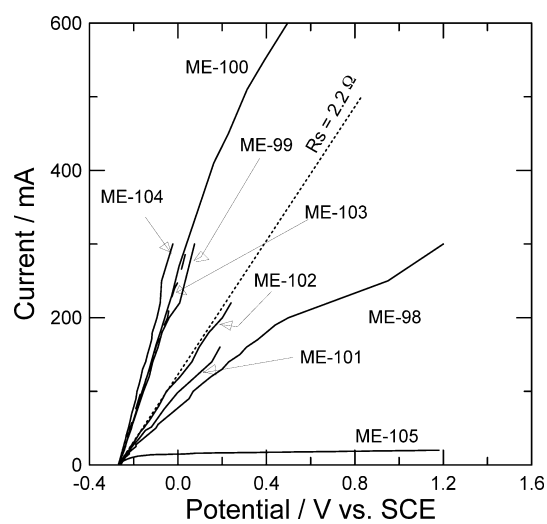


Fig. 3 Polarization curves for selected hydrogen-saturated electrodes

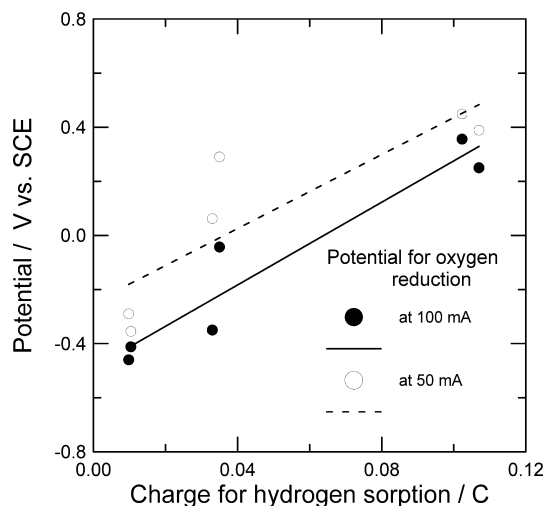
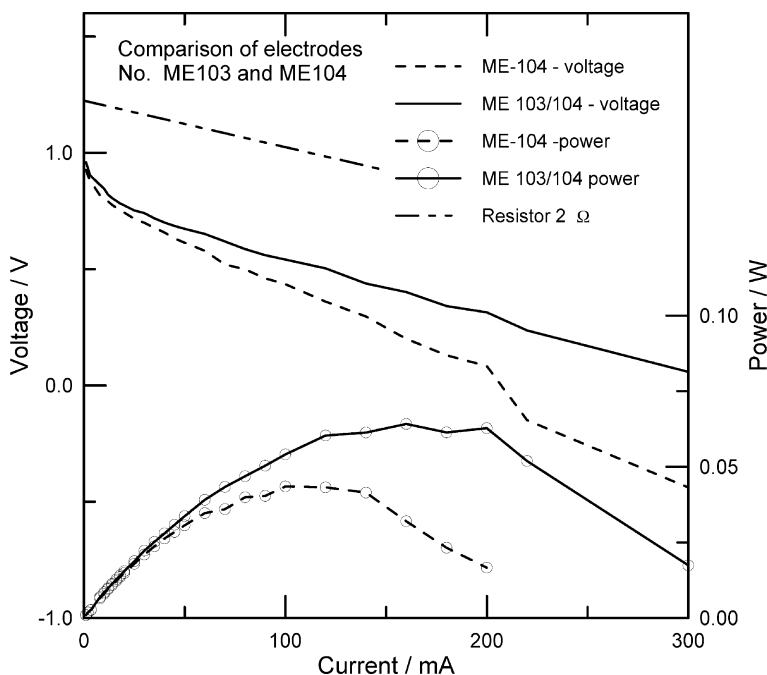


Fig. 4 The catalytic activity of the platinum-containing electrodes (expressed as the current necessary for reaching the selected current) plotted against the charge of adsorbed hydrogen

Correlation between catalytic activity and hydrogen adsorption

The potential necessary for the reduction of oxygen at two selected values of the current density is plotted in Fig. 4 against the charge of adsorbed hydrogen estimated from voltammetric curves on the same electrode assembly. The higher is the active surface area of platinum able to adsorb hydrogen, the higher is the activity of the catalyst and the potentials for oxygen reduction are shifted towards the standard potential of that reaction. It was impossible to find a similar effect in the case of hydrogen oxidation. Apparently, the catalysts were much more active in this case and the overall process is

Fig. 5 Simulation of a complete fuel cell using the best electrodes from Figs. 2 and 3



not so much affected by the active surface area of the platinum.

The electrode assembly impedance spectra series circuits containing the residual resistance (1.5–2.5 Ω) and the capacitance-like constant phase element (CPE = 0.1–0.5 F, phase angle close to 80°) described the properties of the electrode with sufficient precision. The meaning of the series resistance is just the description of ohmic losses in the electrode assembly.

Simulation of a complete fuel cell

A complete fuel cell was simulated numerically by a combination of the best positive electrode (samples ME-104 and ME-103) with a negative electrode (sample ME-104) and by subtraction of their polarization curves (see Fig. 5). Hypothetical values of the cell voltage were obtained in this way. The power could then be calculated as the product of current and voltage. Current densities up to 3500 A m⁻² and specific power close to 1 kW m⁻² were reached. The cell voltage at the maximum power corresponds to an efficiency of 60–65%. Again, the ohmic resistance of the membrane assembly and the overvoltage of the oxygen electrode seem to be the most critical points of the fuel cell design.

Conclusions

The use of non-fluorinated cationic ionex membranes for fuel cells was tested using a half-cell technique. The complete cell was simulated mathematically. The maximum power was close to 1 kW m⁻² with the efficiency ca. 60–65%. The catalytic activity is more important for

the oxygen electrode and it influences the onset of the electrochemical reactions. With a good selection of electrocatalysts, however, the mass transport and the series resistor of the system play overwhelming roles at the higher densities which correspond to real applications of fuel cells.

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