ION EXCHENGE MEMBRANES

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ABSTRACT

The possible application of anion exchanging membranes in chemical power sources is an interesting challenge. For example, its alkaline reaction means much lower requirements on the corrosion resistance of all materials used in power sources. We have measured the impedance and resistivity towards carbonate ions of several samples of membranes.

1 INTRODUCTION

Alkaline fuel cells(AFC) are an attractive, non-convention source of energy. AFC offer several advantages over the more commonly used and researched PEMFC. The kinetics of the electrode reactions are superior in an alkaline environment(AFC) compared to acidic environment (PEMFC). The inherently faster kinetics of the reactions in an alkaline fuel cell allows the use of non-noble metal electro-catalysts like nickel, silver, platinum. AFC exibit much higher current densities and electrochemical efficiencies at comparable temperatures over PEMFC. Moreover, AFC electrodes are stable and not prone to poisoning caused by carbon monoxide (CO), which poisons the platinum catalyst of the PEMFC. Therefore,considering the cost and simplicity of operation, AFC are more advantageous as compared to PEMFC and have better prospects in the commercialization of the fuel cells. However, AFC are inherently plagued by problem of carbon dioxide poisoning, which limits their use as air-breathing energy sources. The poisoning reaction depletes the alkaline KOH electrolyte directly by the following reaction:

$$CO_2 + 2KOH(aq) \rightarrow K_2CO_3(aq) + H_2O \qquad (1)$$

However, Gulzow and Schulze report that reported that, although carbon dioxide poisoning degreases an AFC performance, it does not cause any degradation of the electrodes [1].

2 EXPERIMENTAL

Following membranes were used for comparison:

- NAFION® No. 117
- Anion exchanging heterogenous membrane RALEX AM

  (MEGA Inc., Czech Republic)
- Bipolar membrane FuMA-Tech Ion Exchange Membrane (FT-BP)
- Anion exchanging membrane manufactured according to J.F. Fauvarque et al [2]. This material was synthesized by addition of DABCO (diazobicyclooctane) on polyepichlorhydrine and trimethylamine. APE screen was soaked by the liquid form of the ion exchanger and dried; this procedure was repeated several times.

The procedure was described by Fauvarque [*l.c.*] bu a condensation of polyepichlorhydrine with diazo bicycle octane (DABCO) followed by the addition of a ternary aliphatic amine. This way, a colloid was obtained and carefully deposited onto a PE screen or similar material. Then, it was hardened using thermal irradiation. The membrane was compared to the membrane RALEX AM (Mega Inc., Straz pod Ralskem, Czech Republic). The membrane was mounted between two compartements containing Pt current collectors and proper reference electrode (SCE and Hg/HgO).

A simple glass vessel with two compartments was designed. The tested membrane was clamped between two parts of the vessel, on which polished flanges were formed. Usually, 1M KOH solution was used. In order to estimate the influence of carbonate ions, the hydroxide was in the course of experiment replaced by 1 M solution of K_2CO_3 + 1M KOH. The behavior at d.c. polarization using a potentiostat Autolab (Ecochemie, The Netherlands) served as the source of polarization and for impedance measurements. The morphology of membrane surfaces was observed by an environmental SEM.

3 RESULTS AND DISCUSSION

The voltammograms are presented in Figs. 1 to 2. In general, the lowest conductivity of unipolar membrane was detected in the case of reinforced DABCO membrane. This was confirmed by impedance spectroscopy. The worse conductivity of DABCO membrane can be explained by the presence of reinforcing screen, which reduced the effective cross-section of the membrane, and which increased membrane thickness.

The formation of a space charge in a bipolar membrane polarised in blocking direction is clearly visible both from voltammetry and impedance measurements.

Both parts were filled by 1M KOH at the beginning and constant current (50 mA/cm^2 approx.) was applied. After a steady state had been reached, the electrolyte was replaced by the 1 M solution of K_2CO_3 and the steady state was reached again. Finally, the vessel was filled by the 1M KOH again.

The exchange of electrolytes was performed without interruption of electric circuit. The change of voltage was recorded. Admittance spectroscopy of the membrane measured in the steady state and in an open circuit conditions.

The course of voltage is indicated in Figs. 3, from which we see the increase of

resistance in the system by the introduction of carbonates, as well as the comparison between membranes RALEX AM and DABCO

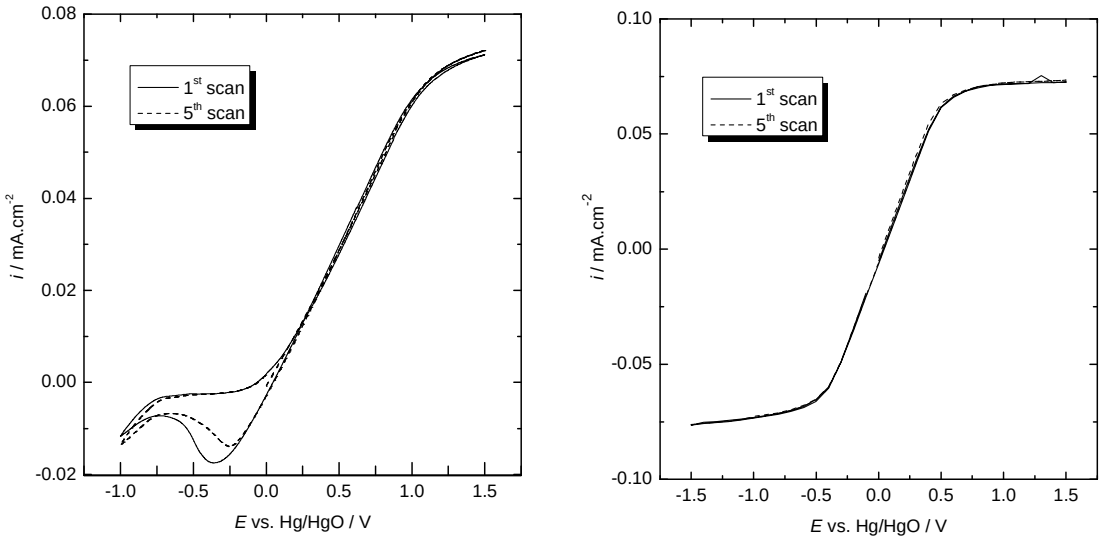

Fig. 1: *Cyclic voltammograms of the bipolar membrane FT-BM (left) and the cationic membrane Nafion® (right) – 1st and 5th scan (scan rate 10 mV.s-1, working electrode platinum).*

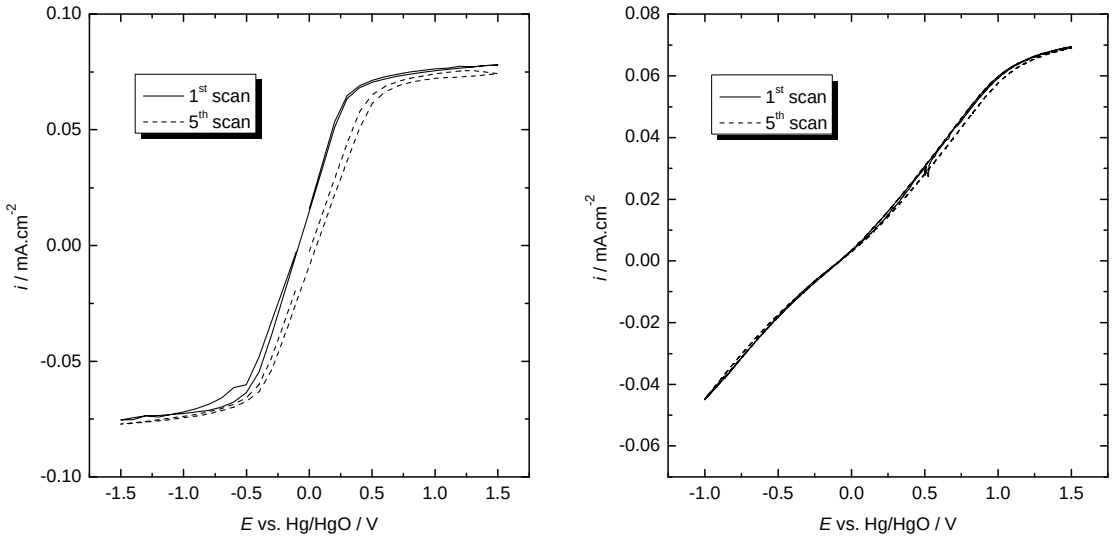

Fig. 2: *Cyclic voltammograms of the RALEX AM membrane (left figure) and the Dabco membrane (right) – 1st and 5th scan (scan rate 10 mV.s-1, working electrode platinum).*

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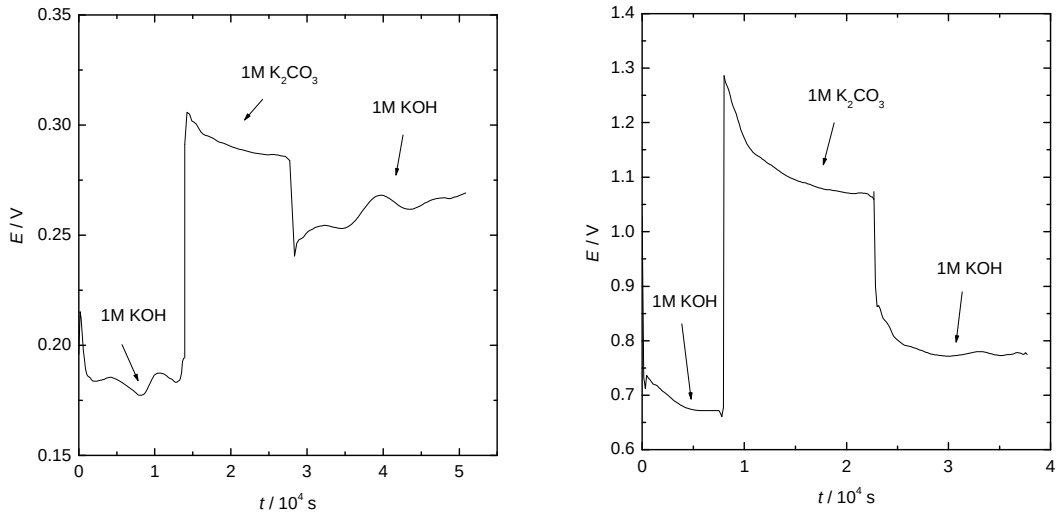

Fig. 3: *(left) Chronopotentiometrical measurement of RALEX AM membrane (current density 50 mA.cm^{-2}).*
(right) Chronopotentiometrical measurement of DABCO membrane (current density 50 mA.cm^{-2}).

4 CONCLUSION

The famous example of polyelectrolyte is the Nafion membrane, which is extensively used in numerous industrial processes and particularly in PEMFC. This cationic membrane is very strong acidic as electrolyte and gives excellent results. Pt/C catalysts only can be used with them in EMFC. Our aim is checking the possibility of an anionic or bipolar membrane with a catalyst MnO_x/C and/or NiO_x/C for FC [3, 4].

Anionic membranes are supposed to work under the influence of CO_2 from air used for positive electrode. The observation of this influence will be described in the presentation.

A) The conductivity of DABCO based membrane seems to be lower than that of membrane RALEX AM.

B) The reinforcement by a PE screen increases the conductivity several times.

C) The carbonate ions increase the resistivity of the membrane by a factor of 2 – 3, but this increase is almost reversible. Hence, these membranes can be used in any fuel cell with positive electrode fed by air instead of oxygen.

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REFERENCES

[1] Schulze, M., Gulzow, E.: Power sources 127(2004) 252-263

[2] Vasal, N., Salmon, E., Fauvarque, J.F.: Electrochim. Acta 45, 1527 (2000).

[3] Agel, E., Bouet, J., Fauvarque, J. F.: Power Sources 101, 267 (2001).

[4] Vondrák, J., Klápště, B., Velická, J., Sedlaříková, M., Novák, V., Reiter, J.: New Mat. Electrochem. Syst. 8, 1 (2005).

[5] Vondrák, J., Klápště, B., Velická, J., Sedlaříková, M., Reiter, J., Roche, I., Chainet, E., Fauvarque, J.F., Chatenet, M.: New Mat. Electrochem. Syst. 8, 209 (2005).