PERMEABILITY AND MORPHOLOGY OF POLYPYRROLE FILMS SYNTHESIZED WITH VARIOUS NUCLEOPHILES

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Polypyrrole represents one of the promising materials for preparation of composite electrodes in PEMFC. Utilization of Pt catalyst is one of most important present problems of PEMFC. As reported in literature [1,2] Pt particles integrated in conducting polymer matrix exhibit higher resistivity against catalyst poisoning in comparison to bare Pt. Also low Pt load is sufficient to reach electrocatalytic activity comparable to Pt. Main advantages of polypyrrole (PPy) represents high chemical and electrochemical stability and simple preparation from water solutions.

This work deals with the influence of the nature of the nucleophile incorporated into the PPy film on its morphology and hydrogen/proton permeability. Sulphate, Chloride, Polystyrene sulphonate (PSS) and Nafion 117 were used as the nucleophiles.

The PPy film was prepared potentiostaticaly at 0.75 V (vs. SCE) from solution of 0.1 M pyrrole and 0.1 M counterion (i.e. Cl^-, SO_4^{2-} or PSS^{n-} (related to monomer)). Commercial 5% solution of Nafion in isopropylalcohol with water was used to prepare solution for synthesis with the use of Nafion as counterion. The Nafion solution content from 10 to 70 % in synthesis solution was used. The film thickness was controlled by integrating the charge passed during synthesis.

Scanning electron microscope (SEM) was used to study PPy films morphology and impact of nucleophile nature on it. Also dependence of film thickness on charge passed was determined from SEM pictures.

The PPy permeability for hydrogen/proton was determined using a limiting current technique [3]. It is based on the division of the total current density on rotating disc electrode (RDE) into the three parts according to the following equation:

$$\frac{1}{j}=\frac{1}{j_{L(H_2)}}+\frac{1}{j_{f(H_2)}}+\frac{1}{j_{ads(H_2)}}+\frac{1}{j_{kin}}+\frac{1}{j_{f(H^+)}}+\frac{1}{j_{L(H^+)}}$$

where j is the total current density, j_{ads} highest obtainable current density related to adsorption of hydrogen on Pt surface, j_{kin} kinetic current density of hydrogen oxidation, j_L Levich current density controlled by the external diffusion and j_f maximal diffusional current density through the PPy film. In the present case PPy film was deposited on Pt electrode, At sufficiently high anodic potentials it is possible to neglect $1/j_{kin}$ term on this electrode.

As it was observed the nucleophile nature has an important effect on the electrochemically synthesised film morphology. Small nucleophiles as sulphate or chloride provide film with very rough surface (Fig. 1a,b). Especially chloride ions form typical “Cauliflower like” structure, whereas PPy film with incorporated PSS as a nucleophile shows compact structure with a smooth surface (Fig. 1c). In the case of Nafion nucleophile the synthesis from water/alcoholic solution provide PPy film disrupted with a defects across the whole film thickness (Fig. 2). The films synthesized from the solution containing more than 10 vol. % of Nafion solution are compact and smooth as expected for polymeric nucleophile (Fig. 1d).

Limiting currents for every type of film were measured with potential step of 0.1 V in range -0.2 to 0.5 V (vs. SCE). The RDE rotation rate were measured in range 50 to 3000 rotation per minute (rpm). Typical results are sown on Fig. 3. At lower potentials the kinetics of hydrogen oxidation is slow and limits the total current density. At more anodic potentials, the surface of platinum electrode is modified by consecutive formation of platinum oxides. This affects the hydrogen adsorption process and decrease current densities. The maximum current desities was observed in majority of cases around 0 V (vs. SCE). The values of limiting current density at 0 V (vs. SCE) for different film thickness are used to perform Koutecky-Levich analysis. The extrapolation to infinite rotation rate together with measurement on bare platinum electrode without PPy film enables us to evaluate hydrogen/proton coupled permeability of in PPy film. The results are summarized in Table 1.

nucleophile type	k [10^{-11} mol·m^{-1}·s^{-1}]
chloride	4.16
sulphate	1.73
poly(styrenesulfonate)	3.68
Nafion, 60 %	8.56

Table 1: *Values of adsorptive contributions and permabilities of PPy films*

The results indicate, that permeability of PPy film is more dependent on hydrophilicity than on the size or structure of nucleophile.

The Nafion as a counterion is of special interest among other anions because it is used as proton conducting membrane in PEMFC. Good compatibility of PPy film based electrode and Nafion membrane is required for fuel cell construction. It is possible to conclude that PPy films prepared from solution with higher content than 10 % of Nafion solution can be used as electrode. The permeability of PPy/Nafion film increases with the content of Nafion in the synthesis solution.

Acknowledgement

The financial support of this research by the Grant Agency of the Czech Republic, project number 104/02/0664, and EC project under contract number ENK5-CT-2001-00572 is gratefully acknowledged.

References

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Figures

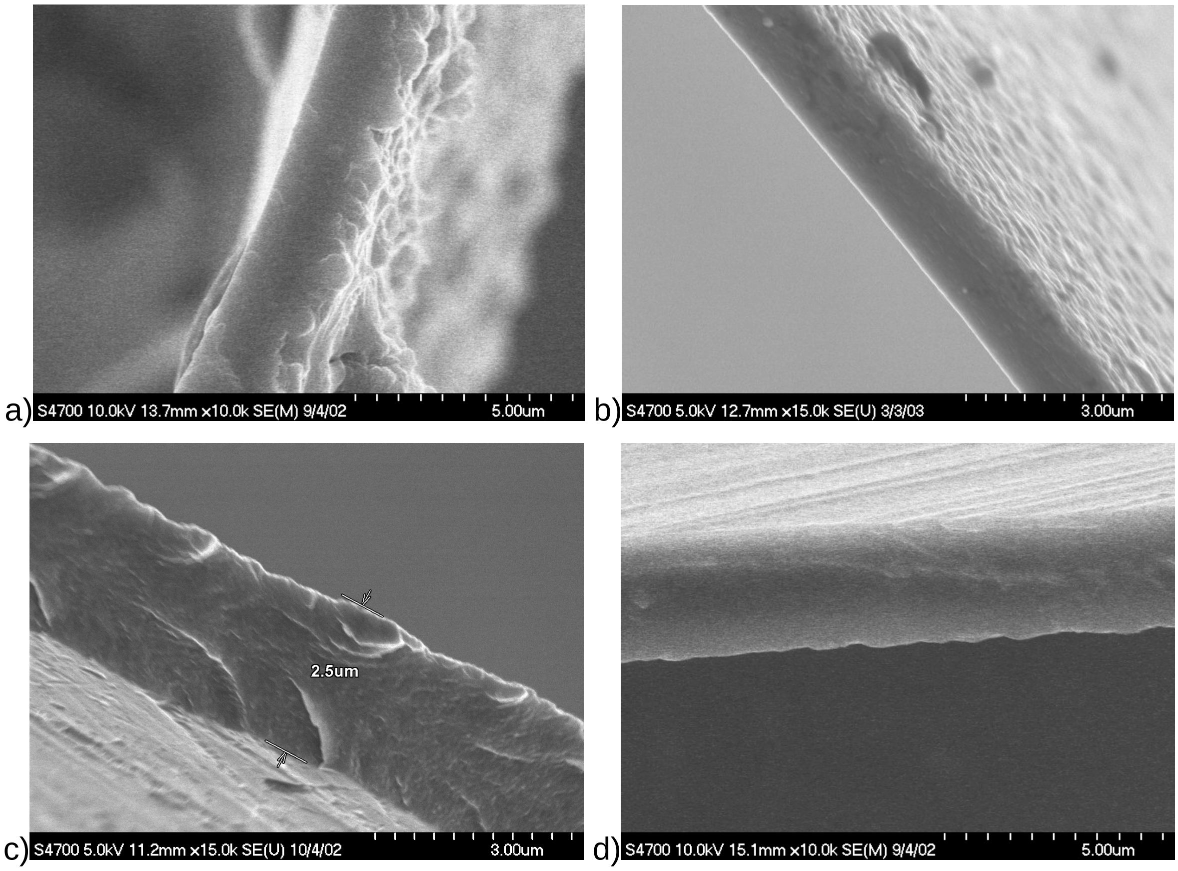

Fig. 1. *SEM image of cross-section of PPy film with nucleophile: a) Cl^-; b) SO_4^{2-}; c) PSS^-; d) Nafion.*

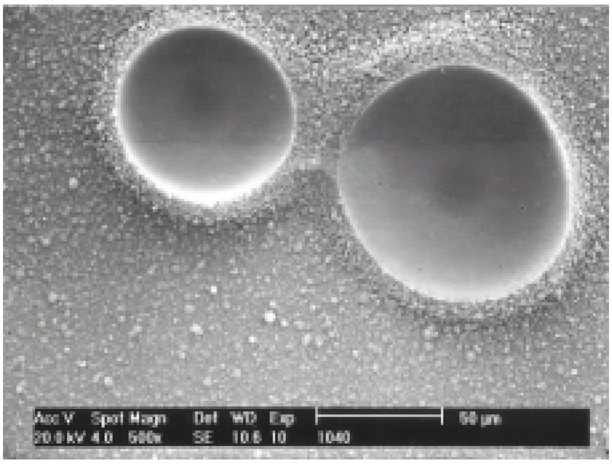

Fig. 2. *SEM image of surface of PPy film with nucleophile Nafion (synthesized from solution of 10% Nafion solution).*

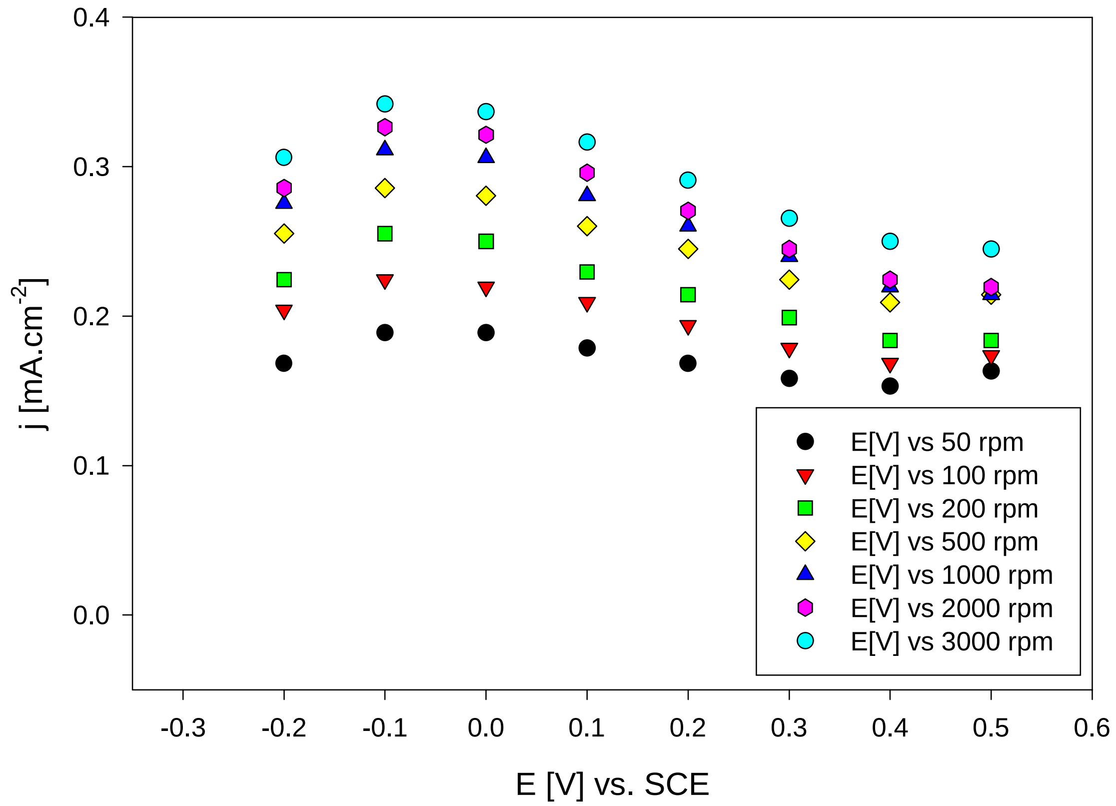

Fig. 3. *Polarization curves of PPy/PSS film, thickness 1.4 μm.*