

Stability study of PEMFC ionomers through model molecules mimicking polymer repeat units

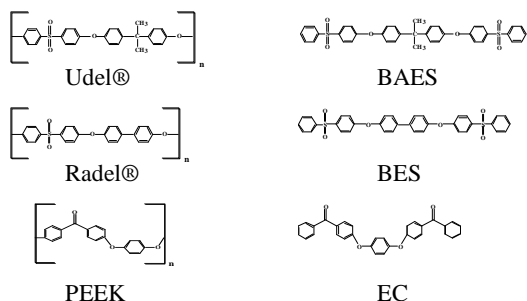
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PEMFC membranes are clearly identified as a technological bolt. A rather broad range of proton-conducting ionomers may fulfil the conductivity requirements but not the lifetime one [1]. Former work [2] proposed the advantage of composite membranes, i.e. polyelectrolytes filled by an inorganic proton-conductor such as phosphatoantimonic acids. Among the ionomeric materials free of fluorine, thermoplastics based on polyaromatic skeleton e.g. polyethersulfone [3] or polyetheretherketone are often selected [4]. We undertook in particular optimization works of the polysulfones sulfonation process [5]. The properties of these polymers and their sulfonated form to a lesser extent are rather well known [6, 7] but few studies deal with their electrochemical stability [8]. In order to accelerate the potential electrochemical instability, we selected to focus the study, by cyclic voltammetry, on model molecules. They mimic the polymer repeat units, e.g. of UDEL® and RADEL® from AMOCO and polyetheretherketone (PEEK) as well as their sulfonated forms. After their synthesis, their characterization was performed by ¹H NMR and carbon ¹³C NMR. Their thermal and electrochemical properties were thereafter evaluated

Syntheses

We carried out the synthesis of the model molecules of three polymers (see below) as well as theirs sulfonic forms.



Thermal testing

Thermogravimetric analysis (TGA) was performed on the materials in order to appreciate their thermal stability. Melting points and glass transition temperatures were measured using DSC and modulated DSC.

Electrochemical stability study

Choice of a solvent

We chose the sulfolane as solvent for our study with respect to its main characteristics:

- high boiling point (280°C) allowing studies at high temperature,
- a good solvent of the model molecules,
- a wide enough electrochemical window from -2V to +1V vs. Ag/Ag⁺ 10mmol, includes that of water.

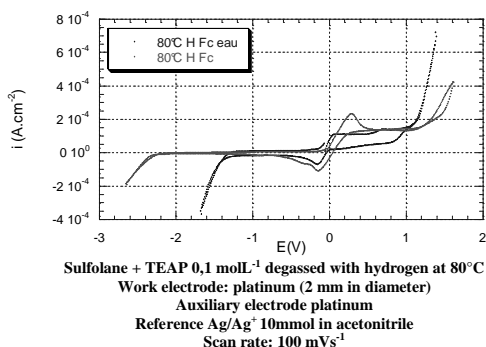
Ferrocene was added in the same concentrations as the studied molecules to have a well-known redox couple, used as internal reference. This molecule is generally used in solution, with regard to its fast and reversible redox couple little influenced by the nature of used solvents. It makes it possible to have a potential of reference well defined and quasi-independent of solvent. Moreover, this introduction makes it possible to check, by comparison of current density vs. that of ferrocene, that all the conditions necessary to the observation of an electrochemical signal are met.

Study segmentation

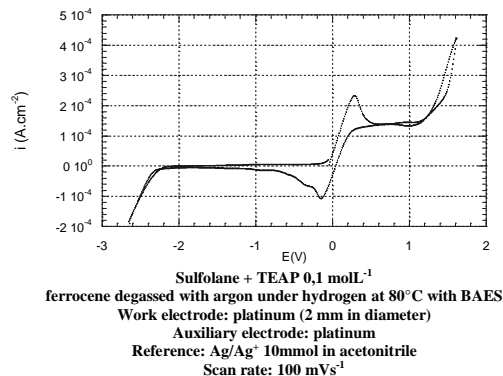
The electrochemical study plan follows gradual complexation logic to reach the closest conditions which the polymer used in a PEMFC. The molecules are studied at 30°C then 80°C under argon, under oxygen then under hydrogen. The conditions closest to operation of a PEMFC which we want to reach are an Etek® electrode, under hydrogen.

Results

The sulfolane is well adapted to our study since its stability redox field is more significant than that of water. We also check on the same graph which follows the stability of the couple Fc^{+/0}.



The following cyclic voltammetry is typical of those obtained for the model molecules. It shows their stability in the electrochemical window of sulfolane and, therefore in water.



The various model molecules did not show any instability under these experimental conditions. However, these preliminary studies proceeded in a medium chemically far away from the conditions met in the Fuel cells. It is obvious that it cannot be inferred that an instability of molecule model may inevitably induce a dramatic decrease of the membrane lifetime, but on the contrary an electrochemical stability of the repeat unit is a warrant of the associated polymer one.

References

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