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Time-resolved ESR investigation on energy transfer processes in Nafion photochemistry

Fosca Conti [a,*], *Enrico Negro* [a], *Vito Di Noto* [a], *Gordon Elger* [b], *Thomas Berthold* [c], *Stefan Weber* [c]

[a] *Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova, Italy*
[b] *Global Technology Development Aachen, Philips Techology GmbH, Philipsstr. 8, 52068 Aachen, Germany*
[c] *Institute of Physical Chemistry, Albert-Ludwigs-University of Freiburg, Albertstr. 21, 79104 Freiburg, Germany*

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ABSTRACT

A solid film of Nafion has been prepared on the inner wall of a quartz tube. After pulsed photoexcitation, time-resolved electron spin resonance (TR-ESR) spectra have been recorded in the temperature range of 290–15 K. The spectra exhibit strongly electron-spin polarized signals in full absorption arising from the excited triplet state of Nafion. The absence of any resolved spectral features and the unusual narrowing of the TR-ESR signal linewidth with decreasing temperature are discussed in terms of the spin Hamiltonian of an excited triplet state with dynamic dipole–dipole interactions between the two unpaired electron spins. The existence of a triplet–triplet energy transfer process is considered, and a prominent role of hydrogen bonds of the surrounding water network is suggested. Finally, the time evolutions of the TR-ESR signals have been analysed, and the corresponding decay parameters have been obtained at low temperatures. Our results provide insight on the role of water as a medium for the conductivity mechanism in Nafion membranes.

1. Introduction

The energy demand in the world is constantly growing, both because of the thrust of industrialized nations, and the increase in energy consumption of the developing countries. The latter arises from their increasing populations and growing industrialization. Recent international agreements have indicated one feasible solution to make the development compatible with the environment: the widespread adoption of technologies to reduce energy consumption and the environmental impact of human activities. In this context, fuel cells (FCs) play an important role among the energy conversion devices that constitute a real prospect in the medium and long term.

An FC is a device that converts the chemical energy of its reagents into electrical power, without resorting to a thermal cycle [1]. For this reason, FCs are characterised by an energy conversion efficiency much higher than that of traditional thermal engines. FCs may be fed with hydrogen; in this case, no greenhouse gases are produced and the maximum efficiency is reached [2,3].

All FCs consist of two electrodes separated by an appropriate electrolyte [4]. The electrochemical reactions involved in a cell take place on the electrolytic active sites of the electrode configurations. There are several types of FCs, characterised by specific functional materials and different operating temperatures. In particular, polymer electrolyte

* *Corresponding author*. Tel.: +39 049 8275118; fax: +39 049 8275829.
E-mail address: fosca.conti@unipd.it (F. Conti).
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membrane FCs (PEMFCs) have raised considerable interest as they are characterised by a high efficiency of energy conversion, high energy density, ease of assembly and silent operation [5]. Finally, since PEMFCs operate at low temperatures, they do not produce gaseous pollutants such as SO_x and NO_x, nor fine particulate. However, despite significant recent technological advances, the large-scale manufacturing and the marketing of PEMFCs are still restricted due to the high production costs and the lack of durability of state-of-the-art functional materials.

Perfluorinated polymers functionalized with sulfonic groups are commonly used in PEMFCs as the electrolyte membrane [6]. The cell is fuelled by hydrogen or methanol at the anode, and oxygen or air at the cathode, and is based on the discovery that oxygen and hydrogen can react to produce electricity: the membrane allows hydrogen ion (H^+) transport in one direction only, from the anode to the cathode, while preventing electron conduction, so that electrons move to an external electric circuit, and electricity is produced [7,8].

Nafion is the material of choice for polyelectrolyte membranes in many FC applications due to its superior physicochemical properties, in particular its high proton conductivity, chemical resistance and thermal stability [9]. Made by DuPont in the late 1960s, Nafion is a polymer consisting of a perfluorinated backbone and oligoether pendant chains terminated by sulfonic acid groups ($-SO_3H$). The conductive properties mainly depend on the equivalent weight (EW), which is the mass that contains 1 mol of $-SO_3H$ groups.

Although Nafion has demonstrated stable performance in FC applications, evidence of polymer degradation has been observed even at an operating temperature of 320 K by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) [10]. The type of structural damage seems to be different at the anode and cathode sides [11]. Previous studies [12] suggested that the chemical degradation of membranes occurs by oxidative processes during red-ox reactions in FCs, and that reactive oxygen-containing radicals are involved. The radicals are active intermediates, which can ultimately lead to membrane thinning and pinhole formation.

The paramagnetic nature of radicals makes electron spin resonance (ESR) an attractive tool in the determination of their presence and in the identification of their structural and electronic properties [13]. ESR, often also called electron paramagnetic resonance (EPR), is a method based on the absorption of electromagnetic radiation, usually in the microwave frequency region, by a paramagnetic sample exposed to an external magnetic field. The absorption takes place only for definite frequencies and magnetic-field combinations, depending on the sample characteristics. The first ESR experiment has been performed more than 60 years ago in Kazan by E.K. Zavoisky, a physicist who used samples of $CuCl_2 \cdot H_2O$, a radiofrequency source operating at 133 MHz and a variable magnetic field operating in the range of few Gauss provided by a solenoid magnet. Nowadays, ESR is used in various branches of science, such as chemistry, physics, biology, earth science, and material science. Modern ESR spectrometers can be used with a large number of samples (crystalline solids, liquid solutions, powders, etc.) and in a broad range of temperatures. The parameters characterizing the ESR spectrum are related to the structure of the species giving rise to the signal, to their interactions with the environment, and to the dynamic processes in which the species are involved [14].

Steady-state ESR techniques have evidenced the absence of any paramagnetic species in pure Nafion membranes before their use in FCs, and an effect of the electrocatalytic metal during the red-ox reactions in FCs has been suggested [15,16]. Several research groups investigate the formation of reactive oxygen-containing radicals. A localisation of the degradation [17] and a full elucidation of the underlying mechanism would open the possibility to prevent deterioration by selective measures [12,18].

By measuring the direct ESR detection without magnetic-field modulation following pulsed laser excitation, time-resolved ESR experiments (TR-ESR) can be carried out [19,20]. The limit in time resolution is nowadays on a lower nanosecond time scale so that TR-ESR spectroscopy is a powerful technique to study short-lived paramagnetic species and excited states in Nafion membranes. Kinetic processes involving the photochemical and photophysical dynamics of the transient species can also be investigated. Very often the species are generated in an electron spin-polarized fashion, i.e., with populations of the spin levels very different from those found at thermal equilibrium (Boltzmann populations). This phenomenon [21] gives rise to a strong signal enhancement, either in absorption or in emission.

We have recently presented, in a short communication, the first TR-ESR observation of the photochemistry of Nafion [22]. The presence of an absorptive signal following pulsed UV irradiation of a Nafion film has been related to the sulphonic acid groups located at the end of the side oligoether chains of Nafion. In particular, we have evidenced the formation of a photoinduced mobile triplet state in this material, and we have invoked a photoinduced triplet–triplet energy transfer process, to which the hydrogen bonds between water molecules of the surrounding network and sulfonic acid groups were suggested to be essential.

In this paper we present the results of TR-ESR studies of the photochemistry of Nafion in a wide range of temperatures (15–290 K). The Nafion film is UV irradiated and the transient ESR signals are analysed as a function of the temperature. The observed Nafion photochemistry confirms the attribution of an excited triplet state. We consider electron spin polarization involving mobility of the triplet state, and as a consequence, the transfer of energy. Finally, we present a spectral analysis of the ESR data which is in line with the Dexter exchange mechanism [23]. Our results allow us to obtain crucial information on the local water cluster morphology and dynamics near the sulphonic acid groups of Nafion matrix. This information is of fundamental importance in order to elucidate the role of water in the conductivity mechanism of Nafion.

2. Experimental

2.1. Materials and sample preparation

Nafion 117 was purchased from Ion Power, Inc. and purified as described previously [24,25].