



Studies of structure formation in Nafion-based nanocomposites for fuel cell membranes

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Report:

The proton-exchange membrane (PEM) is a central, and often performance-limiting, component of all-solid H₂/O₂ polymer electrolyte fuel cells (PEFCs). Most actual PEMs based on perfluorosulfonic polymers like Nafion from DuPont, offer the set of properties such as high protonic conductivity, chemical and mechanical stability required to perform in PEFC [1]. The previous studies show that the cylindrical inverted micelles which are formed in the material upon hydration can serve as ion-channels for PEFC devices [2-3]. To increase the important characteristics of the material like water uptake, retain hydration at higher temperatures and tolerance to impurities (CO, H₂S) new class of composites prepared by sol-gel process to grow silica nanoparticles (PEOS) in the membrane.

In the present work the comparative analysis of structure and morphology of membranes based on perfluorosulfonic polymers and their composites with PEOS nanoparticles was performed. The films with different humidity were prepared to address the role of water molecules in structure development.

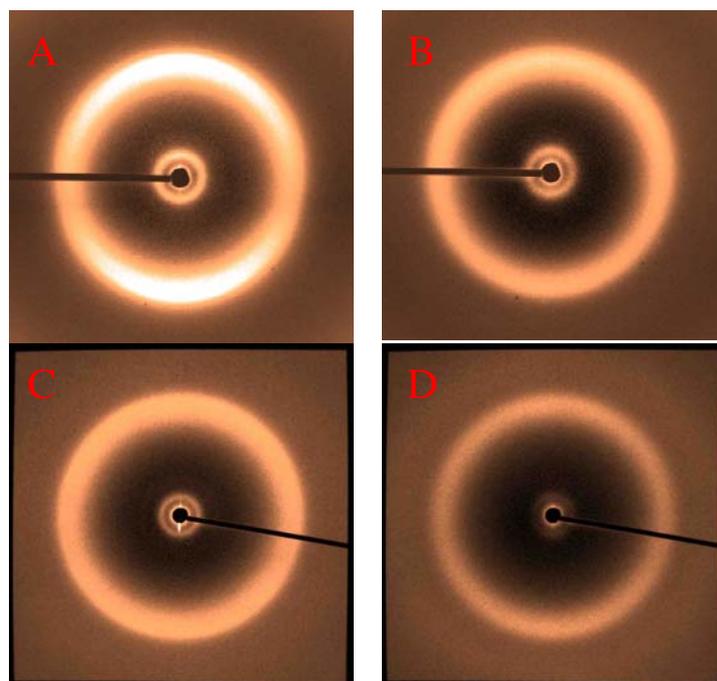


Fig.1: WAXS patterns of pure membranes (A,C) and with 10% of PEOS particles (B,D) at room humidity (A,B) and wet samples (C,D).

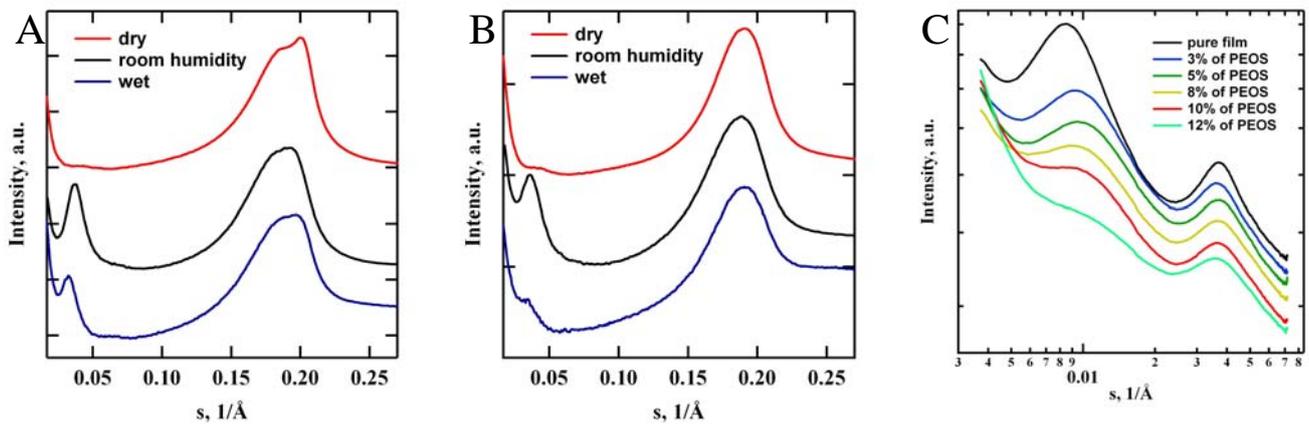


Fig.2: Integrated 1D WAXS patterns of pure membrane (A) and composite with 10% of PEOS (B) at different humidity. SAXS curves of composite with different content of PEOS (C)

Wet samples were stored in water for several hours and extracted directly before measurements. Dehydrated films were prepared by drying in vacuum oven for 48 hours at 100°C. Then the films were closed in dry capillaries. All measurements were performed in transverse direction.

The diffractograms measured in transverse geometry of pure film and composite with 10% of PEOS show orientation of the peaks on meridian (Fig.1). The first visible peak at 30Å is attributed to the inter-cylinder distance (Fig.1A). The orientation of this peak indicates that the ion channels are parallel to the film substrate. For the composite the intensity of this reflex decreases because of distortion of channel structure by PEOS particles (Fig.1B). The second peak is found to be double (5.4 and 5.7Å) and correspond to the distorted crystal structure of PTFE. The intensity and orientation of this peak does not depends on PEOS concentration. The 2D WAXS patterns of wet samples indicate significant disorientation of the peaks at 5.7 and 5.4Å because of presence of high amount of water in the material (Fig.1C,D). In addition, the reflex at 30Å almost disappears for the composites and becomes weaker for pure membrane. Probably, upon swelling in water the high degree of hydration of sulfonic groups prevents formation of regular narrow ion channels. Meanwhile, low intensity of the inter-channel peak was found for all dry samples indicates crucial role of water in channels formation (Fig.2A,B). However, the peaks of PTFE structure are better pronounced for the dry material. It should be mentioned that intensity of these reflexes consequently decreases with growth of PEOS content for both dry and wet membranes.

The SAXS curves of composites at room humidity show the presence of peak at 120 Å (Fig.2C). With increase of PEOS content the intensity of this peak decreases. The nature of this peak is referred to lamellar organization of the material which is disturbed by incorporated PEOS particles.

In conclusion, the analysis of WAXS and SAXS data shows an effect of water presence on crystalline structure of the membranes. The variation of the inter-channel peak intensity reveals that the room humidity is optimal for their formation. The dehydration leads to the collapse of empty cavities and disappearance of phase contrast. The presence of PEOS particles in the material limits the formation of water-rich channels or completely disturbs them in wet samples. They also penetrate into interlamellar regions and hinder regular lamellar stacking. Thus, the membrane structure is sensitive to the presence of filler on nanometer scale.

References:

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