Structure of the hydrophilic phase and its impact on the conductivity of graft copolymer ionomers at low hydration level

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ABSTRACT

SAXS studies indicate that the spatial distribution of ion-rich clusters is not uniform in radiation grafted polymer electrolytes based on a semi-crystalline polymer matrix. Due to the matrix microstructure, certain domains of the polymer electrolyte are rich in these hydrophilic clusters, while other domains are devoid of them. Therefore, the hydrophilic phase is not continuous on the nano-scale, which results in fluctuations in the volumetric number density of ion-rich clusters. The length-scale of fluctuations within the electrolyte is larger than the characteristic distance between ionic aggregates, and we argue that at low hydration level it has a negative impact on the percolation and connectivity of the aqueous phase. However, an increased number density of hydrophilic clusters within grafted domains or an increased volume fraction of grafted domains within the semi-crystalline polymer both have favorable impact on the conductivity at low-hydration levels. We anticipate that a polymer electrolyte with a less heterogenous distribution of hydrophilic clusters would have considerably improved proton conductivity at low-hydration levels, because a uniform distribution on the one hand decreases the percolation threshold of the aqueous phase and one the other hand increases the connectivity of the hydrophilic clusters.

1. Introduction

Radiation-grafted ion-containing copolymers are materials of interest for use as electrolyte membranes in electrochemical cells, owing to the their potentially low-cost synthesis [1] and versatile nature due to the possibility of introducing various types of functionalities into polymer substrates [2]. Both the base polymer and the graft component(s) can be selected from a wide range of commercially available materials. This allows the design of graft copolymers with tailored functional properties. In general, the grafted polymer can have very different properties compared to the base polymer, e.g. strongly hydrophilic styrene sulfonic acid (SSA) grafts attached to a hydrophobic, perfluorinated base polymer [3]. In particular, radiation-grafted copolymers containing sulfonic acid have attracted considerable attention as candidates for cost-competitive electrolytes in the polymer electrolyte fuel cell [4–7]. In this case the polymer electrolyte has two elementary functions: enable the transport of protons from anode to cathode and prevent

the passage of the reactant gases and electrons. For a lifetime of several thousand hours both mechanical and chemical stability are necessary. The cycles of water absorption and drying can lead to degradation in terms of mechanical stability. Consequently, a lower water uptake may improve the lifetime, but unfortunately it also entails lower conductivity. A challenging task is to moderate the loss in proton conductivity at low water content [8]. The proton conductivity strongly depends on the proton concentration and the structure and connectivity of the aqueous phase [9], whose percolation is driven by the gradual coalescence of the aqueous domains upon increasing the amount of absorbed water. The aqueous phase may form only because of the presence of ion-rich clusters containing aggregated SSA groups phase separating from the polymer matrix [10]. The spatial arrangement of these clusters is likely to govern the connectivity of the aqueous phase, especially at low level of hydration where the swelling of these hydrophilic domains is moderate, and therefore, so is their coalescence and connectivity. The composition and architecture of the polymer are expected to have essential impact on the ion-rich phase. Due to the increasing interest in radiation grafted copolymer systems, the influence of the graft composition on the structure, and the influence of the structure on the ion-rich phase are now better understood for certain systems [11–13]. An insight into of the

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structure–property relationships in polymer electrolytes is of high priority, and it will potentially lead to the synthesis of low-cost yet high-performance membranes [14]. The subject of this paper is the study of a sulfonated copolymer based on poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) co-grafted with styrene and methacrylonitrile (MAN). The use of MAN as a co-monomer was found to improve the chemical stability and lifetime of radiation grafted membranes under fuel cell operating conditions [15]. To vary the ionic content of the pendant chains, the ratio of the two co-monomers is varied systematically. The primary goal of the paper is to gain insight into the relationship between the dry-state structure of the hydrophilic phase and the proton conductivity at low hydration levels. We investigate the copolymer in terms of 1) graft topology, 2) chemical microstructure of the pendant chains, and 3) structure of the ion-rich phase containing the SSA groups aggregated in the dry state. The results are compared with Nafion, being ever the most studied material among polymeric electrolytes.

2. Materials and experimental

2.1. Copolymer synthesis

The synthesis of the radiation-grafted copolymer is detailed elsewhere [15,16]. A 25 μm thick ETFE (Tefzel (R) 100LZ DuPont, USA) film was used as the base polymer. The electron pre-irradiation method, under air within doses of 1.5 kGy and 3 kGy, was used to graft styrene and methacrylonitrile (MAN) onto the ETFE backbone, as illustrated in Fig. 1.

The grafting solution consisted of 20% (vol./vol.) monomer (various mixtures of styrene and MAN), 70% isopropanol, and 10% water. The grafting reaction was carried out under a nitrogen atmosphere at 60 °C. The graft level is defined as the relative weight increase of the film upon grafting

$$G \doteq \frac{m_g}{m_0} - 1, \qquad (1)$$

where m_0 and m_g represent the weight of the film before and after grafting, respectively. The mole fraction of styrene with respect to the total monomer content was varied systematically in the grafting solution.

2.2. Grafted chain composition

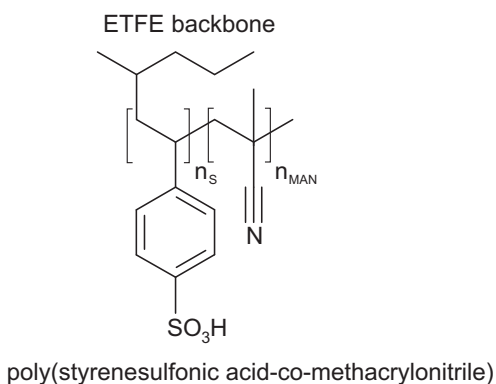The mole fraction of styrene with respect to the total monomer content in the grafted copolymer

ETFE backbone

poly(styrenesulfonic acid-co-methacrylonitrile)

Fig. 1. The proposed structure of the ETFE-g-poly(styrene sulfonic acid-co-methacrylonitrile) polymer electrolyte.

$$X \doteq \frac{n_S}{n_{MAN} + n_S}, \qquad (2)$$

where n_S and n_{MAN} are the numbers of styrene and MAN units, respectively, was measured by means of Fourier transform infrared spectroscopy [17] using a Perkin Elmer FTIR System 2000, Waltham, USA. Bands of specific interest are the C=C aromatic stretching vibration at 1494 cm^{-1} for styrene, the C≡N stretching vibration at 2234 cm^{-1} characterizing MAN, and the C–H deformation vibration at 1325 cm^{-1} for ETFE [15]. Each infrared spectrum was collected with a frequency resolution of 4 cm^{-1} and was analyzed using the GRAMS/385 software (version 7.01, Galactic Industries, Salem, USA). Two groups of films were synthesized. For the first group (A) the target graft level was constant: $G = 40\%$. For the second group (B) the target ion-exchange capacity (IEC) was constant: IEC = 1.5 mmol/g. The ion-exchange capacity is defined as the number of SO$_3^-$ exchange sites per dry mass of the polymer, IEC $\doteq n(SO_3^-)/m_{dry}$. The proton exchange membranes were prepared by sulfonation in a solution of 2% chlorosulfonic acid in dichloromethane at room temperature for 5 h, followed by hydrolysis in water for 8 h at 80 °C. The ion-exchange capacity was measured by titration (SM Titrino 702 instruments, Metrohm, Herisau, Switzerland). The membranes were exchanged from the H$^+$ form to K$^+$ form using KCl solution (0.5 mol/L), and the titration was performed using KOH solution (0.05 mol/L). The degree of sulfonation, s, which is defined as the percentage of styrene units bearing acidic groups, was estimated from the monomer composition and IEC of the polymer [13]. The properties of the polymers are summarized in Table 1. The Nafion PFSA membrane (NR-212, solution cast, IEC = 0.98 ± 0.04 mmol/g) was purchased from DuPont and was used as received.

2.3. Isothermal water sorption and desorption in the vapor phase as a function of the relative humidity

The isothermal water sorption/desorption in the vapor phase was measured by a high-throughput dynamic vapor sorption analyzer (DVS-HT) (Surface Measurement Systems LTD, UK). To establish the dry mass, the membranes were dried in the acid form under a continuous air flow. Afterwards they were exposed to partial pressures of 0–80% relative humidity at 70 °C. No hysteresis was found between sorption and desorption.

Table 1
The properties of the two sets of copolymer membranes. The target graft level is $G = 40\%$ for series A. The target IEC is 1.5 mmol/g for series B. X is the mole fraction of styrene with respect to the total monomer content in the grafted copolymer as defined in Equation (2). The degree of sulfonation, s, was estimated from the monomer composition and from the measured IEC.

Name	IEC [mmol/g]	s	G [%]	X [%]
A-0	0	–	40.4	0
A-1	1.05 ± 0.11	1.01 ± 0.12	41.8	30.5 ± 2.3
A-2	1.18 ± 0.08	0.93 ± 0.07	41.6	39.5 ± 1.9
A-3	1.32 ± 0.04	0.86 ± 0.03	38.8	53.0 ± 4.2
A-4	1.50 ± 0.11	0.90 ± 0.08	39.8	58.9 ± 4.4
A-5	1.73 ± 0.08	0.99 ± 0.05	41.7	62.4 ± 4.1
A-6	2.02 ± 0.08	1.03 ± 0.05	41.5	76.3 ± 5.2
A-7	2.25 ± 0.14	1.05 ± 0.08	42.4	87.2 ± 1.0
A-8	2.33 ± 0.19	1.10 ± 0.11	37.5	100.0
B-1	1.43 ± 0.05	0.92 ± 0.04	38.0	56.1 ± 1.8
B-2	1.47 ± 0.05	0.91 ± 0.04	35.2	64.2 ± 4.2
B-3	1.54 ± 0.02	0.98 ± 0.01	23.1	100.0
B-4	1.55 ± 0.01	0.99 ± 0.01	34.2	63.5 ± 4.4
B-5	1.59 ± 0.03	1.00 ± 0.02	61.3	39.1 ± 2.4
B-6	1.61 ± 0.05	1.03 ± 0.04	28.6	77.4 ± 4.1