Transmission electron microscopy study of silica reinforced polybenzimidazole membranes

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ABSTRACT

The incorporation of silica nanostructures in polymer membranes is beneficial for the chemical, mechanical and the life time stability of high temperature proton exchange membrane fuel cells. Since the properties are closely related to the morphology and chemical composition of the constituents, their detailed investigation is of importance. In this paper transmission electron microscopy is utilized to study cross-linked silica nanoparticles in phosphoric acid doped polybenzimidazole membranes, which are formed by an *in-situ* sol–gel reaction using varying reaction parameters. The results show that by an additional heating step before membrane casting, several hundred nanometer large, ellipsoidal silica particles are formed in the membrane. Small, elongated nanoparticles with sizes in the range of about 20 nm are present in all samples independent of the heat treatment. In-depth energy dispersive X-ray spectroscopy and electron energy loss spectroscopy analysis proved the homogeneous distribution and composition of the amorphous silica nanoparticles and revealed that no enrichment occurs at the interface between nanoparticles and polymer. The *ex-situ* membrane investigations reveal a higher chemical and mechanical stability for membranes containing the large, ellipsoidal particles. However, the membrane with only smaller silica nanoparticles shows a better degradation behavior than the membrane with large particles.

1. Introduction

The development and optimization of proton exchange membrane fuel cells (PEMFC) as promising systems for efficient, environmentally friendly energy conversion have gained considerable attention in research over the last several years [1]. One research focus is the introduction of new membrane types, which can be operated above 100 °C and thereby overcome the limitations of commonly used Nafion® membranes. By operating at higher temperatures (150–200 °C) the high temperature PEMFC (HT-PEMFC) exhibits features like an increased CO tolerance, an increased electrocatalytic activity, simplified water management and in addition no need for a complex thermal management

system [2]. The most widely used material for HT-PEMFC membranes is polybenzimidazole (poly(2,2′-*m*-phenylene-5,5′-bibenzimidazole), PBI) [3–5]. It combines advantageous properties like high thermal and mechanical stability as well as low gas permeability with a high CO tolerance [3]. The long-term stability of the phosphoric acid doped PBI-based membranes under fuel cell operation conditions is a crucial prerequisite for the development of stable and efficient HT-PEMFCs. In this regard, leaching of the phosphoric acid and low proton conductivity are some of the known challenges of PBI-based membranes. Different strategies were applied to improve the stability and the properties of these kinds of membranes for the use in HT-PEMFC. By modifying the polymer structure to adjust the basicity of PBI higher proton conductivity was obtained [6]. To enhance the mechanical strength and oxidative stability of PBI-based membranes the preparation of hyperbranched and cross-linked PBI was reported to be a successful approach [7,8]. Another promising method is the incorporation of inorganic nanofillers in the polymer matrix to form organic–inorganic composite membranes. Pure or functionalized silica particles introduced in PBI-based membranes enhanced their mechanical stability and improved their acid retention capability and therefore their proton conductivity [9–16]. These positive effects were also observed for silica doped Nafion®

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membranes [17]. The incorporation is often realized by an *in-situ* sol–gel reaction of the particles during membrane casting [18]. By doing so, the agglomeration of the silica particles is prevented. Saxena et al. reported that control over the spacing between silica domains can be achieved by applying polyethylene glycol of different molecular weights during synthesis [11]. In order to maintain high conductivity the formation of percolation pathways at the interface between the polar and nonpolar domains in the functionalized membrane is important [19].

Altogether control over the size and distribution of the incorporated inorganic particles are crucial for the development of efficient HT-PEMFC membranes. Most of the applied analysis methods in literature focus on *ex-situ* and *in-situ* techniques which give an averaged behavior of the membrane properties. Regarding the electrodes of HT-PEMFC detailed electron microscopic work was performed [20,21]. In case of membranes only basic scanning electron microscopy and transmission electron microscopy (TEM) measurements were mostly conducted to get information on the size and agglomeration behavior of the introduced particles [9,10,12–14,17,21]. Detailed studies of the distribution of the occurring elements *via* analytical measurements such as energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) are rare. The electron microscopy analyis of organic materials such as the PBI-based membrane is challenging due to several reasons [22]. The interaction of electrons with organic matter results in inelastic scattering processes which cause ionization and break chemical bonds. In addition, the sample suffers from mass loss, fading of crystallinity and heat generation [23]. Thus, polymers decompose and damage quickly under electron bombardment.

In our recent work [18] we showed that silica nanoparticles embedded in a PBI-based membrane significantly enhance the chemical and mechanical stability as well as the performance of the resulting membrane electrode assemblies (MEA). We found that a certain amount of silica doping give the best results and that larger silica nanoparticles seem to have a beneficial influence on the MEA performance. In the present work the influence of an additional heating step during the membrane synthesis on the size, distribution and composition of the embedded silica particles is investigated. We also demonstrate that TEM is a well-suited method to obtain local information on the size, distribution and composition of silica nanoparticles in a PBI-based membrane as well as to study possible segregation phenomena which might occur at the particle/polymer interface. The applied techniques include high-angle annular dark-field (HAADF) imaging in the scanning TEM (STEM) mode for the determination of the sizes and distribution of the silica particles in the membrane as well as EDS and EELS for the chemical composition analyses. In addition, the chemical and mechanical properties of the membranes are studied. The cycle stability as well as the long-term fuel cell operation stability was examined to investigate the suitability of the newly synthesized silica stabilized PBI-membrane electrode assemblies in HT-PEMFC applications.

2. Experimental

2.1. Synthesis

2.1.1. Membrane and MEA preparation

Two different membranes based on the polymer PBI were prepared. First, PBI was dissolved under pressure by stirring in N,N-dimethylacetamide (DMAc, Merck) over 3 h at 200 °C. After filtering using a 20 μm filter, the product was mixed with a solution of tetraethoxy silane (TEOS, Alpha Aesar) and (3-glycidyloxypropyl)-trimethoxysilane (GPTMS, Alpha Aesar) in DMAc.

Potassium hydroxide (Sigma Aldrich) was added to the resulting viscous solution. Stirring at 70 °C, filtration and coating on a carrier foil resulted in membrane M I. For comparison we used a membrane which had been studied in our previous work and which was stirred at room temperature while all other parameters were the same [18]. This reference membrane is labeled M II in the following. For both membranes an amount of 40% TEOS with regard to the PBI was introduced. The membrane thickness was ~50 μm. By the chosen synthesis procedure the silica nanoparticles are cross-linked *via* GPTMS to the PBI chains of the membrane. In order to fabricate HT-PEM MEAs, the membranes were hot-pressed with phosphoric acid doped gas diffusion electrodes as described elsewhere [24].

2.2. Characterization methods

2.2.1. Ex-situ membrane testing
2.2.1.1. Chemical stability.
Chemical stability of the two membranes was tested by extraction in the solvent DMAc. Samples were dried overnight at 150 °C in an oven to obtain the basic weight. The membrane pieces were covered with DMAc in a round bottom flask and heated to 130 °C for 1 h. Within one additional hour the solution was cooled to room temperature. The extracted samples were dried at 150 °C overnight, weighted and the extraction residue was calculated.

2.2.1.2. Swelling ratio and liquid uptake.
Swelling behavior and liquid uptake were determined as percentage weight increase and dimensional growth by immersing the samples in phosphoric acid at 130 °C for 30 min. The changes in weight and dimension between the undoped and phosphoric acid doped membranes were measured.

2.2.1.3. Mechanical properties.
Stress–strain curves of the samples were measured on a BT1-FR0.5TN.D14/500 N Zwick from Zwick at room temperature. The average thickness of the membrane pieces was evaluated with a thickness gauche from Sylvac.

2.2.1.4. Morphology and chemical composition analysis.
In-depth investigations of the silica particles in the membrane regarding their morphology as well as their chemical composition were performed using TEM based techniques. Cross-sectional TEM samples were prepared using the procedure reported by Strecker [25]. By glueing a piece of the membrane between two spacers (aluminum or brass) a sandwich was obtained which was subsequently glued into a brass tube with an outer diameter of 3 mm. Thin discs (200 μm) were sliced off this tube with a diamond saw and thinned using a grinder and dimpler from GATAN. Further thinning of the samples with a beam of argon ions (using a precision ion polishing system from GATAN; 3 keV, 5°, double mode) was performed until electron transparency was achieved. For all TEM investigations a FEI Titan 80-300 (S)TEM equipped with an EDAX detector for EDS measurements was used. The Titan was operated at 80 kV and at 300 kV. Beam damage of the membrane material could be minimized by keeping the accumulated electron dose lower than ~10^5 e/nm^2. This was achieved by carefully choosing the spot size, the condenser aperture and the acquisition time. An attached HAADF detector from Fischione Instruments (Model 3000) was used for STEM imaging. EELS measurements were performed in STEM mode with a Gatan Tridiem image filter. The full width at half-maximum (FWHM) of the zero loss peak was around 0.9 eV. We used a 2 mm entrance aperture and a dispersion of 0.1 eV per channel leading to a satisfying energy resolution and a good signal to noise ratio. The camera length was varied between 128 mm and 196 mm leading to collector angles of 13.5 mrad and 9.3 mrad, respectively.