Metallic Plate Corrosion and Uptake of Corrosion Products by Nafion in Polymer Electrolyte Membrane Fuel Cells

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Nafion contamination by ferrous-alloy corrosion products, resulting in dramatic drops of the Ohmic potential, is a suspected major failure mode of polymer electrolyte membrane fuel cells that make use of metallic bipolar plates. This study demonstrates the potential of scanning transmission X-ray microscopy combined with X-ray absorption and fluorescence microscopy for exploring corrosion processes of Ni and Fe electrodes in contact with a hydrated Nafion film in a thin-layer cell. The imaged morphology changes of the Ni and Fe electrodes and surrounding Nafion film that result from relevant electrochemical processes are correlated to the spatial distribution, local concentration, and chemical state of Fe and Ni species. The X-ray fluorescence maps and absorption spectra, sampled at different locations, show diffusion of corrosion products within the Nafion film only in the case of the Fe electrodes, whereas the Ni electrodes appear corrosion resistant.

Introduction

The two most critical barriers that hinder the widespread commercial application of polymer electrolyte membrane fuel cells (PEMFCs) are their excessive weight and limited durability. Currently, about 80% of the weight and 45% of the costs are due to the use of graphite bipolar plates (BiPs).[1] Thinner, lighter, and cheaper BiPs can be fabricated with metals, but the lack of knowledge of the corrosion resistance of these materials under relevant fuel-cell (FC) operating conditions urgently requires dedicated research efforts. The main problems related to the corrosion resistance of BiPs are (1) the release of cationic species that interact with other critical FC materials, resulting in damage to the proton-exchange membranes and poisoning of the catalysts; (2) the formation of layers of high resistance at the BiP/gas diffusion layer (GDL) interface; and (3) the loss of hydraulic tightness across the BiPs, owing to the formation of perforating pinholes. BiP corrosion primarily results from galvanic contact with the more noble, carbon-based GDL materials in the presence of condensed water that contains ionic species released from the Nafion, such as F⁻.

Chemical degradation of membranes is a major cause of PEMFC failure, mainly manifested in unacceptably high drops of the Ohmic potential, not excluding additional contributions from fuel crossover. In all-graphite PEMFCs the typical cause for chemical degradation is attack by radicals (e.g., *OH, *OOH).[2] With BiPs a new degradation pathway can occur, in which the proton groups of the Nafion side chains may be exchanged with metal ions from the corroding BiPs. In particular, it has been proven that the presence of trace amounts of metallic ions, such as Fe²⁺ or Cu²⁺, enhances the attack on Nafion by radical species,[3] because both the main and side chains degrade at similar rates via a depolymerization route. By contrast, it seems that Cr³⁺ and Co³⁺ do not have such detrimental effects.[4] The membrane is especially vulnerable to corrosion products because the sulphonate group has a higher affinity to metal cations (with the exception of Li⁺) compared to H⁺.[5] The membrane conductivity decreases with increasing cationic charge.[5] In turn, the H⁺ displacement reduces the membrane hydration, which results in a lower ionic conductivity, enhanced brittleness, and a higher concentration of H₂O₂, increasing the rate of chemical attack.

To design and fabricate efficient, stable, and long-lasting PEMFCs, the degradation modes of the electrodes and polymer membrane occurring in working devices need to be understood. A major obstacle is that appropriate morphologically and chemically sensitive methods with sufficient lateral resolution are needed, to monitor relevant local processes induced under electrochemical conditions. This obstacle has recently been overcome by using soft X-ray transmission microscopy (SXTM), combined with microspot X-ray absorption spectroscopy (µ-XAS) for characterization of complex multiparticular sys-
tems in electrochemical environments with sub-micrometer lateral resolution.20–24

Herein, we report on the corrosion of Fe and Ni electrodes in contact with a hydrated Nafion film in a thin-layer cell, combining the potential of SXTM and μ-LEXRF with low-energy X-ray fluorescence (LEXRF) spectroscopy. The major efforts in this investigation are focused on elucidating the processes that lead to the release of corrosion products deriving from metallic (typically Fe-based alloys containing Ni) BPs, with eventual uptake by the Nafion membrane. The explored fundamental aspects of Nafion contamination by ferrous-alloy corrosion products are believed to be the cause of the observed dramatic Ohmic drops.

Results and Discussion

The morphological and chemical changes, related to the corrosion processes under consideration, were evidenced by combining transmission X-ray and LEXRF imaging with μ-LEXRF and μ-XAS spectroscopy from representative areas selected from X-ray images. The advantage of μ-LEXRF is that it detects all elements that emit characteristic X-rays following irradiation with the selected photon energy, but owing to the low energy resolution of the fluorescence detectors it lacks chemical speciation. μ-XAS accesses only single elements by tuning the photon energy scan around the selected elemental edge, but it can provide the missing information for the chemical state because of the much better energy resolution of the detector. The use of chromatic zone plate (ZP) lenses to access the different constituent elements by XAS required changes in the optical setup of the X-ray microscope, which prolonged the measurement time. The elemental distribution and the chemical speciation of Fe or Ni were not affected by the photon radiation during the measurements. The X-ray microscopy results were complemented by preliminary optical microscopy and electrode potential measurements (see the Supporting Information for details).

Electrocorrosion of the Fe electrode in contact with hydrated Nafion

The STXM images in Figure 1 a–c, taken by using photon energies below and across the Fe L edge, reflect the density distribution and complex morphology developed as a result of corrosion processes that occurred under electrochemical working conditions, encompassing residues of the solid electrode as well as precipitated corrosion products migrated several micrometers into the electrolyte. The contrast in the 701.0 eV map taken below the Fe L edge is dominated by the morphology (thickness variations) and relative absorptive properties of the material’s constituent elements away from their absorption edges. The left region of the Fe electrode appears a bit darker owing to stronger absorption of the X-rays by Fe compared to the surrounding low-density electrolyte. Within the Fe electrode region different contrast levels can already be distinguished, reflecting thickness and density variations induced by the corrosion process. More quantitative information about the Fe distribution is conveyed by maps taken above the L edge (> 703 eV), where a dramatic intensity drop occurs in the Fe electrode region and in locations containing Fe species. Dividing the 706.3 eV map by the 701.0 eV map affords the Fe concentration distribution map. In this quantitative map two very bright “cracks” can be clearly distinguished inside the Fe electrode as well as several “bubble-like” brighter areas, resulting from localized corrosion. This observation is in accordance with the optical microscopy images shown in the Supporting Information. The released Fe contributes to the gradually fainting darkness moving away from the electrode edge (highlighted by the dashed line), indicating the diffusion of Fe species released from the electrode as a result of the electrochemical reactions. The corresponding process in a full-scale FC implementing commercial materials would be the release of $\text{Fe}^{2+}$ from Fe-based alloys—possibly enhanced by the ubiquitous presence of contaminants such as $\text{Cl}^{-}$, deriving from Nafion fabrication and cathodic reactant flux—and its solubilization, favoring transport to the fixation sites within the proton-exchange membrane. In practice, the geometrical effects of damaging the BP itself are expected to be negligible.13

The spatial variations in Fe concentration were confirmed by μ-XAS Fe L$_3$ spectra, measured in selected spots (Figure 1 d), which are highly sensitive to the Fe chemical state.14–15 Our spectra showed the expected general trend of Fe signal attenuation approaching the edge of the Fe electrode, which reflects the increasing loss of Fe resulting from the corrosion process. More quantitative information about the
process. Moreover, because the corrosion process occurs in a nonhomogeneous manner, variations in the Fe L3 intensity measured in spots inside the electrode (points A and B, where the bubbles are seen in the normalized Fe L3 map) were also observed. Along with the variations in the local Fe concentration, the Fe oxidation state can be judged from the lineshape of the XAS spectra. As fingerprints, we used the known energy positions of the Fe L3 peaks corresponding to the stoichiometric oxides FeO, Fe2O3, and Fe3O4. The FeO spectrum is similar to that of Fe, whereas features shifted by 1.7 and 1.4 eV with respect to the metallic Fe position (706.5 eV) characterize the Fe2O3 and Fe3O4 states. The FeOOH spectrum is very similar to that of Fe2O3; the Fe L3 spectral fine structures measured for single-phase oxides could not be distinguished in the amorphous specimens in this study, because of overlap between components corresponding to several different phases. As shown in Figure 1 d, to probe the variations of the Fe oxidation state within the electrode and of the detached Fe species that have diffused away, two broad components were used for the deconvolution of the Fe L spectra. The first peaked at ca. 706.5, representing metallic (Fe0) and lower oxidation states (Fe2+), and the second at ca. 708.0 eV, accounting for the higher oxidation states (Fe3+,4+); the latter including FeOOH, as well. The lineshape of the Fe L3 spectra and the position-dependent ratio of the components and their maxima denote variations in the Fe “average” oxidation states. The general trend is that the relative amount of Fe species in higher oxidation states and FeOOH is increasing in the heavily corroded areas (spectrum B) and in areas that are closer to the edge. As can be expected the oxidized forms dominate the species that have diffused away from the electrode (spectra F–H). This result contributes to an understanding of in situ processes at the molecular level, with spatial resolution of the detailed chemistry of Fe-based corrosion products. This result contributes to the in situ understanding at the molecular level and with space resolution of the detailed chemistry of Fe-based corrosion products—both in solution phase and as precipitated into solid scales or fixed into ion-exchange materials, that is still an open question, notwithstanding the comprehensive insight into the underlying electrochemistry.

Figure 2 shows the X-ray fluorescence (XRF) maps of C, F, O, and Fe, including the area reported in Figure 1, along with a simultaneously acquired STXM image for morphology reference. The STXM image contains two main features: a residual portion of the electrode, preserving an approximately square shape after oxidation, and strongly absorbing Nafion flakes. Overall, the XRF results complement the XAS data, allowing more insight into the spatial distribution of cell constituents. A strong correlation between C and F can be noticed, corresponding to the location of the fluorocarbon polymer. The apparent difference in the extension of the Nafion particle between the STXM and XRF images is due to strong absorption by thicker portions of the polymer. The Fe map correlates with the O map, indicating that the residual portion of the oxidized electrode is in fact composed of Fe oxo-hydroxides, coherent with the µ-XAS results. The electrode edges are smeared out, apparently due to corrosion.

Electrocorrosion of the Ni electrode in contact with hydrated Nafion

STXM, XAS, and XRF results highlighting the corrosion behavior of the Ni electrode are reported in Figure 3 and 4. In particular, two regions of the Ni electrode were studied: (A) an area including the corner of the Ni electrode, and (B) the side of the Ni electrode facing the Au counter-electrode (for details about the corresponding current density distributions, see the Supporting Information). The STXM maps of zones A and B in Figure 3 a show that the electrode edges have remained essentially unchanged, indicating negligible corrosion. As far as Nafion is concerned, some thicker islands (darker features scattered throughout the imaged area including the electrode) can be noticed. This observation is supported by the µ-XAS spectra measured in different regions of the Ni electrode, in Figure 3 b. Deconvolution of the spectra taken inside the electrode area was performed by considering the reported spectra corresponding to NiO (single component at ca. 853.1 eV) and NiO (two components at ca. 854 eV and 855.8 eV). Inspection of the spectra shows some degree of lateral inhomogeneity in the thickness of the NiO passivating layer. The part of the Ni electrode covered by a Nafion layer (point C1) seems slightly less oxidized. No Ni species were found in regions outside the electrode,
confirming the passivation ability of Ni in the relevant environment, at variance with the corrosion mode of the Fe electrode. The corresponding XRF maps in Figure 4 yield coherent information. A correlation of the C and F maps locates the Nafion flakes, and essentially no Ni can be found outside the electrode area. Moreover, O is shared by both the Ni and Nafion areas, in agreement with the polymer composition and the NiO passivation layer formed under the prevailing electrochemical conditions. A comparison with optical microscopy during the initial stages of the oxidation process can be found in the Supporting Information. Of course, passivation is an advantage from the point of view of corrosion resistance in a strict sense, but in the case of BiP applications the additional necessary requirement is a high electronic conductivity of the surface. This point calls for further material development—possibly including the use of coatings applied to ferrous alloys, accompanied by suitable fundamental information on the space-dependent chemical evolution and structural development in systems as close as possible to the real physico-chemical conditions of operating FCs.

Conclusions

We report an investigation of the corrosion of Fe and Ni in the presence of a hydrated Nafion film, carried out by synchrotron-based X-ray microscopy combining imaging with absorption and fluorescence microspectroscopy. The obtained information is relevant to the fabrication and application of metallic BiPs for PEMFCs, in particular concerning how Fe and Ni films of nanometer-scale thickness are corroded by galvanic coupling to Au in a thin-layer configuration. The obtained morphological and chemical details of the corrosion process and of the fixation of the corrosion products in the Nafion film reveal that corrosion of Fe is characterized by the diffusion of Fe species into the Nafion film, accompanied by changes of the Fe chemical state. As expected, Ni corrosion products are essentially localized at the surface of the Ni electrode without release of Ni species.

This pioneering investigation of an electrochemical system, simultaneously employing soft X-ray imaging and two space-resolved X-ray spectroscopy techniques, demonstrates the power of such an approach, not only to the system investigated—with potential impact in the acquisition of fundamental information relevant to fuel-cell technology—but potentially to all fields of electrochemical materials science and bioelectrochemistry.

Experimental Section

Experiments were carried out by using the STXM module of the TwinMic X-ray microscope at the Elettra synchrotron facility in Trieste (Italy), operated in the 280–2200 eV photon energy range. In STXM the X-ray beam could be focused down to sub-100 nm spot size by zone plate diffractive optics, and the specimen was raster-scanned across the X-ray probe to obtain morphological and chemical maps. In the present study the X-ray probe size was varied between 200 nm and 1 μm, according to the dimensions of the features of interest and the photon flux needed for the chemical speciation. The transmitted X-rays were monitored with an IXON Andor-Technology EMCCD camera, simultaneously providing absorption and phase information, and Si detectors for XRF.
In the corrosion experiments, the electrolyte was an aqueous Nafion solution of composition: Nafion 0.25 wt%, isopropyl alcohol 3.75 wt%, balance ultra-pure water, pH regulated to 4 by NaOH. The solution was aerated to mimic the more aggressive, cathodic conditions. Anodic polarization of the working electrodes was achieved by short-circuiting them externally with the Au counter electrode. The ensuing corrosion transient could be followed in situ in terms of the corrosion potential, which was found to stabilize after ca. 3000 s. More information about the corrosion process can be found in the Supporting Information.

The corrosion reaction was followed ex situ under a visible-light microscope, terminated after an adequate reaction time, and transferred for characterization in an adequate state into the sample compartment of the X-ray microscope. The characterization required a combination of chemical and lateral resolution that could be provided only by using the bright and tunable synchrotron radiation.

For adapting the experimental set-up to the requirements of the measurement station we deployed a second-generation electrochemical cell, based on the design proposed in Refs. [7] and [8], but improved for a better definition of the electrolyte volume, current density distribution, and vacuum sealing. The cell consisted of a Si₃N₄ X-ray window with four square sputter-deposited electrodes of which, two were 40 nm thick Au counter- and quasi-reference electrodes and two were 75 nm thick Fe or Ni working electrodes. Lateral electrolyte containment was ensured by a 500 nm thick resist layer, deposited on top of the Si₃N₄ window/electrode assembly. The X-ray microprobe normally hit this assembly and the X-rays, transmitted through the cell, and the emitted fluorescence X-ray signal were simultaneously monitored using CCD and Si drift detectors, respectively.[23] More details on the cell construction, illustrated in Figure 5, and experimental conditions is given in the Supporting Information.

Figure 5. Layout of the electrochemical cell. Figure not to scale.

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