

[Electronic Supplementary Information]

Imaging Heterogeneity and Transport of Degraded Nafion Membranes

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Experimental

Chemical and Materials

All chemicals were used as received without further purification. A potassium chloride (Macron Chemicals, Phillipsburg, NJ) solution with a concentration of 0.1 M was filtered with 0.22 μm PVDF filter membranes (Millipore Corp., Billerica, MA) and utilized as the supporting electrolyte. Potassium dihydrogen phosphate (J. T. Baker, Phillipsburg, NJ) and potassium dibasic phosphate (J. T. Baker, Phillipsburg, NJ) were used for pH adjustment. Hexaammineruthenium(III) chloride (Strem Chemicals, Newburyport, MA) was dissolved in supporting electrolyte and the ionic form, $\text{Ru}(\text{NH}_3)_6^{3+}$ was used as the redox mediator for SICM-SECM measurements. All aqueous solutions were prepared from de-ionized water (resistivity = 18 $\text{M}\Omega\cdot\text{cm}$ at 25°C, Millipore Corp, Billerica, MA). Sodium hypochlorite (13% active chlorine, Acros, Morris Plains, NJ) and potassium iodide (Mallinckrodt, Phillipsburg, NJ) were used to prepare nanoporous membranes. Dichloro-[2,2]-paracyclophane (parylene C dimer, SCS Coatings, Indianapolis, IN) was used for electrode insulation. Samples of Nafion® 212 (Fuel Cells Etc, College Station, TX) with a thickness of 51 μm and an equivalent weight of M.W. 1100 were cut from a larger sheet and had dimensions of approximately 1 \times 1 cm. Ferrous sulfate heptahydrate (Sigma Life Science, St. Louis, MO) and 30% hydrogen peroxide solution (Macron Chemicals, Phillipsburg, NJ) were used for Fenton's reaction.

Electrode Fabrication and Characterization

Quartz capillaries (Q100-70-7.5, Sutter Instruments, Novato, CA) with 1.0 mm outer diameter and 0.7 mm inner diameter were pulled with a P-2000 CO_2 -laser pipette puller

(Sutter Instruments, Novato, CA) to produce two symmetric sibling nanopipettes. Puller program parameters are as follows, heat: 690; filament: 3; velocity: 45; delay: 165; pull: 190. A Cr adhesion layer (10 nm at 2 Å/s), followed by an Au layer (250 nm at 5 Å/s) was deposited on one half of the nanopipette via a thermal evaporator (BOC Edwards, Auto 306 Vacuum Coater, West Sussex, United Kingdom) and the resulted Au crescent was used as the SECM electrode. Next, Au-coated nanopipettes were placed in the deposition chamber of a parylene deposition system (PDS 2010, SCS coating, Indianapolis, IN) in an upright position and chemical vapor deposition of parylene C on the nanopipette surface was carried out with vaporizer and furnace temperature settings at 175°C and 690°C, respectively. Finally, a Zeiss Auriga® Modular Cross Beam work station (Oberkochen, Germany) was used to mill the end off the insulated electrodes. The “Mill for Depth” function was selected in SmartSEM® V05.05 XB operating software. A 100 µm depth and a 30 kV, 600 pA beam current was used. Typical electrode configurations consisted of an Au crescent (~250 nm in thickness) and an open pore (~100-200 nm in radius) at the tip of a quartz nanopipette. Scanning electron microscopy (SEM) was used to determine the diameter of the pipette tip opening and the thickness of the Au crescent electrode. Both cyclic voltammetry (CV) and current-voltage (I-V) measurements were performed to further estimate the size of the Au crescent electrode and the pipette tip opening.

Nanoporous Membrane Preparation and Characterization

Nanoporous membranes were prepared from ion-tracked polyimide films (track density 10^6 tracks/cm², thickness 25 µm, it4ip, Belgium) through the track-etch process, as previously described.^{1,2} Briefly, a polyimide membrane was first etched in 13%

hypochlorite solution at 70 °C, followed by immersion in a 1 M potassium iodide solution for 30 minutes to neutralize residual etchant. Finally, membranes were rinsed with de-ionized water.

Membrane Pre-treatment

Prior to degradation, N212 membrane samples were pretreated according to the standard pretreatment procedure.³ The membrane samples were first treated in 30% H₂O₂ at 80°C for 1 h to remove any organic impurities, followed by rinsing in boiling water for 1 h. Next, the membrane samples were treated in 0.5 M sulfuric acid at 80°C for 1 h, and finally washed repeatedly with boiling water. Pre-treated membrane samples were stored in de-ionized water for future use.

X-ray Photoelectron Spectroscopy Mapping

X-ray photoelectron spectroscopy (XPS) experiments were performed using a PHI Versa Probe II instrument equipped with a monochromatic Al K α focused source. Instrument base pressure was ca. 8×10^{-10} Torr. The PHI dual charge compensation system was used on all samples. All XPS spectra were recorded using PHI software SmartSoft – XPS v2.0 and processed using PHI Multipak v9.0.

For mapping experiments, a 9.0 μm beam at 1.0 W and 15 kV was used at an X-ray incidence and take off angle of 45°. Maps were collected over a 200x200 μm area at 149x149 pixels. For C1s, O1s and F1s maps, 20 frames were acquired. XPS results are shown in **Figure 2**.

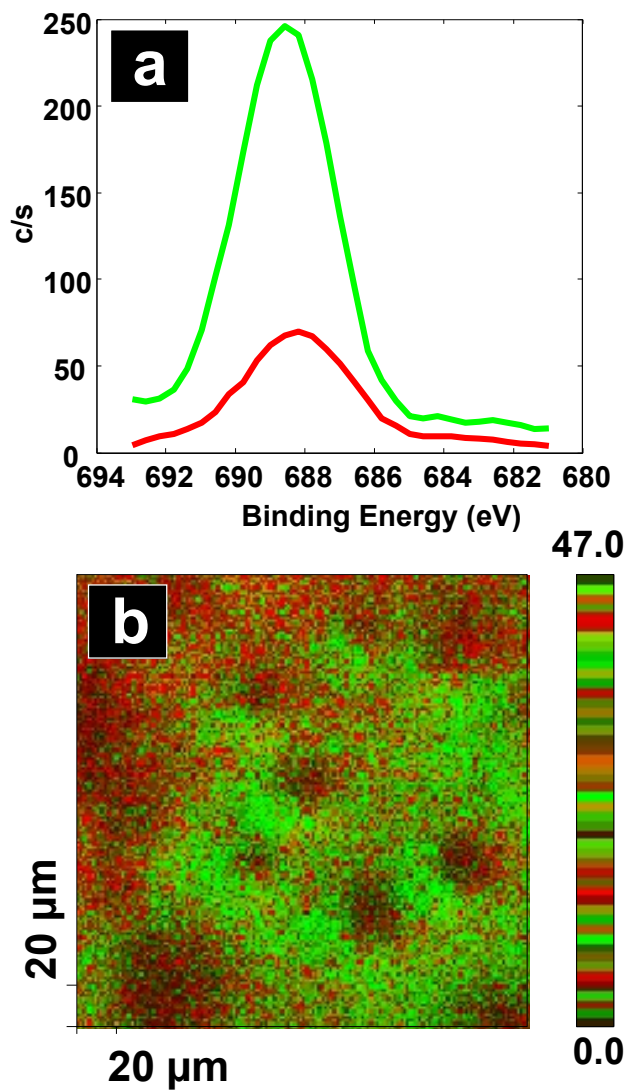


Figure S1. (a) XPS spectra for F1s “on” surface defects (red) and “off” the surface defects (green). (b) XPS map for F1s.

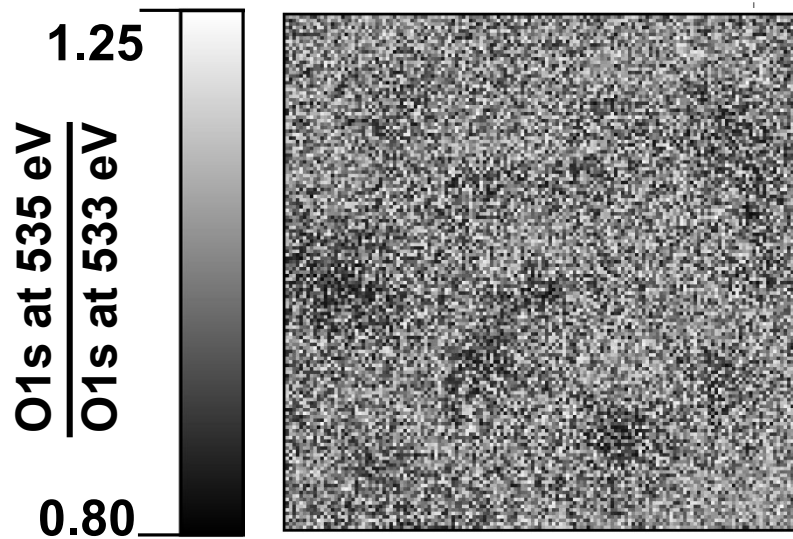


Figure S2. XPS ratio map obtained by dividing the O1s map at 535 eV and at 533 eV.

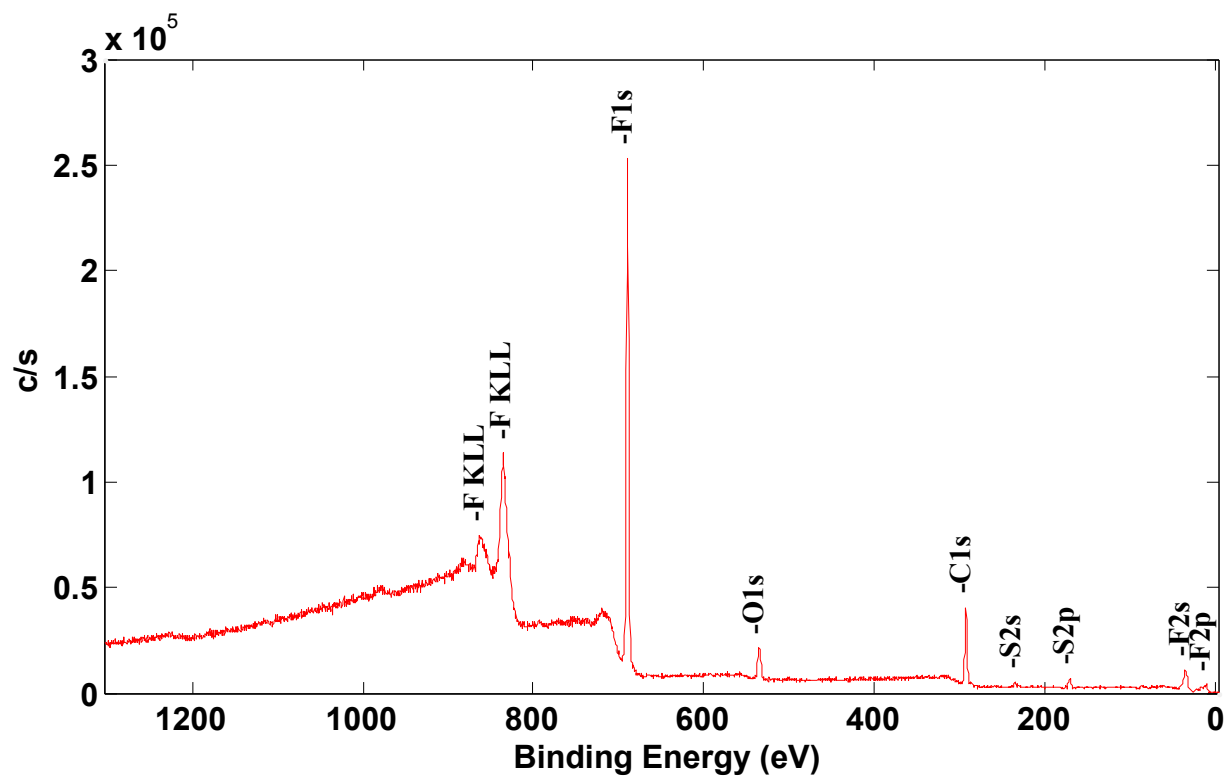


Figure S3. XPS survey scan spectrum for as-purchased Nafion[®] 212.

1. C. C. Chen, M. A. Derylo and L. A. Baker, *Anal Chem*, 2009, **81**, 4742-4751.
2. C. C. Chen, Y. Zhou and L. A. Baker, *ACS Nano*, 2011, **5**, 8404-8411.
3. D. Linden, *New York, McGraw-Hill Book Co.*, 1984, 1075 p. No individual items are abstracted in this volume., 1984, **1**.