

SUPPLEMENTARY INFORMATION

Chemical and electrochemical characterization of Nafion containing silver nanoparticles in stripe-like distribution

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SI.1. XPS measurements detailed protocol.

Nafion-117 surface modification due to the presence of the Ag-NPs was determined by XPS measurements, which were recorded with a Physical Electronic PHI 5700 spectrometer with X-ray MgK_{α} radiation (300W, 15 kV, 1253.6 eV) as the excitation source. High-resolution spectra were recorded at a take-off angle of 45° by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 mm diameter analysis area; the Au $4f_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu $2p_{3/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. Charge referencing was done against $-CF_2-$ carbon of Nafion (C 1s, 292.0 eV). Hydrated samples (kept in distilled water) were evacuated for several hours in high vacuum (pressure lower than 5.0×10^{-6} Pa). PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were fitted using Gauss-Lorentz curves following the methodology described elsewhere.¹ Atomic concentration percentages of the elements in the membranes surfaces were determined considering the area sensitivity factor for the different measured spectral regions.² Controlled erosion of the Nafion-117/Ag-NP membrane surface by argon sputtering (4 kV and 1.5 mA) during 2 minutes was also performed in order to eliminate contributions associated to surface species.

SI.2. XRD measurements detailed protocol.

XRD patterns were collected on a PANalytical X'Pert Pro automated diffractometer. Powder patterns were recorded in Bragg-Brentano reflection configuration by using a Ge(111) primary monochromator (Cu Kalfa1) and the X'Celerator detector with a step size of 0.0167° (2θ). The powder patterns were recorded between 10 and 80° in 2θ with an equivalent counting time of ca. 60 sec/step.

SI.3. XANES measurements detailed protocol.

The X-ray radiation was monochromatized by using a double crystal Si311 monochromator cooled by liquid nitrogen. The contribution of higher harmonics was rejected by a collimator and a focusing mirror by selecting on both the rhodium coating using a rejection angle of 2.0 mrad and 0.72 mrad, respectively. This setting corresponds to a beam size of $200 \times 200 \mu m^2$ at the sample position. Spectra were collected in transmission mode and incoming and out coming photon flux from and to the sample were measured by

ionizations chambers filled with the appropriate gases. Data normalization and linear combination was done using Athena package.³ The linear combination range was -30 to +150 eV around the absorption Ag K-edge. The goodness of the fitting was evaluated by the R-factor.

References

[1] M.J. Ariza, J. Benavente and E. Rodríguez-Castellón. The Capability of X-ray Photoelectron Spectroscopy in the Characterization of Membranes: Correlation between Surface Chemical and Transport Properties in Polymeric Membranes, in Handbook of Membranes: Properties, Performance and Applications, pp. 257-290. Nova Science Publishers, Inc., New York, 2009.

[2] J. Lukas and B. Jezek. *Collection Czech. Chem. Commun.*, 1983, **48**, 2909-2913.

[3] B. Ravel and M. Newville. *J. Synchrotron Radiat.*, 2005, **12**, 537-541.