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Significant improving H^+/VO^{2+} permselectivity of Nafion membrane by modification with PDDA in aqueous isopropanol

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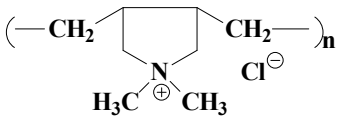
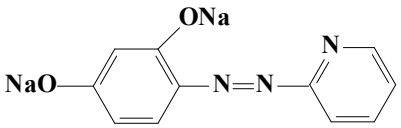
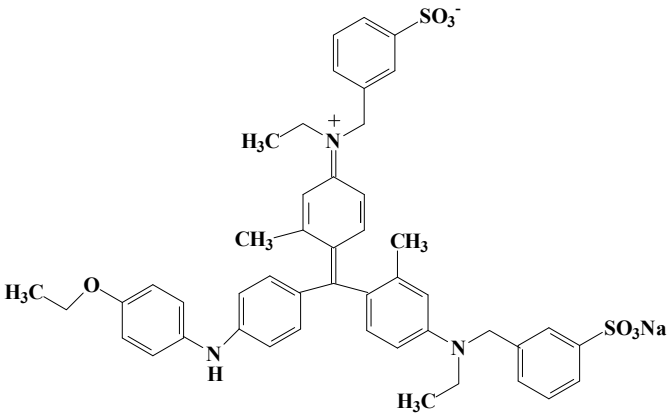
S1. Structures of organic compounds



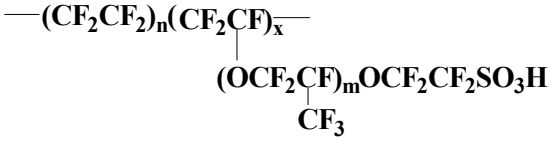
PDDA



PAR



Coomassie Brilliant Blue G250 (CBB)



Nafion

S2. Laboratory instruments used in the study

Spectroscopic measurements were carried out using a Perkin-Elmer Lambda EZ 201 UV/VIS spectrometer (United States).

Mettler Delta 350 pH-meter (Switzerland) equipped with a glass micro pH combination electrode (Sigma-Aldrich) was used for pH measurements.

IR spectra of the membranes were recorded using a Nicolet iS59 FR-IR spectrometer (Thermo Scientific Intertech).

The impedance was measured using SP-300 (“Bio-Logic SAS”, France) instrument.

S3. Experimental details

Prior to the modification, commercial Nafion 112 membrane (Sigma-Aldrich, USA, equivalent mass 1100 g mol^{-1}, thickness 51 μm) was pretreated according to conventional procedure.[S1] To perform the modification, weighed 2x2 cm or 4x4 cm specimens of water-swollen Nafion 112 membrane were incubated in modification solution during 20–24 h, thoroughly washed with bidistilled water, and kept in 2.5 M sulfuric acid before use. Modification solutions (20 ml) comprised 5–15 mM PDDA (M_w 157 kDa as per light scattering data, Wako Pure Chemical Industries, Ltd., Japan) and 10–35 wt% isopropanol in deionized water. The PDDA concentration was determined *via* precipitation titration with sodium dodecylsulfate[S2,S3] and expressed in mol/L of the ionic groups. The molar ratio of PDDA ionic groups to the membrane sulfo-groups exceeded 1 in all cases.

The membranes permeability (P, cm^2 min^{-1}) towards vanadyl ions was determined using a two-compartment static cell and calculated using a conventional diffusion equation.[S4] Due to extremely low concentration of vanadyl ions to be measured, it was determined by means of spectrophotometry upon conversion in the 1:1 complex with 4-(2-pyridylazo)resorcinol disodium salt (PAR).[S5] Through-plane proton conductivity (σ) was determined by means of impedance spectroscopy using a Teflon cell equipped with platinum electrodes (area 1 cm^2).[S6] Equilibrium swelling degree (α) was measured by means of gravimetry and expressed as the mass of the solvent in the swollen specimen per gram of dry membrane. Ion-exchange capacity (IEC, mol of protons per 1 g of dry membrane) was determined by potentiometric titration of protons released from the membrane upon keeping in 2 M NaCl solution for 5 days. Staining of the membranes in the Bradford reagent solution[S7] (based on Coomassie Brilliant Blue G250) was performed during 1.5 min and 24 h.

References

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