

Polymer Electrolyte Membranes and their Applications to Membranes, Fuel Cells and Solar Cells

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ABSTRACT

Polymer electrolyte membranes are developed for the applications to facilitated transport membranes, fuel cells and solar cells. The polymer electrolyte membranes containing silver salt show the remarkably high separation performance for olefin/paraffin mixture in the solid state; the propylene permeance is 45 GPU and the ideal selectivity of propylene/propane is 15,000. For fuel cell membranes, the effects of the presence and size of the proton transport channels on the proton conductivity and methanol permeability were investigated. The cell performance for dye-sensitized solar cells employing polymer electrolytes are measured under light illumination. The overall energy conversion efficiency reaches 5.44 % at 10 mW/cm², to our knowledge the highest value ever reported in the polymer electrolytes.

INTRODUCTION

Polymer electrolytes are formed when metal salts are dissolved in a polymer matrix and consequently dissociated into metal cations and corresponding counter anions. They are ionically conductive and thus have received considerable attention owing to their versatile applications in lithium polymer batteries,¹ solar cells,² fuel cells³ or membrane separation.⁴⁻¹¹ The dissolution of metal salt in a polymer matrix occurs due to the coordinative interaction between metal ions and polymeric ligands.

EXPERIMENTAL

For facilitated transport membranes, polymer/silver salt solutions were coated onto a microporous polysulfone substrate using an RK Control Coater. After evaporation of the solvent in a convection oven at room temperature under nitrogen, the membrane was dried completely in a vacuum oven for two days. For fuel cell membranes, a solution of 5wt % SBS in toluene with 5wt % of the photoinitiator of SBS was prepared. The solution was poured into a glass dish and held at room temperature until complete evaporation of solvent had taken place. The residual solvent was evaporated under vacuum. Dye-sensitized solar cells were assembled using a film of the polymer electrolyte sandwiched between the photoanode and the counter electrode. The methodology employed the deposition by casting TiO₂ pastes onto conducting glass substrate, followed by firing at 450 °C for 30 min. The resultant TiO₂ films were coated with the Ru535bisTBA dye by immersing the film in an alcoholic solution of dye. Afterwards, the electrode was washed with ethanol and dried in a moisture-free atmosphere. The transparent platinized counter electrode was prepared by spin-coating of 0.05 mol/L solution of H₂PtCl₆ in isopropanol onto the conducting glass, followed by firing at 400 °C in air for 20 min. Polymer solution was spread over the sensitized TiO₂ electrode and then pressed against the counter electrode.

RESULTS AND DISCUSSION

(1) Facilitated Transport Membranes: Solid state facilitated transport membranes comprising carriers dissolved in a polymer matrix have demonstrated to be very effective in simultaneously improving gas permeability and selectivity, which are normally in conflict for common polymeric materials.¹² Thus, facilitated transport membranes are considered to be an alternative approach to overcome the permeability/selectivity trade-off behavior of conventional polymeric membranes. For example, the separation performance of facilitated transport membranes consisting of silver polymer electrolytes⁴⁻¹¹ for propylene/propane mixtures is improved by several orders of the magnitude compared to that of conventional polymeric membranes¹² such as polyimides, polysulfone, poly(phenylene oxide), ethyl cellulose, poly(dimethyl siloxane), etc. as shown in Fig. 1. The propylene permeance reaches more than $4.5 \times 10^{-5} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ sec cmHg}$ and the ideal selectivity of propylene over propane is extremely high at several thousands.

In facilitated olefin transport through silver polymer electrolytes, the threshold concentration was observed at a silver mole fraction of approximately 0.25 for AgBF_4 or AgCF_3SO_3 dissolved in poly(2-ethyl-2-oxazoline) (POZ) or poly(N-vinyl pyrrolidone) (PVP), below which facilitated transport was not observed.⁶ However, the selectivity of propylene over propane increased nearly linearly with the silver concentration at silver concentrations above the threshold concentration as shown in Fig. 2. The threshold concentration is found to be strongly associated with the coordination behavior of the silver ion by both carbonyl oxygens and olefins molecules.⁶ The coordination numbers (m: by carbonyl, n: by propylene) of silver ions in POZ/ AgCF_3SO_3 are plotted against the mole fraction of silver salt as shown in Fig. 3. It is clear from the figure that m decreases exponentially with the silver concentration whereas n increases slightly. Surprisingly, the total coordination number, (m+n), becomes nearly invariant and is around 3. This result strongly suggests that the most favorable coordination number of the silver ion dissolved in a polymer matrix under propylene environment is ~ 3 . It was also found from IR spectra and theoretical calculations that the interaction of silver ion with carbonyl oxygen of POZ is slightly stronger than that with olefin molecules. Therefore, the relationship between the threshold concentration and the most probable coordination number of silver ion can be deduced from the favorable coordination number and difference in the interactions. When $m \geq 3$, silver ions may not be able to interact with surrounding olefin molecules, implying that the silver ion does not act as an olefin carrier. However, when $m < 3$, the coordination sites of the silver ion are not completely occupied by carbonyl oxygen and thus vacant sites are available for olefin coordination. Therefore, it is concluded that silver ions can act as an olefin carrier only when $m < 3$, in other words, the threshold concentration of the mole fraction of the silver salts is 0.25, which is consistent with Fig. 2.

(2) Fuel Cell Membranes: In order to constrain the swellability and consequently to reduce the cross-sectional size of the ionic channels, microphase-separated poly(styrene-butadiene-styrene) (SBS) triblock copolymer membranes were crosslinked by UV irradiation in the presence of a photoinitiator, and then sulfonated by acetyl sulfate. The crosslinked SBS (cSBS) and sulfonated SBS (csSBS) membrane shows a high proton conductivity of $2.3 \times 10^{-2} \text{ S/cm}$, comparable to that of Nafion, and a low methanol permeability of $2.7 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 10 wt% methanol, more than one order of the magnitude smaller than that of Nafion. SAXS was used to study the size and the spatial arrangement of the microdomains of SBS triblock copolymers. Typical SAXS data for the pristine SBS, cSBS, and csSBS films in both dried and water-swollen states are shown in Fig. 4. The microdomain morphology of a block copolymer can be determined from the q values of higher-order peaks relative to the first-order peak for the interparticle scattering because such materials exhibit different arrays depending on the dominant shapes of their microdomain structures, such as spheres

in a cubic lattice, cylinders in a hexagonal lattice and lamellar arrangements. Fig. 4 shows that the intercylinder distance for the cSBS sample is almost the same as that of the pristine SBS film. The cylindrical morphology of the triblock copolymer is maintained with cross-linking, but it starts to disappear with increasing sulfonation. However, this cylindrical morphology is maintained for each sulfonated film up to scSBS1.5. The spatial arrangements of the microdomains for the water-swollen scSBS1.5 membrane are indistinct.

(3) Dye-Sensitized Solar Cells: Current-voltage curves for dye-sensitized solar cell employing PEO/PPG/NaI/I₂ electrolytes are measured under light illumination. The mole ratio of ethylene oxide unit in PEO to sodium ion was fixed at 10, where highest ionic conductivity is obtained. As seen in Fig. 5, the introduction of PPG in PEO matrix leads to the significant increase of cell performance, especially current density. The lower molecular weight of PPG, the higher cell performance for the solar cells is achieved. Maximum cell performance is short circuit current density (J_{sc}) of 1.38mA/cm², open circuit voltage (V_{oc}) of 0.67V, fill factor (FF) of 58.1% and the overall energy conversion efficiency (η) of 5.44% for PEO/PPG_{Mn725} electrolytes at 10 mW/cm². It should be noted that the increase of cell performance is more significant than that of ionic conductivity upon addition of PPG; the former is increased by 80 (from 0.07 to 5.4 %) whereas the latter is increased by 15 (from 1.6×10^{-6} to 2.5×10^{-5} S/cm).

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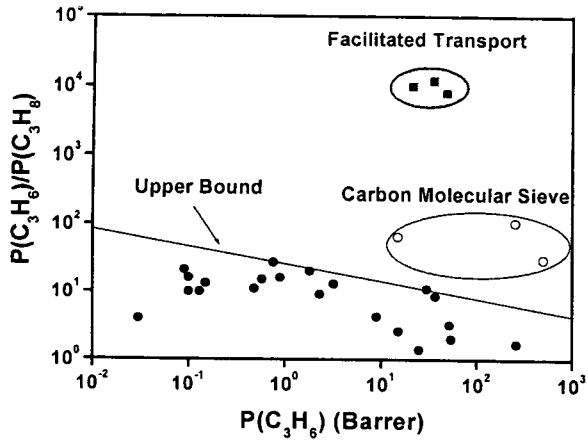


Fig. 1. Relationship between propylene permeability and its ideal selectivity over propane.^{4-6,12}

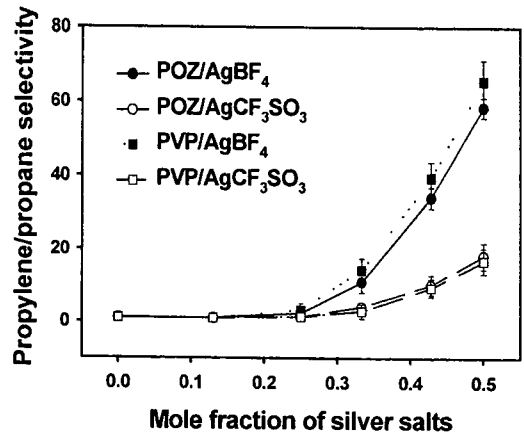


Fig. 2. Mixed-gas propylene/propane selectivity for silver polymer electrolyte membranes at 23 °C, $\Delta p=276$ kPa.

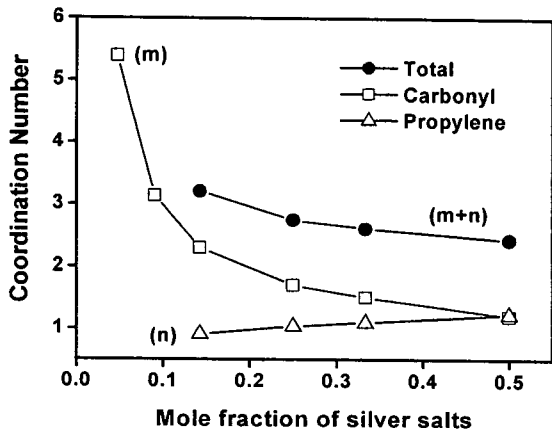


Fig. 3. Coordination numbers of silver ion by carbonyl oxygen and propylene in POZ/AgCF₃SO₃ as a function of the silver salt concentration.⁶

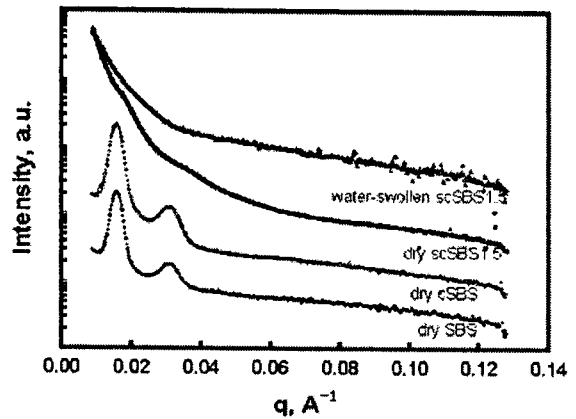


Fig. 4. SAXS profiles of dry SBS, dry cSBS, dry scSBS1.5, and water-swollen scSBS1.5 samples.³

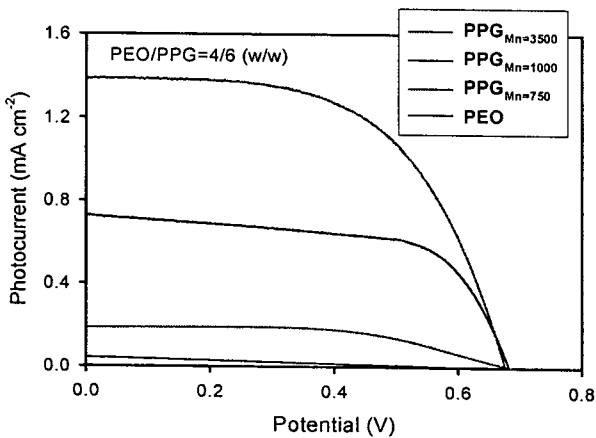


Fig. 5. J-V curves for dye-sensitized solar cells employing PEO/PPG blend polymer electrolytes with various molecular weights of PPG.