

V.N.14 Surface-Initiated Ionomer Films Based on Modified Poly(n-alkylnorbornene)s

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Objectives

The overall goal of the proposed research is to prepare an integrated network to support gas diffusion, catalyst, and ionomer inside the pores of a nanoporous support and use this well-defined three-phase boundary to molecularly optimize the design of PEM fuel cell cathodes. The two major objectives of this project are to (1) use surface-initiated polymerizations to construct new classes of non-fluorinated and partially fluorinated ionomer coatings and (2) employ a template-assisted growth process to prepare well-defined nanoporous cathodes that contain catalyst-coated pore walls and ionomer-filled pores.

Technical Barriers

The technical barriers for this project are largely related to the new chemistry that we are employing. For example, the synthesis of fluoroalkylnorbornenes can be challenging, and the ring-opening metathesis polymerization of these compounds from surfaces has never been reported. Sulfonation of polynorbornenes is also not well established in the literature. Additionally, once we begin to grow polymer films within the nanoporous materials, we will need to accurately characterize the chemical state and uniformity of the film grown within the pores.

Abstract, Progress Report and Future Directions

Abstract

While the majority of ionomers for proton exchange membranes are prepared via solution polymerization and the subsequent casting onto a membrane, the employment of surface-initiated polymerization of ionomer films from the electrode surface offers the

advantages of uniform coverage throughout complex electrode architectures and precise tailoring of the catalyst/ionomer interface. We propose a new type of ionomer based on surface-initiated ring-opening metathesis polymerization (ROMP) of n-alkylnorbornenes and subsequent sulfonation to achieve films with controlled thicknesses up to 100 nm, hydrophobic packing, and abundant channels for proton transfer. The feasibility of our approach is demonstrated via the growth and chemical modification of a series of poly(n-alkylnorbornene) films from a two dimensional gold surface. We present the influence of alkyl side chains on the structure, barrier and surface properties, and the growth kinetics of surface-initiated ROMP-type polynorbornene films. Reflectance-absorbance IR spectroscopy is used to show the molecular-level packing within the polyalkylnorbornene films is disrupted by the alkyl side chains, producing a more liquid-like film that collapses to eliminate defects. The methyl terminus of the alkyl side chains increases the hydrophobicity of the alkylnorbornene films ($\theta_A(\text{H}_2\text{O}) = 109^\circ\text{-}114^\circ$) beyond that of a typical polynorbornene film ($\theta_A(\text{H}_2\text{O}) \sim 106^\circ$). The polymerization rate constant decreases by two orders of magnitude from norbornene ($k_p \sim 15.16 \text{ M}^{-1} \text{ s}^{-1}$) to decylnorbornene ($k_p \sim 0.004 \text{ M}^{-1} \text{ s}^{-1}$). Upon sulfonation, the thin films transform into good proton conductors.

Progress Report

In the first year and a third of this project, we have completed the following tasks:

1. Grow polynorbornene (pNB) films from a 2-D surface by ring-opening metathesis polymerization and sulfonate the pNB to create ionomer films. Investigate the proton conductance of the films. This part of the work is being written up as a communication that will be submitted to *Macromolecules* as soon as issues with the sulfonation chemistry are resolved.
2. Grow poly(alkylnorbornene) films from a 2-D surface by ring-opening metathesis polymerization and investigate the effect of the alkyl substituent on the structure, barrier properties, and kinetics of film growth. This part of the work is being written up as a full length article that will be submitted to *Macromolecules* in the spring of 2007.

Future Directions

There are several tasks that we plan to complete by the end of August, 2007. These include the following:

1) Modify the norbornene monomer with fluorocarbon side chains prior to polymerization and sulfonation to investigate the effect of ionomer composition on structure, and the effect of film structure on proton conductivity. 2) Upon growing these films from 2-D surfaces that contain catalytic Pt nanoparticles, determine the effect of ionomer composition and structure on the rate of the oxygen reduction reaction. 3) Define target or optimum ionomer film compositions from work on 2-D surfaces to aid the design of 3-D systems. We will begin growing these films within nanoporous electrode supports in the third year of the project.

Publications (Including Patents) Acknowledging the Grant or Contract

Two publications are in preparation, as described above.