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Effects of surfactants on the transport properties of redox species through Nafion® membranes

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Abstract

Previous research in our group has employed tetraalkylammonium bromides to alter the micellar structure of Nafion® membranes to affect flux of redox species through the membrane. However, research by Patist et al. has shown that maximum micellar stability occurs when the chain lengths of the both the main micellar component and the surfactant are the same in sodium dodecyl sulfate micelles (SDS). When considering the steric hindrance of large, spherical ammonium salts and the effect of chain length compatibility on micellar stability, it was determined that *n*-alkyltrimethylammonium and *n*-alkyltriethylammonium surfactants may be more favorable in altering the pore structure. This research focuses on mixture-casting Nafion® with ammonium-based surfactants in order to form more stable Nafion® membranes with larger pore structures and a less acidic environment that will be more biocompatible with entrapping dehydrogenase enzymes within the membrane. *n*-Alkyltriethylammonium and *n*-alkyltrimethylammonium surfactants decreased the number of available exchange sites to proton (proton exchange capacity) of the membrane and they altered the transport of redox species through the membrane. Phenyltrimethylammonium bromide treated Nafion® membranes and triethylhexylammonium bromide treated Nafion® membranes were found to successfully immobilize dehydrogenase enzymes while maintaining enzyme activity.

Keywords: Ion-exchange membranes; Electrochemistry; Membrane electrodes; Nafion; Surfactants

1. Introduction

Nafion® is a perfluorinated cation exchange polymer with a micellar pore structure. The selectivity of Nafion® against anions is frequently increased by heating Nafion® above its glass transition temperature, which inverts the micellar structure [1] thereby, increasing in the ionic charge density at the orifice of the pore by decreasing the volume of the orifice. Nafion® has been widely used to modify electrodes for sensor and fuel cell applications [2–6]. However, researchers have found Nafion® to have two main limitations. The two limitations are that the small, micellar pore structure of Nafion® prohibits the transport of large redox species through the membrane and the acidity of Nafion® has limited its usefulness to entrap enzymes and proteins.

Previous research in our group has shown that mixture-casting Nafion® with tetraalkylammonium bromides can alter the electrochemical flux of redox couples through the membrane and allow for larger redox species (such as erythromycin) to diffuse to the electrode surface [7]. As a suspension of the protonated form of Nafion® is mixed with tetraalkylammonium salts, the proton on the sulfonic acid group is exchanged with the tetraalkylammonium cations and this induces micellar growth, while decreasing the total number of micellar pores. Our research has focused on tetraalkylammonium bromides ranging from tetramethylammonium to tetrapentylammonium. Alkyl chain lengths larger than tetrapentylammonium salts destroy the micellar pore structure of the polymer, so they were not employed. The tetraalkylammonium bromide treated Nafion® membranes have a secondary advantage beyond increasing the pore size of Nafion®. Since the sulfonic acid groups of Nafion® have a higher affinity for large hydrophobic groups than for proton,

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the number of available exchange sites to proton decreases dramatically as the size of the tetraalkylammonium salt increases [7,8]. Therefore, the membranes have a higher buffer capacity when in the presence of acidic solutions. This is of interest in biosensors and biofuel cells, because if the Nafion® membranes re-exchanges protons then the immobilized enzymes and proteins will be denatured in the acidic conditions of unmodified Nafion®.

Although tetraalkylammonium salts were a reasonable first choice for tailoring the chemical and physical properties of Nafion® due to literature reports of tetraalkylammonium salts inducing growth of micelles [9,10], they are not necessarily the ideal ammonium salt for tailoring the chemical and physical properties of the micellar pore structure. Research has shown that maximum micellar stability occurs when the chain lengths of the both the main micellar component and the surfactant are the same in sodium dodecyl sulfate micelles (SDS) [11]. The sulfonic acid side chain is approximately the same length as a tetrabutylammonium cation. However, when considering the steric hindrance of large, spherical ammonium salts and the effect of chain length compatibility on micellar stability, it was determined that *n*-alkyltrimethylammonium and *n*-alkyltriethylammonium surfactants may be more favorable in altering the pore structure while maintaining a stable micellar pore. Research has also shown that addition of *n*-alkylamines will induce growth of SDS micelles [12]. This research described in this paper will focus on mixture-casting Nafion® with ammonium-based surfactants in order to form more stable Nafion® membranes with larger pore structures and a less acidic environment that will be more biocompatible for entrapping enzymes within the membrane.

This study examined two types of modified Nafion® membranes. The first type of membrane is a mixture-cast membrane where the ammonium salt is mixed in a suspension of Nafion® and cast on a surface. The second type of membrane is a salt-extracted membrane where a mixture-cast membrane is formed and then soaked in water to extract all the excess HBr salts. After all the excess HBr salt are extracted from the membrane, the membrane is re-suspended in alcohol and can be re-cast on the surface of an electrode. These re-cast membranes are more stable due to a decrease in salt voids within the membrane. The re-cast membranes have been shown to be more biocompatible for immobilizing enzymes for sensor and biofuel cell applications [13]. This paper will also examine the ability to immobilize dehydrogenase enzymes within the surfactant modified Nafion® membranes.

2. Experimental

2.1. Preparation of casting solutions

Seven bromide salts were combined with 5 ml of 5 wt.% suspension of Nafion® (Aldrich) and vortexed for 15 min. The salts included triethylhexylammonium bromide (Aldrich, TEHABr), octyltrimethylammonium bromide (Fluka, OTMABr), phenyltrimethylammonium bromide (Acros, PTMABr), tetrapentylammonium bromide (Aldrich, TPentABr), tetraethylammonium bromide (Fisher, TEABr), tetrapropylammonium bromide (Aldrich, TPABr), and tetrabutylammonium bromide (Sigma, TBABr). An unmodified Nafion® control casting solution and was employed for all studies. All mixture-casting solutions were prepared so the concentration of ammonium salt is in excess of the concentration of sulfonic acid sites in the Nafion® suspension. After optimization, it was determined that the most stable and reproducible membrane has an ammonium salt concentration that is three times the concentration of the exchange sites in the membrane.

2.2. Preparation of salt-extracted membrane casting solutions

Mixture-cast membranes of Nafion® and ammonium salts were prepared as discussed above. One milliliter of the ammonium salt/Nafion® casting solution was placed in a weighing boat and allowed to dry. Previous studies have shown that all of the bromide ions that were introduced into a membrane were ejected from the membrane upon soaking that membrane in water [8]. Therefore, 7.0 ml of 18 MΩ water were added to the weighing boats and allowed to soak overnight. The water was removed and the films were rinsed thoroughly with 18 MΩ water and dried. Then, the films were re-suspended in 1.0 ml of lower aliphatic alcohols.

2.3. Preparation of electrodes

All electrodes are cleaned by polishing the glassy carbon electrode on a 0.05 μm alumina covered polishing cloth (Buehler). The electrodes were soaked in concentrated nitric acid and thoroughly rinsed with 18 MΩ water. A 2.0 μl aliquot of casting solution was pipetted onto the surface of a clean glassy carbon electrode (CH Instruments, diameter = 3.0 mm). After the solvents evaporated, the membrane-coated electrodes were placed in the vacuum desiccator for 30 min to ensure that all remaining solvent was removed.

2.4. Electrochemical measurement

All membrane coated working electrodes were allowed to equilibrate in the redox solution before electrochemical measurements were performed. All solutions contained 1.0 mM of redox species and 0.10 M electrolyte. The redox couples employed in this study were tris(2,2′-bipyridyl) dichlororuthenium hexahydrate ($Ru(bpy)_3^{+2}$,Aldrich), *N*,*N*,*N*′,*N*′-tetramethylphenylenediamine (TMPD, Sigma), methylviologen dichloride (MV, Aldrich), sodium 2,6-dichloroindophenol (DCPIP, Aldrich), potassium ferricyanide (Sigma), and caffeine (Sigma). Sodium sulfate was used as the electrolyte.