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# Pentablock Copolymer Morphology Dependent Transport and Its Impact upon Film Swelling, Proton Conductivity, Hydrogen Fuel Cell Operation, Vanadium Flow Battery Function, and Electroactive Actuator Performance

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## ABSTRACT

Ionomer composition and morphology impacts functional group distribution, water and ion-transport, and physical properties related to toughness, and degradation resistance. NEXAR MD9100 a pentablock copolymer (PBC) film morphology was dramatically altered when solution-cast into a film using tetrahydrofuran (THF) versus a cyclohexane:heptane (C:H) mixture. Film property and morphology changes were evaluated using Transmission Electron Microscopy (TEM), Small-Angle X-ray Scattering (SAXS), and electrochemical impedance spectroscopy. These changes were compared to Nafion 117 and Nafion 212. Average sulfonated inter-domain spacing through the film's thickness increased from 22.3 nm (C:H cast) to 30.5 nm (THF cast) that was estimated using SAXS. TEM revealed that PBC solution-cast films from C:H contained a random distribution of discrete sulfonated domains. An ordered PBC morphology consisting of lamella and hexagonally packed ion groups were created from a THF solution-cast film. These changes were attributed to favorable solvent-ionomer interactions during solvent evaporation and film densification. This ordered morphology led to increased conductivity (4.5 mS/cm versus 47.8 mS/cm), improved fuel cell power (19 mW/cm<sup>2</sup> versus 160 mW/cm<sup>2</sup>), enhanced ionomer actuation (3.0 cm versus 6.9 cm), and modest self-discharge improvements for a vanadium redox-flow battery. This study demonstrates that morphology impacts ionomer physical properties, transport, and device function.

**Keywords:** *Ionomer Solution Processing into Films; Morphology; SAXS and TEM; Water Swelling and Ion Transport; and Fuel Cell, Flow Battery, and Actuator Function*

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## 1. INTRODUCTION

Ionomers are characterized by three principal attributes related to ion conductivity, hydrophilicity, and fixed charge carriers within an electrically neutral structure [1-3]. These materials contribute to very diverse fields such as electrodialysis, electrolysis, dialysis, biomedical, analytical chemistry, sensors, actuators, batteries, and fuel cells [4]. For example, a polymer-electrolyte fuel-cell (PEMFC) uses an ionomer to transport ions produced during the electrochemical conversion of H<sub>2</sub> and O<sub>2</sub> into electricity, water, and heat [5]. Nafion is considered a state-of-the-art membrane used within a PEMFC, ionomeric polymer-metal composite (IPMC), and vanadium

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