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Impact of Cation form on Structure/Function Relationships of Perfluorosulfonic Acid Ionomers. AHMET KUSOGLU, SHOUWEN SHI, MERON TESFAYE, ADAM WEBER, Energy Technologies Area, Lawrence Berkeley Natl Lab — Perfluorosulfonic-acid (PFSA) ionomers are widely used as ion-exchange solid-electrolytes in electrochemical devices, where their behavior are influenced by the interactions among its sulfonate groups, mobile cations, and water. The properties of a PFSA depends on its hydration, which drives its phase-separated morphology and controls the extent of sulfonate-cation interaction. Thus, cation-form and hydration collectively affect the structure/transport relationship, yet their interplay is still not well known. To elucidate this interplay, water uptake and conductivity of cation-exchanged PFSA are studied at various relative humidities (RHs) and in water, which are then correlated with mechanical properties and nanostructure. With increasing cation size and valence, the modulus increases, while swelling and conductivity decreases. The extent to which the cations impact the conductivity depends on hydration; at low RH the controlling factor is the cation (interactions), while with increasing RH, the key factor becomes water (swelling), although it is also controlled by the cations. Changes in conductivity with cations and RH are analyzed to establish a universal conductivity-hydration correlation, by accounting for charge density and water content.

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