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Role of Substrate/Film interactions in Controlling Structure and Swelling of Nafion Thin Films¹ ADAM WEBER, AHMET KUSOGLU, LBNL, MICHAEL HICKNER, Penn State University, KUNAL KARAN, U. Calgary — Nafion is the prototypical ionomer in electrochemical energy devices due to its good ionic conductivity and permselectivity. In most devices, bulk ionomers are in contact with the catalysts. When confined to nanometer-thick 'thin' films, Nafion's structure/property relationship deviate from bulk, resulting in a complex polymer behavior dependent on thickness, environmental and casting conditions, and substrate material. In this talk, results of a systematic investigation on the substrate/film interactions of Nafion will be presented. The nanostructure of hydrated films is studied by Grazing-incidence X-Ray Scattering and analyzed along with swelling and water uptake measured by ellipsometry and QCM. Overall, films exhibit phase-separation with 4 to 6nm water-domain spacing and 10 to 15% swelling. Film thickness has a universal impact on properties such that thicker films (ca. 100nm) behave like bulk, whereas thin films (20 to 100nm) exhibit confinement effects with reduced swelling, regardless of the substrate. However, thin(ner) films (ca. 20nm) have no separated-structure and demonstrate significant swelling. Moreover, metallic substrates induce more ordered and anisotropic structure accompanied by additional reduction in swelling.

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