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Controlling self-assembly and transport properties of ionomer thin films MIGUEL MODESTINO, RACHEL SEGALMAN, University of California, Berkeley and Lawrence Berkeley National Laboratory — Electrochemically active materials, such as ionomer composites, allow for both ionic and electrical conduction. Commonly, these materials involve inorganic electrocatalytic particles surrounded by ionomer thin films. This work presents insights in the effects of confinement and wetting interactions in the self-assembly and transport properties of perfluorosulfonic acid ionomers thin films. Using in situ grazing-incidence X-ray scattering (GISAXS), we demonstrate that interfacial interactions and thin-film confinement can significantly affect phase separation, domain orientation and dynamics of ionomer films during water uptake. Thin-films casted on hydrophobic substrates result in parallel orientation of ionomer domains, while films prepared on SiO₂ surfaces result in isotropic orientation of these domains. These morphological characteristics, translate directly into effects on their macroscopic swelling behavior, where parallel orientation of ionomer domains limits the maximum water uptake of films. Furthermore, confinement to thickness below 10 nm hinders microphase separation of the material and results in high levels water uptake.

Miguel Modestino
University of California, Berkeley and
Lawrence Berkeley National Laboratory

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