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The Donnan Potential Revealed

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Highly selective, rapid ion transport across membranes is essential in biological ion channels and electrochemical and water purification membranes. Ion exchange membrane (IEM) based technologies play a critical role in meeting increasing global demands for energy and water because charged groups tethered to the polymeric chains enable selective permeation of ions based on their charge/valence.¹ In 1911, permselectivity of charged membranes was postulated for the first time by Prof. Frederick G. Donnan, regarding the formation of an electrical potential at the membrane/solution interface.² The so-called Donnan potential was found to be responsible for the selective transport of ions. Despite rich literature across various fields, many fundamental molecular interactions underpinning ion selectivity in IEMs are poorly understood. In addition, the direct measurement of Donnan potential has been thought to be unmeasurable^{3,4} and has never been accomplished in the over 100 years since the original Donnan theory was proposed.

In this talk, I will present the direct measurement of the Donnan potential of an IEM equilibrated with aqueous salt solutions using tender (hv = 4 keV) ambient pressure X-ray photoelectron spectroscopy (APXPS).^{5,6} Our results directly reveal the dependence of the membrane's Donnan potential on external salt concentration and counter-ion valence, as suggested by Donnan himself.⁷ In addition, by comparing our experimental results with well-known thermodynamic models, we show that the classic Donnan model assuming ideal behavior fails to predict experimentally measured Donnan potentials, while an improved model (Donnan/Manning) incorporating some of the thermodynamic non-idealities shows reasonable correlation. The ability to discern the various models is highly important, since current models fail to capture all non-idealities (e.g., mobile ion association, ionic cross-linking, non-electrostatic interactions, etc.). We anticipate that our methodology will be an important step toward better understanding permselectivity in membranes that are important in cellular processes as well as in energy storage and conversion and water purification applications.

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