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# Fundamental water and salt transport properties of polymeric materials

Geoffrey M. Geise, Donald R. Paul, Benny D. Freeman\*

The University of Texas at Austin, Department of Chemical Engineering, Texas Materials Institute and Center for Energy and Environmental Resources, 1 University Station, Mail Code: C0400, Austin, TX 78712, USA

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### ABSTRACT

Fundamental water and salt transport properties of polymers are critical for applications such as reverse osmosis (RO), nanofiltration (NF), forward osmosis (FO), pressure-retarded osmosis (PRO), and membrane capacitive deionization (MCDI) that require controlled water and salt transport. Key developments in the field of water and salt transport in polymer membranes are reviewed, and a survey of polymers considered for such applications is provided. Many polymers considered for such applications contain charged functional groups, such as sulfonate groups, that can dissociate in the presence of water. Water and ion transport data from the literature are reviewed to highlight the similarities and differences between charged and uncharged polymers. Additionally, the influence of other polymer structure characteristics, such as cross-linking and morphology in phase separated systems, on water and salt transport properties is discussed. The role of free volume on water and salt transport properties is discussed. The solution–diffusion model, which describes the transport of water and ions in nonporous polymers, is used as a framework for discussing structure/property relations in polymers related to water and salt transport properties. Areas where current knowledge is limited and opportunities for further research are also noted.

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\* Corresponding author. Tel.: +1 512 232 2803; fax: +1 512 232 2807.  
E-mail address: [freeman@austin.utexas.edu](mailto:freeman@austin.utexas.edu) (B.D. Freeman).

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## 1. Introduction

Two inexorably intertwined, pressing global challenges are providing: (1) sufficient clean water to satisfy agricultural, industrial, and municipal needs, and (2) reliable and efficient access to clean energy to support ever-increasing demands [1–7]. These issues are highly interconnected because thermoelectric power generation, which accounts for 89% of the energy produced in power plants in the U.S. [8], requires large volumes of purified water [4,9], and energy is invariably required to purify water. In 2005, approximately 50% of all water used in the United States was for power generation at thermoelectric power stations [10]. Future thermoelectric power plants in the U.S. are projected to require as much as an additional 2.6 billion gallons of water per day by 2030 (a ~40% increase from 2010) [11]. Furthermore, production of oil and natural gas through operations such as hydraulic fracturing can consume millions of gallons of water per well and generate substantial amounts of flowback water, which must be purified or otherwise managed [9,11,12]. Additionally, as population growth continues and fresh water sources become more scarce, we will rely more heavily on desalinated water from seawater as well as increasingly saline inland sources to generate sufficient purified water to satisfy human consumption as well as agricultural and other needs [2,3,5]. Consequently, improvements in technologies for energy-efficient water purification are of great interest from scientific, technological, and social viewpoints [1].

Today, polymer membranes play a key role in addressing these needs since reverse osmosis (RO) membranes are the dominant technology for desalination due, in part, to their low energy requirement relative to other technologies [2,5,7,13–17]. Desalination has traditionally been accomplished using thermal processes to vaporize water from a saline source and then condense this vapor to recover pure water [2,18,19]. The specific energy required to desalinate seawater by thermal technologies such as multiple effect distillation (MED) and multiple stage

flash (MSF) is approximately 18–30 and 24–37 kW h m<sup>-3</sup>, respectively, though these estimates vary widely in the literature [18,20]. In contrast, the specific energy required for membrane seawater desalination is less than 4 kW h m<sup>-3</sup> [3,14,18,20], so membranes require significantly less energy than conventional thermal technologies. Consequently, membranes are used worldwide to produce over 50% of all desalinated seawater [3].

The scale of water desalination is extraordinarily large. Membrane desalination plants having more than 10<sup>6</sup> m<sup>2</sup> of membrane surface area are in operation [21]. In 2010, approximately 16 billion gallons (~61 billion liters) of desalinated water were produced worldwide per day [5]. To place the extraordinary size of this figure in perspective, the worldwide production of crude oil (another fluid processed in large amounts) in 2010 was 3.7 billion gallons (~14 billion liters) per day [22], so the production rate of desalination of water is more than four times that of oil. With a theoretical minimum energy requirement to desalinate seawater at 75% recovery of 1.29 kW h m<sup>-3</sup> [3], improving the separation properties of membranes may contribute to even lower energy costs to desalinate water.

Technologies such as membrane capacitive deionization (MCDI) [23–31], electro dialysis (ED) [19,32–37], and forward osmosis (FO) [38–46], which all could further enhance the role of polymer membranes in desalination, are being actively explored. Additionally, membrane-based renewable energy technologies (e.g., reverse electro dialysis (RED) [47–56] and pressure retarded osmosis (PRO) [45,47,50,57–62]) can generate electrical energy by harnessing the chemical energy inherently released when streams of different salt concentrations are mixed, for example where a freshwater river flows into the sea. The generation of energy from the sea by methods such as RED and PRO is often called “blue energy”. Because the concentrate produced by a seawater reverse osmosis plant has an even higher salt concentration than that of seawater, a PRO plant could be fed with this highly saline water and seawater, thereby providing a membrane-based plant

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