



Thermoelectric effects in solid-state polyelectrolytes

Suk Lae Kim^a, Jui-Hung Hsu^b, Choongho Yu^{a,b,*}

^a Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA

^b Department of Material Science and Engineering, Texas A&M University, College Station, TX 77843, USA



ARTICLE INFO

Keywords:

Polymer thermoelectric
Soret effect
Polyether ether ketone
Nafion
Polyvinyl alcohol
Poly(diallyldimethylammonium chloride)

ABSTRACT

Solid-state polyelectrolytes have recently been reported to exhibit extremely high thermally induced voltage in contrast to conventional thermoelectric materials, showing great promise in energy harvesting for wearable and flexible electronics. Nevertheless the thermoelectric behaviors of polyelectrolytes have been barely studied. Here we provide comparative experimental studies about the thermoelectric behaviors of three different types of solid-state polyelectrolytes - cation conductors with negatively charged immobile backbones (Nafion and S-PEEK), conductors with both cations and anions (basic PVA-NaOH and acidic PVA-H₃PO₄), and an anion conductor (PDDAC). We observed that the proton conductors (Nafion and S-PEEK) exhibited large thermopower values up to ~5.5 mV/K. Higher humidity rendered the thermopower of S-PEEK larger but that of Nafion smaller, which is attributed to the opposite thermo-diffusion direction of water. When both cation and anion are thermally diffused (PVA-NaOH and PVA-H₃PO₄), the absolute values of thermopower was relatively small 1–1.5 mV/K and independent of humidity. In PDDAC, we observed extremely large thermopower values up to 19 mV/K, which could be attributed to more rigorous dissociation of Cl⁻ in the hotter side rather than the thermo-diffusion of Cl⁻. Our experimental results provide useful data for developing practical thermal energy harvesters and storage devices with high output voltages for wearable and flexible electronic devices.

Low-grade heat is one of the most sustainable, clean, and promising energy sources owing to its abundance and accessibility for standalone self-powered systems including wearable and portable electronics and remote systems inaccessible to power grids [1–3]. For example, the waste heat from human and animal bodies can be utilized as power sources to operate wearable electronic devices [4–6]. Thermoelectric energy conversion is well suited to this type of applications due to the direct conversion of thermal energy into electrical energy without complicated moving parts [7]. Traditional thermoelectric materials are typically made of brittle inorganic semiconductors [8], and recently emerged organic thermoelectrics have been studied due to the benefits of mechanical flexibility and easier synthesis processes [1,5,9–12].

These conventional thermoelectric materials utilize electron diffusion under temperature gradients called the Seebeck effect [13]. Under a small temperature gradient with low-grade heat, the voltage produced by these thermoelectric materials is fairly small on the order of 0.01–0.1 mV/K, requiring many modules connected in series for practical applications typically needing at least ~1 V [5,11]. On the other hand, thermogalvanic cells operate based on temperature-dependent electrochemical redox potentials of liquid electrolytes, producing relatively high voltages (~2 mV/K) [14–18]. However, heat convection makes it difficult to maintain temperature gradients in the liquid

electrolytes of thermogalvanic cells. Liquid-type systems also require bulky packaging to prevent leakage, which is not favorable to wearable and flexible applications.

Recently, the thermo-diffusion of ions called the Soret effect in electrolytes or ion conductors have been studied for harvesting low-grade heat because much larger thermoelectric voltage can be generated. It has been reported that the ion concentration gradient created by temperature gradients can produce output voltage up to ~11 mV/K in liquid electrolyte systems [19,20]. Solid-state polymer electrolytes such as polystyrene sulfonate can produce a large voltage up to 7.9 mV/K by utilizing the thermo-diffusion of ions for simultaneous thermal energy harvesting and storage [4] and thermoelectric power generation with conventional leg-type structures [21]. These types of ion conductors have great potentials in generating large thermally induced voltages, but there are only a handful of papers. Here we report thermally induced voltage generation from three different kinds of solid-state polyelectrolytes, and propose their mechanisms. The first kind is proton (single ion) conductors, sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion) and sulfonated polyether ether ketone (S-PEEK), which have been used for electrochemical cells due to their outstanding proton and water transport characteristics. Then the thermoelectric behaviors of binary ion (cation and anion) conductors made

* Corresponding author. Department of Mechanical Engineering, Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA.
E-mail address: chyu@tamu.edu (C. Yu).

of polyvinyl alcohol (PVA) as a matrix and NaOH or H₃PO₄ as a supplier for cation and anion were comparatively studied, followed by an anion conductor, poly(diallyldimethylammonium chloride) (PDDAC).

The thermo-diffusion of ions under a temperature gradient creates an ionic-charge gradient, leading to a potential gradient. A thermally-induced ion current for each mobile ion can be expressed as [22–24]:

$$\mathbf{J}_{\pm} = -D_{\pm} \left(\nabla n_{\pm} + 2n_{\pm} \alpha_{\pm} \frac{\nabla T}{T} \mp n_{\pm} \frac{e\mathbf{E}}{k_B T} \right) \quad (1)$$

which comprises the normal diffusion term with the Einstein coefficients D , the thermo-diffusion term with the reduced Soret coefficient α , and the electrophoresis term for monovalent ions. Here, e is the electron charge; n_i is the ion density; k_B is the Boltzmann constant; \mathbf{E} is the thermoelectric field (∇V); and T is absolute temperature. Assuming a steady-state condition ($\mathbf{J}_{\pm} = 0$) and a zero net charge condition ($\nabla n_{+} - \nabla n_{-} = 0$) in an electrolyte with cation and anion, thermopower by thermo-diffusion of ions can be expressed as follows.

$$S = (\alpha_{+} - \alpha_{-})(k_B/e) \quad (2)$$

We first tested the proton conductors, Nafion and S-PEEK. As shown in Fig. 1a, they consist of sulfonate anions tethered to the polymer backbone and mobile protons. Electrical conductivity was obtained from linear current-voltage relations (confirming Ohmic contacts) using the 4-point probe method. For thermopower measurements, 6–8 different temperature differences (ΔT) across the sample were made, and then thermally induced voltage (ΔV) at steady-state were recorded for each temperature difference. Thermopower was found from the linear slope of the $\Delta T - \Delta V$ relation. Fig. 1b displays a representative transient response (thermoelectric voltage) of Nafion under a 50% relative humidity (RH) condition as a function of temperature difference. The relatively slow responses indicate that the electrical properties are governed by ion transport.

Fig. 1c and d displays the thermopower and electrical conductivity of Nafion and S-PEEK measured at room temperature over a RH range

from 30% to 70%. We noticed that the electrical conductivity of both Nafion and S-PEEK was strongly dependent on humidity. For example, the electrical conductivity of S-PEEK at 70% RH was around 0.3 S/m, which is 50 times higher than that at 30% RH. The largely increased electrical conductivity with a higher humidity suggests a higher water uptake promotes the dissociation of the proton as well as renders the proton more mobile since electrical conductivity is proportional to the concentration and mobility of proton.

The thermopower of Nafion was measured to be very high (~ 4.2 mV/K), which is much higher than the reported thermopower from conventional thermoelectric materials [25,26] and thermo-electrochemical cells [14,27]. While the thermopower of Nafion slightly decreases at higher humidity conditions, S-PEEK exhibited remarkable increases at higher RH. For instance, the thermopower of S-PEEK was measured to be ~ 5.5 mV/K at 70% RH in comparison to ~ 1.2 mV/K at 30% RH. It is also interesting to see that both the thermopower and electrical conductivity of S-PEEK increased simultaneously at higher humidity conditions, which are different from the inversely proportional behaviors [13,26] observed in traditional thermoelectric materials. This behavior can be attributed to the different major carriers for the electrical transport: ions for the current study vs. electrons for the traditional thermoelectric materials.

The dissimilar behaviors for the thermopower of Nafion and S-PEEK in contrast to the similar trend in electrical conductivity despite the same transport carriers (protons) need more detailed discussion. It is well known that water transports through Nafion and S-PEEK, and the water channels are more percolated at a higher humidity condition [28–30]. At a low RH condition, there are more segregated water clusters than a case at a high RH condition [28], as illustrated in Fig. 2. The two most prominent ways of transporting protons are considered to be the Grotthuss (proton hopping between H₂O) and vehicle mechanisms (H₃O⁺ diffusion) (Fig. 2a). When the water content gets higher, the more percolated pores promote proton hopping and H₃O⁺ diffusion [29–33]. In addition, a higher water uptake increases the concentration

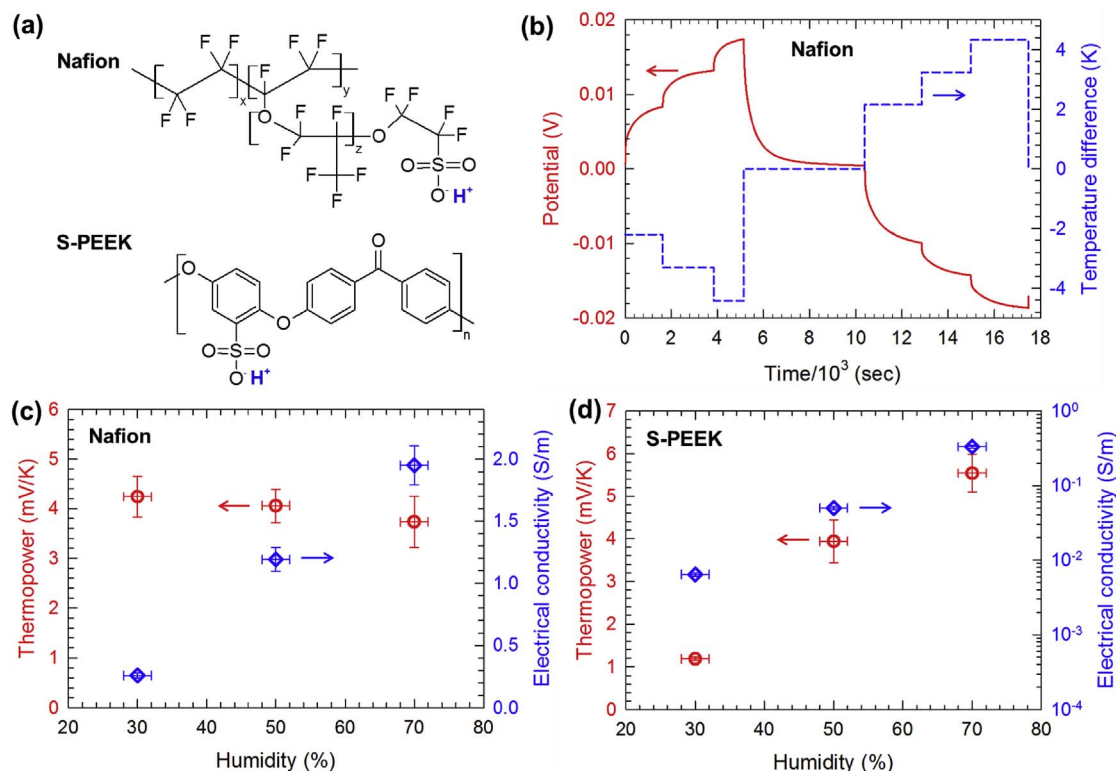


Fig. 1. (a) Chemical structures of Nafion and S-PEEK. (b) Thermally induced voltage and corresponding temperature difference at room temperature as a function of time for Nafion under a 50% relative humidity (RH) condition. Thermopower and electrical conductivity of (c) Nafion and (d) S-PEEK as a function of RH.

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