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Ionic Thermoelectric Figure of Merit for charging of supercapacitors

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Thanks to natural heat gradients, for example, generated by the sun, and the large amount of heat being wasted in combustion engines (35-40% efficiency), there is a strong interest in heat-to-electricity conversion to contribute in powering our modern society. Thermoelectric applications are typically based on thermodiffusion of electronic charge carriers (electrons or holes) in semiconductors, semimetals or metals. This thermoelectric effect is also referred to as the electronic Seebeck effect.^[1] More recently, thermodiffusion of ionic charge carriers in an electrolyte was used to convert heat to electrical energy stored in a supercapacitor. This new device concept, together with the discovery that some electrolytes can provide ionic Seebeck coefficients that are hundred times larger than the electronic Seebeck coefficient of good thermoelectric materials,^[2] motivates a fair comparison between electronic and ionic thermoelectric devices.

The electronic Seebeck coefficient α_e of a material is defined as the ratio between the open circuit potential V_{oc} and the temperature difference ΔT (compensated for the Seebeck coefficient of the metal contacts). If electrons and holes thermo-diffuse towards the colder side at identical rate no thermovoltage is generated. Hence, a non-negligible Seebeck coefficient is obtained for materials with different conductivities for electrons and holes. This is illustrated for a material displaying majority hole (h^+) conduction in Figures 1a and 1b. The electronic Seebeck effect provides the basic principle of operation for thermoelectric generators (TEGs), which can provide a continuous output current and power (Figure 1c). The efficiency of the heat-to-electricity conversion is directly related to $\sqrt{1 + ZT_e}$, where ZT_e is the dimensionless thermoelectric figure-of-merit, as introduced by A. F. Ioffe already in 1949.^[4] $ZT_e (= \sigma_e \alpha_e^2 T / \lambda)$ is defined by three fundamental properties of the thermoelectric material: the electrical conductivity σ_e , the Seebeck coefficient α_e and the thermal conductivity λ . Today, there is an intense strive to optimize the interplay between those three properties and to maximize ZT_e .^[1] While the major effort is to achieve TEGs based on inorganic materials ($ZT_e=1.2$ at 300K for Bi_2Te_3 alloys),^[5] recent studies also include oxides, carbon based compounds,^[6, 7] and electronically conducting organic polymers entirely based on atomic elements of high natural abundance ($ZT_e=0.2-0.4$ at 300K for PEDOT).^[8, 9, 10] This opens up for mass production of thermoelectric modules using high-volume printing and extrusion technologies.^[8]

We now move from electronic to *ionic* electronic thermoelectric materials. Figure 1d shows an example of an ionic conductor (that is not electrochemically active, thus excluding any contribution from thermogalvanic effects)^[11] that favors the transport of cations over anions when exposed to a thermal gradient. The Soret effect induces ionic concentration differences that generate a thermo-voltage. The ionic Seebeck voltage α_i of the ionic conductor is measured as the open circuit voltage V_{oc} established between the two metal electrodes exposed to different temperatures (assuming a negligible Seebeck coefficient of the metal contacts).^[12] The ionic thermoelectric effect occurs in ionic solids,^[13, 14] liquids or gel electrolytes^[15, 16] as well as in inorganic solid electrolytes.^[17] The thermodiffusion depends on the details of the ion-solvent interactions and it is measured as the so-called heat of transport Q^* , which determines the direction and magnitude of thermo-diffusion.^[18] The contribution from one type of ions to the ionic Seebeck coefficient can be presented $\alpha = Q^*/N_a|e|T$, where N_a is Avogadro's number and $|e|$ is the charge of an electron.^[19] From this, the α_i contribution of diluted ions in water is expected to be in the range of 0.1 mV/K. Analogous to the Seebeck voltage for electronic materials, if cations and anions thermodiffuse at the similar rates, one can foresee that α_i is low. Hence, different mobility or concentration for cations and anions should favor a large α_i . Surprisingly, large ionic Seebeck coefficient up to about 10 mV/K has been measured for asymmetric electrolytes in organic solvent.^[20] The origin of this large Seebeck coefficient is not yet fully understood.

One important difference between the ionic Seebeck effect and the electronic Seebeck effect in energy conversion applications is that thermo-diffused ions cannot pass into an external circuit when reaching a metal electrode (Figure 1e). The ionic thermoelectric effect is therefore not suitable for continuous operation of traditional thermoelectric generators. Instead, ions will accumulate at the metal electrodes to form an electric double layer (EDL), and induce a transient thermo-induced current that decreases to zero over time (Figure 1f). The integrated current represents the charge stored in the EDL capacitors located along the metal electrode-electrolyte interface.^[21] When using suitable (high capacitance) electrode materials, the accumulated charge could be dramatically enhanced and this principle can then be used to charge a supercapacitor^[2, 3] or a battery.^[22] In this way, the ionic thermoelectric effect can convert thermal energy to stored electrical energy that later can be used to power an external circuit on demand. When used to charge a supercapacitor, the device is referred to as an ionic thermoelectric supercapacitor (ITESC).^[2, 3] We note that thermoelectric effects in general are useful for low power energy harvesting, and therefore suitable to slowly charge a battery or a supercapacitor (SC) followed by rapid release and usage of the stored electrical energy as a high power pulse. Hence, the equivalent circuit of the serial connection of a TEG and a SC is one of the key to consider also for thermoelectric applications that are based on electronic materials. Here, we discuss charging efficiency of such circuit, for both electronic and ionic thermoelectric materials. In particular, we demonstrate that the efficiency of the ITESC can be expressed using an ionic thermoelectric figure of merit of the electrolyte $ZT_i = \sigma_i \alpha_i^2 T / \lambda$, where σ_i is the ionic electrical conductivity, α_i is the Seebeck coefficient, and λ the thermal conductivity. This relationship will greatly aid the search for suitable ionic thermoelectric materials, by establishing a map of various families of ionic conductors classified by their ZT_i and calculating their efficiency and energy stored per degree of temperature difference.

The ITESC utilizes thermodiffusion of *ionic* charge carriers to charge a supercapacitor and was recently demonstrated as suitable for intermittent heat sources, ultimately the sun.^[2, 3] As an example of application, the ITESC could store electrical charge during daytime due to heating by the sun, followed by usage of the energy

during night by discharging the device. The basic operational protocol of the ITESC is illustrated in Figure 2.^[2] (i) First, a heater is switched on to establish a ΔT across the electrode-electrolyte-electrode stack, resulting in a thermovoltage reaching $V_{\text{thermo}} = \alpha_i \Delta T$ after a certain time of stabilization (t_{st}). (ii) By connecting the two electrodes, V_{thermo} charges the supercapacitor. The integrated current during charging represents the charge Q_{ch} stored at the electrodes of the ITESC. (iii) After charging, the circuit is disconnected (open circuit) and the heater is switched off. In this cooling step, the thermovoltage decays to zero, such that the open circuit potential is entirely governed by the voltage drop (of opposite sign) from the stored charge along the electrode/polyelectrolyte interface of the ITESC. (iv) Finally, the device can be discharged by connecting the ITESC to an external circuit. The integrated discharge current corresponds to the charge Q_{dis} . Recently, *Suk Lae Kim et al.* successfully made ITESC with similar polyelectrolytes, they observed no leakage current, and the stored charge could be maintained longer than 24 h. For the sake of simplicity in our theoretical description of efficiency and energy, we assume that there is no leakage current and no parasitic self-discharge processes, which leads to $Q_{\text{ch}} = \frac{1}{2} C V_{\text{thermo}}^2 = Q_{\text{dis}}$

Before discussing conversion efficiency and stored energy, it is useful to first resolve what are relevant values for the thermoelectric properties of ionic materials. Here, we provide a study on a well-known polymer electrolyte, polystyrene sulfonate sodium (PSS:Na⁺), and we control the ionic mobility by controlling the humidity, in other words by introducing various amount of water. PSS:Na serves as a polyanionic membrane since the negative charge (sulfonate) is attached covalently to the polymer chain and is effectively immobile while the cations are the only mobile species. PSS:Na films with thickness of about 1.5 μm were prepared by drop-casting on glass substrates with pre-patterned Au electrodes. The Ionic Seebeck coefficient α_i was measured by applying alternating temperature differences ΔT of increasing magnitude from -4K to 4K and following the evolution of the thermovoltage (open circuit voltage) V_{thermo} (the structure of the setup is shown in supplementary information Figure S1). We find a linear relation between V_{thermo} and ΔT , and α_i is obtained as the slope of the linear fit to the experimental data (after subtraction of the Seebeck coefficient of the Au electrodes, see Figure S2). At 100% RH, PSS:Na possesses a large and positive ionic Seebeck coefficient of +4 mV/K (Figure 3b). This indicates that PSS:Na is a cation selective conductor, as expected since the polymer anions are essentially immobile because of their large size (Figure 3a). We measured α_i at various levels of RH in the range from 50% to 100% (Figure 3b). Lowest α_i of only 0.26 mV/K was measured at 50% RH, followed by an increase with increasing humidity, reaching 4 mV/K at 100% RH. The evolution of the ionic conductivity σ_i versus humidity levels is also given in Figure 3b. The ionic conductivity was characterized by a standard method established for electrochemical devices,^[23] as detailed in the supplementary information (Figure S3). The ionic conductivity is lowest at 50% RH (0.026 S/m) and then increases rapidly to slowly saturate around 80% RH, finally reaching 1.18 S/m at 100% RH. These results are in agreement with the fact that cations in dry polyelectrolyte films to a great extent are immobile, since they are localized by electrostatic interaction with the polyelectrolyte chains. With increasing humidity, absorbed water molecules in the hygroscopic polyelectrolyte film screen the ions by forming a solvation shell.^[17] As a result, the electrostatic attraction between the mobile counter ions and the immobile polyions is suppressed and, thus, the activation energy for transport of counter ions decreases.^[24] By further increasing the humidity level, continuous water percolation paths, *i.e.* conduction channels inside the polyelectrolyte film, are created. Finally, at some elevated RH level, the ionic conductivity saturates and reaches a value similar to those measured in pure aqueous solution.^[25] The fact that both σ_i and α_i increase with RH corroborates that ionic diffusion is the main

origin of the resulting thermo-voltage.^[26] Here, we would like to emphasize that α_i for completely hydrated PSS:Na films (100% RH) is about 40 times larger than typical values for conventional high-performing electronic thermoelectric materials.^[12] The power factor, which is defined as $\sigma_i \alpha_i^2$ can be calculated to $19 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 100% RH.

The thermal conductivity of the PSS:Na film at different RH were measured using the 3ω -method,^[27] (see experimental details in SI, Figure S4 and S5). Figure 3c shows that the thermal conductivity λ of the polyelectrolyte films increases from $0.35 \pm 0.02 \text{ Wm}^{-1}\text{K}^{-1}$ at 50% RH to $0.49 \pm 0.03 \text{ Wm}^{-1}\text{K}^{-1}$ at 100% RH. This increase is attributed to an increase in the water content of the films. Water swells the hygroscopic polymer film^[28] and nano-sized aqueous domains and percolation pathways are created. In turn, this increases the net heat transport for the two major transport mechanisms: the phonon transport through the polymer chains and the local convection of water molecules within aqueous-rich domains ($\lambda_{\text{H}_2\text{O}} = 0.6 \pm 0.031 \text{ Wm}^{-1}\text{K}^{-1}$).^[29] Finally, the evolution of λ and ZT_i versus RH are both presented in Figure 3c. ZT_i increases versus humidity, from 1.55×10^{-6} at 50% RH to 0.012 at 100% RH (at room temperature). Hence, varying the humidity has been a useful tool to explore the range of thermoelectric properties available for solid state polymer electrolyte since the ZT_i varies by more than four orders of magnitude.

With this knowledge about the ionic thermoelectric properties of the polyelectrolyte, we now turn to the expected impact when used in thermoelectric energy conversion devices. By using the concept of ITESC, heat is converted to electrical energy stored at the electrodes of the supercapacitor. In a simplified picture, we can evaluate the ITESC using an equivalent circuit based on an internal electric generator providing a voltage V_{thermo} in series with an ideal supercapacitor of capacitance C and a resistor R_s (Figure 4a). This highly resembles a TEG connected in series with a supercapacitor;^[2] which will enable a comparison between the energy and charging efficiency for ITESC and TEG-SC using respectively (α_i, ZT_i) and (α_e, ZT_e) . The charge stored on the electrodes is $Q_{ch} = CV_{\text{thermo}} = C\alpha_i\Delta T$ (Eq. 1) and the stored electrical energy is $E_{ch} = \frac{1}{2} \frac{Q_{ch}^2}{C} = \frac{1}{2} CV_{\text{thermo}}^2$ (Eq. 2). It is clear from these equations that E_{ch} should increase linearly and quadratically with the Seebeck coefficient. Assuming a supercapacitor with $C = 1\text{mF}$ and a temperature difference of $\Delta T = 10\text{K}$, the stored energy in the ITESCs with the PSS:Na electrolyte increases from $0.004 \mu\text{J}$ to $0.6\mu\text{J}$ when humidity increased from 50% to 100%, as shown in Figure 4b. By considering charging of an equivalent supercapacitor connected to a TEG leg (Figure S6. b), we can calculate and compare the stored energy E_{ch} also for electronic thermoelectric materials. The stored energy is 500 and 3000 times lower respectively for Bi_2Te_3 and PEDOT than PSS:Na at RH 100%. This pinpoints the key advantage of high Seebeck coefficients for ionic thermoelectric materials compared to electronic thermoelectric materials. We also report E_{ch} for other types of ionic thermoelectric materials in order to establish a first map of ionic thermoelectric materials, including PEO-NaOH^[2], PSSH^[3] and ionic liquids.^[21]

We will now discuss how the efficiency of the ITESC depends on material parameters expressed as a function of ZT_i . The efficiency of the total heating-cooling cycle is the electrical energy produced divided by the thermal energy passing through the device. There are two major contributions to the thermal energy.^[25] The first is the heat used to warm up the materials, which is proportional to the masses and the heat capacitances of the electrodes and the electrolyte. The second contribution corresponds to the heat absorbed in the device by phenomena similar to traditional thermoelectric generators:^[30] (1) Peltier heat absorption from the hot side to the

cold side due to the thermoelectric current ($\alpha_i T_H \int I_{ch} dt$, where T_H is the temperature at hot side); (2) Joule heating that heats the hot side of the device ($\frac{1}{2} \int I_{ch}^2 R_s dt$), where R_s corresponds to the internal ionic resistance of the electrolyte; and (3) the heat that flows along the ITESC due to the temperature difference ($\lambda A \int \Delta T dt$), where A is the cross-sectional area of the film in the direction perpendicular to the current. We neglect the first contribution which is highly dependent on the geometry of the device, and focus on the material aspect for the first step. Moreover, the initial heating of the materials is also possible to be reused to some extent in more complex device system. Here maximum heat-to-stored electricity conversion efficiency of an ITESC ($\eta_{\Delta T_{ch}}$) is defined as the ratio between the electrical energy that is generated and stored in the ITESC (E_{ch}) during the charging time (t_{ch}), and the heat absorbed during charging (Q_{in}), $\eta_{ch} = E_{ch}/Q_{in}$. For a specific t_{ch} , the heat input to the hot junction of the ITESC is:^[25]

$$Q_{in} = \alpha_i T_H \int_0^{t_{ch}} I_{ch} dt + \lambda A \int_0^{t_{ch}} \Delta T dt - \frac{1}{2} \int_0^{t_{ch}} I_{ch}^2 R_s dt \quad (\text{Eq. 3})$$

By recognizing that $\int_0^{t_{ch}} I_{ch} dt = Q_{ch} = C \alpha_i \Delta T$ (Eq. 4) and $\int_0^{t_{ch}} I_{ch}^2 R_s dt = C (\alpha_i \Delta T)^2$ (Eq. 5), Eq. 3 is reduced to:

$$Q_{in} = \alpha_i T_H C \alpha_i \Delta T + \lambda A \Delta T t_{ch} - \frac{1}{4} C (\alpha_i \Delta T)^2 \quad (\text{Eq. 6})$$

Using the time constant for charging the supercapacitor as $\tau = CR_s$ ($R_s = \frac{L}{A \sigma_i}$) and 5τ as the charging time (99% of the charge has been transferred during this period), the heat absorbed can be expressed as:

$$Q_{in} = \alpha_i T_H C \alpha_i \Delta T + \frac{5C \lambda A \Delta T}{\sigma_i} - \frac{1}{4} C (\alpha_i \Delta T)^2 \quad (\text{Eq. 7})$$

The maximum charging efficiency of ITESC ($\eta_{\Delta T_{ch}}$) can now be expressed as:

$$\eta_{\Delta T_{ch}} = \frac{\Delta T}{2T_H + \frac{10\lambda}{\sigma_i \alpha_i^2} - \frac{1}{2} \Delta T} \quad (\text{Eq. 8})$$

It is clear from Eq. 8 that the maximum charging efficiency is closely related to the same parameters that determines the ionic thermoelectric properties: σ_i , α_i and λ . **Similar to classic electronic materials, the efficiency will increase with higher ionic conductivity and Seebeck coefficient and lower thermoconductivity.** The dependence of these three parameters on the maximum efficiency of ITESC is illustrated in Figure S7 by fixing two of the parameters and vary the third (at $\Delta T = 10$ K and $T_H = 303$ K). This will give useful insights into the importance of the individual properties, while we point out that they are typically not uncorrelated for real materials. As reasoned in the introduction, it would be highly valuable if η_{ch} could also be directly evaluated based on ZT_i . Indeed $ZT_i = \sigma_i \alpha_i^2 T / \lambda$ as defined above, allows us to modify Eq. 8 to:

$$\eta_{ch} = \frac{\Delta T}{T_H} \frac{ZT_i}{2ZT_i + \frac{10T}{T_H} - \frac{1}{2} ZT_i \frac{\Delta T}{T_H}} \quad (\text{Eq. 9})$$

As comparison, the maximum efficiency for traditional electronic thermoelectric generator (TEG) is:

$$\Phi_{max} = \frac{\Delta T}{T_H} \frac{\sqrt{1+ZT_e} - 1}{\sqrt{1+ZT_e} + \frac{T_C}{T_H}} \quad (\text{Eq. 10})$$

For material with the same ZT value, the maximum efficiency from the classic TEGs is higher than from ITESC. This is due to the fact that the output power is not constant in ITESC, instead decrease with time.

Figure 4c shows the dependence of ZT for the efficiency of ITESCs composed of different materials, as well as for the equivalence of electronic TEGs connected to a SC (at $T=298K$, $\Delta T=10K$, $C=1\text{ mF}$). Because ZT varies dramatically with humidity for PSS:Na, the efficiency also spans a large range, from $5\times 10^{-7}\%$ to 0.004%. It is worth mentioning that the efficiency of PSS:Na at high humidity is larger than other ionic thermoelectric materials that have higher ionic Seebeck coefficients, which can be explained by the higher ionic conductivity in the aqueous PSS:Na gels.^[31] Fig. 4c shows that the ionic material with the highest efficiency is PSSH^[3] due to its high ionic conductivity. Indeed the proton mobility in aqueous system is known to be much higher than sodium cation through efficient transport mechanism such as the Grotthuss mechanism at high humidity^[24]. Hence, ionic thermoelectric material can reach efficiencies similar to electronic thermoelectric material for charging supercapacitor with alternative heat sources. The exciting point is that there has been a lot of research on reaching high ionic conductivity, but it remains to reveal how to optimize the ionic Seebeck coefficient in polymer electrolytes. Hence, for that parameter, there is vast potential for improvement.

Finally, we stress the important finding that the charging efficiency of ITESC can be expressed based on an ionic figure of merit ZT_i , in analogy to traditional TEGs. Because ZT_i includes the relevant thermoelectric properties of the material, this enables a direct prediction of efficiency with new improved materials developed in future research. Moreover, for the first time, the energy conversion efficiency of ionic and electronic thermoelectric material is presented together with the same meaning through the equivalence of a ITESCs with a series circuit TEG-SC. This builds the foundation for a new route to develop the technology in case of energy harvesting from intermittent heat sources.

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Figure 1 | Thermoelectric effect with electronic charge carriers in a semiconductor and ionic charge carriers in an electrolyte

a. and b. schematically demonstrate the electronic conductors displaying majority hole (h^+) conduction. c. The thermoelectric generator (TEG) with electronic Seebeck effect can provide a continuous output current and power. d. The ionic conductors with majority cations ($+$) conduction. e. and f. show that ions accumulating at the metal electrodes induce a transient thermo-induced current that decreases to zero over time.

Figure 2 | Operation principle of ionic thermoelectric supercapacitor (ITESC).

Voltage curve and mechanism sketch of a full charge and discharge cycle: (i) establishing the temperature gradient through heating leads to an ionic thermovoltage, (ii) thermoelectric charging of the supercapacitor, (iii) cooling to reach equilibration with $\Delta T = 0$, and (iv) discharging.

Figure 3 | Thermoelectric properties of polyelectrolytes versus humidity.

- (a) Chemical structure of PSS:Na and sketch of the thermodiffusion of cations in a polyanion submitted to a temperature difference. For PSS:Na, the mobile ions (Na^+) diffuse to the cold side. (b) Evolution of the ionic conductivity (σ_i), Seebeck coefficient (α_i) and corresponding power factor ($\sigma\alpha_i^2$) for PSS:Na versus RH. (c) The evolution of the thermal conductivity (λ), and ZT_1 versus RH. All measurements were done at room temperature

Figure 4| Energy of charging and efficiency for PSS:Na and other thermoelectric materials.

(a) (left) Measurement set-up and (right) the equivalent circuit of ITESC in the experimental set-up. (b) The energy transfer to supercapacitor from charging of different thermoelectric material ($\Delta T = 10K$, $C = 1mF$). For ionic materials (PSS:Na, PSSH, PEO-NaOH and ionic liquids) the structure of device is ITESC, and for electronic

material (PEDOT and Bi_2Te_3) the structure of device is by connecting the TEG with a supercapacitor as shown in figure (a). (c) The efficiencies of materials with different ZT.