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Short communication

Thermal-to-electric energy conversion of a nanoporous carbon

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ABSTRACT

As two nanoporous carbon electrodes are soaked by an electrolyte solution and placed at different temperatures, a significant transient potential was measured, providing a novel mechanism for thermal-to-electric energy conversion.

1. Introduction

Generating clean energy from environment, e.g. wasted heat, has been an active area of research for the past few decades [1]. Usually, thermoelectric energy conversion is based on the well-known Seebeck effect. As the two ends of a conductor or a semiconductor are placed at different temperatures, due to the temperature dependence of electron mobility, electrons would diffuse from the high-temperature end to the low-temperature end, transferring thermal energy as a current is formed. The energy conversion efficiency can be measured by the dimensionless figure of merit

$$Z = \frac{\alpha^2}{\kappa\lambda} \tag{1}$$

where $\alpha = \phi/\Delta T$ is the Seebeck coefficient, with ϕ and ΔT being the output voltage and the temperature difference, respectively; κ is the electric resistivity; and λ is the thermal conductivity. For conventional thermoelectric materials, the values of figures of merit are only 0.1–1, and therefore their applications are limited to temperature measurement [2]. Recently, enhanced figures of merit around 3–5 were achieved by using superlattices and nanowires/nanotubes [3–6], which was attributed to the confinement size effect [7,8]. However, their performance was still far from satisfactory. In order to meet the increasingly high requirements, mechanisms of higher energy conversion efficiency need to be discovered.

As a solid electrode is immersed in an electrolyte solution, near the solid–liquid interface solvated ions are subjected to different forces from the solid and from the bulk liquid phase, and thus there structures become anisotropic [9,10]. This electrochemical effect, which is often secondary in ordinary systems, can be significantly amplified by the large surface area in a nanoporous system. For instance, as an external electrical field is applied across two nanoporous electrodes, a large amount of ions can be adsorbed at the nanopore surfaces. As a first-order estimation, the total charge, Ω, can be estimated as

$$\Omega = \sigma A_0 \tag{2}$$

where σ is the surface charge density and A_0 is the total surface area. Since A_0 is typically 100–2000 $m^2\,g^{-1}$ for a nanoporous material, 6–8 orders of magnitude higher than its bulk counterpart, the system becomes a “super-capacitor” [11–13].

2. Experimental

In the current study, we investigated a Norit SX2 nanoporous carbon. The as-received material was in powder form, with the particle size around 50 μm. The pore size was 1–10 nm, and the specific surface area was about 500 $m^2\,g^{-1}$. The experimental setup is depicted in Fig. 1. The nanoporous electrodes were prepared by mixing eight parts of nanoporous carbon, one part of Soltex ACE acetelyene black (AB), and one part of Aldrich 182702 polyvinylidene fluoride (PVF). The mixture was placed in a steel mold and compressed at 20 MPa for 5 min at room temperature, forming

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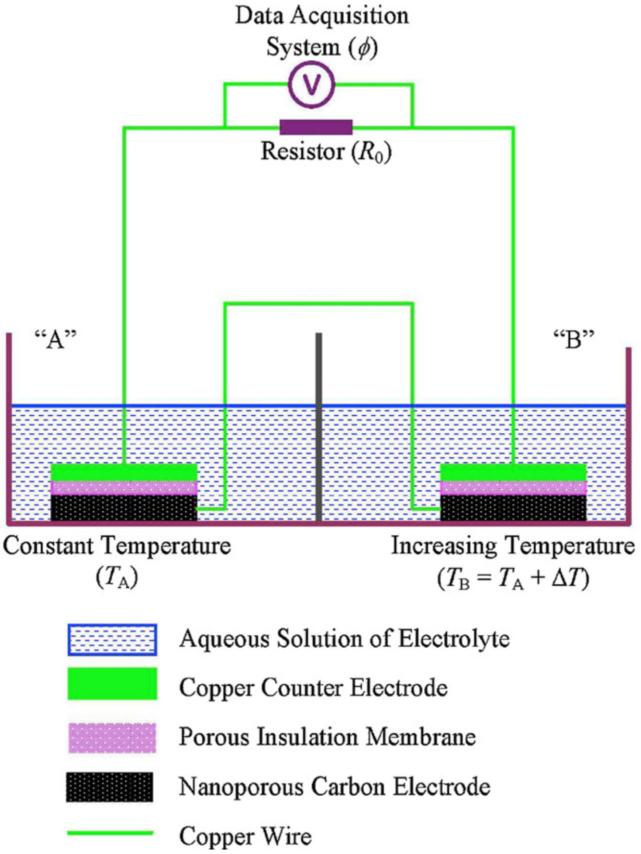

Fig. 1. A schematic of the experimental setup.

disks with the diameter of 19.0 mm. The mass of each disk was $m = 45$ mg.

The nanoporous thermo-to-electric energy conversion system (NTEECS) was produced by immersing two identical sandwich ("A" and "B") in a 26-wt.% sodium chloride solution. Since the ion size is relatively small, the solvated ions could be adsorbed at nanopore surfaces [14,15]. Each sandwich consisted of a copper thin film (the counter electrode), a porous polymer membrane separator, and a nanoporous carbon disk (the electrode). The two nanoporous carbon electrodes were directly connected by a copper wire, and the two copper counter electrodes were connected through an external resistor, R_0. The temperature of one electrode ("A") was maintained constant. The other electrode ("B") was heated using an Aldrich Z28 controlled-temperature coil, with the temperature increase rate lower than 2 °C min^{-1}. The voltage, ϕ, across the external resistor was measured by a National Instrument 6036E data acquisition board. Fig. 2 shows a typical $\phi - \Delta T$ curve ($R_0 = 10\,\mathrm{k\Omega}$), where $\Delta T = T_B - T_A$ is the temperature increase of electrode "B", and T_A and T_B are temperatures of electrodes "A" and "B", respectively.

3. Results and discussion

Through Fig. 2, it can be seen clearly that, with a relatively small temperature variation around 35 °C, the measured output voltage is more than 100 mV, higher than that of conventional thermoelectric materials by nearly two orders of magnitude. This should be attributed to the thermal effect on surface ion density. As temperature varies, since ion mobility rises and the effective liquid viscosity decreases, the interface charge density is lowered. Assume that

$$\sigma = \sigma_0 \left[1 - \exp\left(-\frac{H}{kT}\right)\right] \tag{3}$$

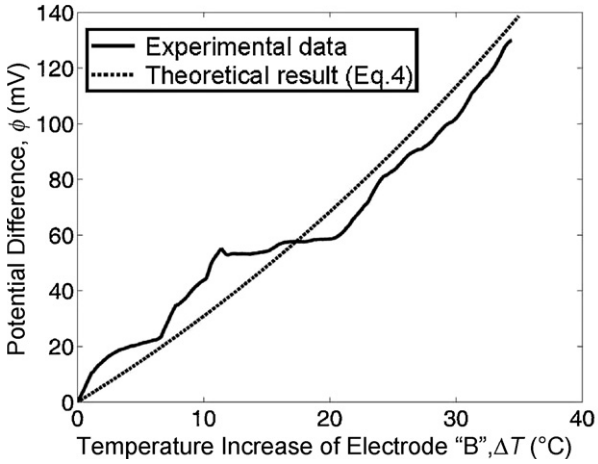

Fig. 2. Typical measurement result of output potential difference.

where σ_0 is the reference charge density, H is the energy barrier that an ion must overcome to diffuse away from the Outer Helmholtz Plane, k is the Boltzmann's constant, and T is the temperature. The voltage between the two electrodes of different temperatures can then be estimated as

$$\phi = \phi_0 \left[\exp\left(-\frac{H}{k(T_A + \Delta T)}\right) - \exp\left(-\frac{H}{kT_A}\right)\right] \tag{4}$$

where $\phi_0 = \sigma_0 RA$ is the reference potential difference, with $A = 18\,\mathrm{m}^2$ being the nanopore surface area of the electrode and R being the effective system resistance, which can be taken as the external resistance, R_0. In order to fit Eq. (4) with the testing data in Fig. 2, σ_0 should be set as 13 mC (s m^2)$^{-1}$, or 5×10^{16} e (s m^2)$^{-1}$; and H should be taken as 2.95×10^{-20} J, or 0.2 eV, where "e" indicates electron charge. Because the electrolyte concentration is high, the Debye length is quite small, around 1 nm. In the sodium chloride solution, in a layer of 1 nm, the effective average ion density is $\sigma^* = 4 \times 10^{18}$ e m^{-2}. That is, $\sigma_0 \Delta t$ is at about 1% of σ^*, where Δt is the characteristic diffusion time, which looks plausible.

According to Fig. 2, in the temperature range under investigation, the output voltage increases with the temperature difference quite linearly. Hence, Eq. (4) can be simplified as

$$\phi = \tilde{\alpha} \ \Delta T \tag{5}$$

where $\tilde{\alpha}$ is the specific thermal sensitivity, an analog to the Seebeck coefficient. According to Fig. 2, the value of $\tilde{\alpha}$ is 3.7 mV °C^{-1}. Since the temperature gradient exists in the liquid phase, the thermal conductivity is dominated by the electrolyte solution, with $\lambda \approx 0.6\,\mathrm{W\,(m\,K)^{-1}}$. The electric resistivity is determined by the counter electrodes, with $\kappa \approx 10^{-8}\,\Omega\,\mathrm{m}$. Thus, by replacing α in Eq. (1) by $\tilde{\alpha}$, the energy conversion efficiency factor of the NTEECS can be calculated as 2.3×10^3.

While in general the potential difference exists at any solid–liquid surfaces, only in a nanoporous system can it be detectable using the current data acquisition system. When the two electrodes are connected, a current would be formed until the new equilibrium is established. If the surface area of the electrode is small, the total amount of excess charges would be negligible, and thus the output electric energy is nearly zero. As the electrode area, A, becomes large, it takes a much longer time for the equilibrium condition to be reached. In the experiment, we observed that it took more than 4 days for the output voltage to decrease by 50%. Once the voltage vanished, the thermoelectric energy conversion capacity of the system was lost. However, as the two electrodes were disconnected, internally grounded with counter

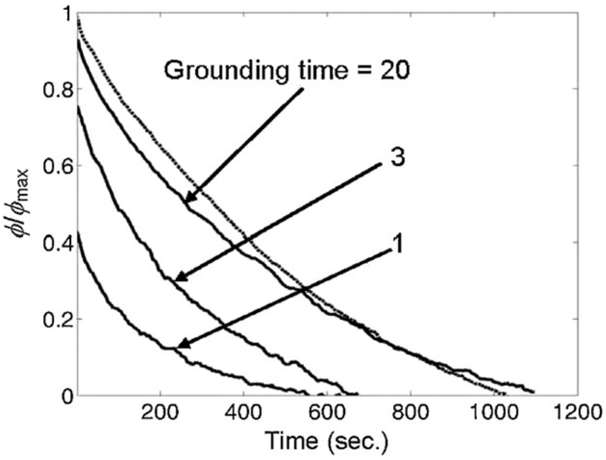

Fig. 3. The output voltage as a function of time. The dashed line indicates the voltage before disconnection and internal grounding. The temperature difference is kept at 50 °C. The external resistance $R_0 = 100\,\Omega$. The maximum output voltage $\phi_{max} = 46.5$ mV.

electrodes, and reconnected, similar energy conversion procedure could be repeated. That is, during the disconnection–reconnection process, the distribution of ions and charges at nanopore surfaces returned to their original configuration, and thus the energy conversion could be performed semi-continuously. The discharge time is highly dependent on the external resistance. For $R_0 = 100\,\Omega$, the decay time was about 10 min. As shown in Fig. 3, after being grounded for 1 min, about 40% of the energy conversion capacity of the system was recovered. The system recovery rate rapidly increased to nearly 75% as the grounding time was 3 min, and converged to the steady-state as the grounding time was longer than 6 min. At the steady-state, in each energy conversion cycle the generated electric density is $E = 4.5$ mJ, and thus the output energy density is $E/m = 0.1\,\mathrm{J\,g^{-1}}$ per energy conversion cycle. At the initial stage of each cycle, the output power density is about $0.5\,\mathrm{mW\,g^{-1}}$. Note that shifting the locations of the two electrodes (i.e. changing their temperatures) can also lead to the recovery of energy conversion capacity.

4. Concluding remarks

In summary, it has been demonstrated through experiments that, due to the temperature dependence of surface ion density, thermal-to-electric energy conversion can be achieved by using a nanoporous carbon. The output voltage is orders of magnitude higher than that of conventional thermoelectric materials. While the current is transient, the system can be reactivated by internal grounding. It is envisioned that as nanoporous electrodes of higher specific surface areas or counter electrodes of lower electric resistivity and thermal conductivity are used, the energy conversion efficiency can be further improved.

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