The Further Improvement of the Ionic Thermoelectric Generator

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Abstract—The power conversion efficiency of the proton-conductive thermoelectric cell is improved by the unidirectional orientation of ionic conductivity in the electrospun Nafion cell. The thermoelectric performance of nanofibers is experimentally demonstrated.

Index Terms—Electrochemical processes, electrospinning, polymer gels, thermoelectricity.

I. INTRODUCTION

The thermoelectric sensitivity of gels was initially reported for the extracellular hydrogel extracted from receptors of marine sharks and skates (rays) [1], [2], while further investigation [3] concluded that the thermoelectric response is related to the thermally activated electrochemical reactions on electrodes [4]–[6]. However, recently the significant thermoelectric (TE) voltage in a temperature gradient has been experimentally demonstrated with natural and synthetic gels at low and room temperatures [7]. The model [8] discussed here is based on the thermally driven transfer of protons between hopping places [9]. Due to the energy barrier between these places, the temperature gradient creates a directional transfer of charge carriers (protons) from the hot side to the colder side as illustrated in Fig. 1.

At the moment, the authors are unaware of any published work by others on the subject of TE effect in ionic conductors besides our work [7], [8]. In the steady state, if there are no gradients of temperature $\Delta T = 0$ and proton concentration $\Delta n$ and if there is no net exchange between the two states (1 and 2) and equal probability of hopping in both directions, then $\omega_{12} - \omega_{21} = 0$, as illustrated in Fig. 1 (left side) and shown in (1)

$$\omega_{12} = \omega_{21} = \text{Const} \cdot n \cdot f(T) \cdot \exp \left( -\frac{W_b}{kT} \right)$$

where \(f(T)\) is the frequency of oscillations of ions (attempts to go over the barrier \(W_b\)).

Fig. 1. Asymmetric displacement of protons between hopping places in the gradient of temperature that creates the gradient of proton concentration (space charge).

Fig. 2. Hopping proton exchange between two neighboring states when the electric field is applied.

A gradient in temperature creates the net flow because the probability to hop toward the lower temperature prevails as illustrated in Fig. 1 (right side). This thermally driven displacement of charge carriers (protons) produces the space charge that results in the internal electric field; the colder side of the material becomes positively electrochemically charged. A gradient in electric potential $E = -d\varphi/dx$ leads to the asymmetry of the energy barrier because of the difference in electric potential over the hopping distance $\delta$, as Fig. 2 shows.

If the dc current is blocked (open circuit), the material is polarized until the net electric current $j = j_{1,2} - j_{2,1} = 0$. The extrapolation of local deviations ($\Delta T$ and $\Delta n$) to the macroscopic range leads to the direct expression for the proton concentration

$$n = n_0 \exp \left[ \frac{2W_d + q\delta E}{2k} \left( \frac{1}{T_0 + \alpha \cdot x} - \frac{1}{T_0} \right) \right]$$

where $\alpha$ is the temperature gradient (d$T$/dx), $n_0$ and $T_0$ are the proton density and temperature at the cold end, respectively, and $W_d = W_{dis} + W_b$ includes the enthalpy of dissociation $W_{dis}$ to account for proton generation at varied temperature.

As a result, the created space charge (thermal polarization of a gel) causes the electric potential difference between the electrodes. Steady state is established when the transfer of
protons due to the temperature gradient is compensated by the backward diffusion flow due to the gradient of concentration. Fig. 3 shows that the RedOx potential of electrolyte is inclined along the temperature gradient. This supports the reduction of protons to atoms of hydrogen near the cold electrode (anode) while assisting the oxidation of hydrogen on the hot electrode (cathode).

Fig. 3 shows that the electron flow (electric current) in the external circuit is produced due to the electron exchange on electrodes. To achieve the practically useful power conversion from such an ionic thermoelectric generator (iTEG), three problems must be solved: the potential barrier to electron exchange on electrodes, the recirculation of protons by the return of hydrogen to the hot electrode (cathode), and the ionic conductivity of the gel. This work addresses the improvement of ionic conductivity in the Nafion media.

Synthetic proton-conductive membranes, specifically Nafion (a tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid copolymer) from DuPont Corp., are commercially available because they are used in fuel cells. Wet Nafion microphase separates into hydrophilic domains containing sorbed water that is surrounded by a hydrophobic polymer matrix. These hydrophilic domains provide paths for proton transport similarly to hydrogels. The proton conductivity of bulk Nafion film is highly dependent on the percolation of protons through the nanoscale ionic morphology of Nafion. In fact, protons migrate along the surface of nanopores. Recently, it has been shown [10], [11] that Nafion nanofibers exhibit significantly higher (an order of magnitude) proton-conducting properties than bulk (extruded or solution cast) films due to the straight path of protons along the fiber, and higher surface area available for the ionic current due to the more uniform distribution of voids between fibers than that of pores in the bulk material. Originally, Nafion nanofibers were discovered via scanning electron microscopy of fuel cell electrodes, where they naturally form under certain fuel cell operating conditions [12]. However, the intentional fabrication of Nafion nanofibers required the use of a carrier polymer (e.g., poly(ethylene oxide), PEO; poly(vinyl alcohol), PVA; or poly(acrylic acid), PAA) [10]. In this paper, we report the results of an experimental study with the goal of increasing the proton conductivity in the Nafion media.

II. Experiments

The deposition of the Nafion fibers by electrospinning is based on the Coulomb force between the meniscus of the electrically charged liquid (Nafion solution) and the grounded conductive substrate. This technology involves a combination of electrospray and dry spinning of microfibers. The process is initiated as electrospray when the electrostatic repulsion on the charged surface of the liquid meniscus counteracts the surface tension. At some voltage and corresponding density of charge, a stream of liquid erupts from the surface of the meniscus as a charged liquid jet known as a Taylor cone. In the case of liquid, which easily evaporates, the jets become thinner, the density of the electric charge exceeds the Rayleigh limit, and the jet explodes as a cloud of charged microdroplets. However, in the case of a liquid polymer solution, the evaporation of the solvent (dry spinning) leads to the creation of polymer fibers that are stretched by the electric field. Electrospinning may be done by different kinds of spinnerets from thin metal or dielectric hollow needles with polymer solution inside to sharp needles externally coated with the polymer solution.

Nanofibers were electrospun from a solution of 98:2 wt% Nafion: PEO, in 2%, 3%, and 4% solid concentration in the isopropyl alcohol (IPA) and water (3:1, IPA:H2O) solvent. The high molecular weight (and so the long molecular chain) of the polymer is needed to form nanofibers because the Nafion itself creates only the agglomerate of micelles with pores between them. The long-chain polymer molecules serve as a holder for a linear Nafion structure with a single axial channel inside the polymer “tube.” As a result, the random percolation of protons in the labyrinth of pores is replaced by the straight transfer along the giant length “pore” that dramatically, by more than an order of magnitude, increases the proton conductivity of the material.

For the arrangement of fibers, the test substrates were mounted on a rotating mandrel (drum) as shown in Fig. 4, and nanofibers were deposited directly on the copper electrodes of these substrates shown in Fig. 5. The rotation of target (mandrel) allows for the alignment of produced fibers.
The following parameters guided the electrospinning:

1) drum rotation rate = 500 rot./min (set by the controller of the drum motor);
2) needle-to-drum distance = 15 cm;
3) voltage = 9–10 kV (monitored by the embedded voltmeter of the high-voltage source);
4) flow rate = 0.6 mL/h (set by the controller of the syringe pump).

Fig. 6 shows the distribution of the electrospun fiber diameter, while Fig. 7 presents the SEM images of the samples produced.

Fig. 6 clearly illustrates that electrospun fibers exhibit a thickness (diameter) that increases with the content of solids in the solution, as shown in Table I.

Electrospun Nafion samples were tested for the TE performance by applying a temperature difference along the fibers. The setup for these tests is shown in Fig. 8.

The Keithley 2100 digital multimeter (6.5 digit) was used as a millivoltmeter. The Agilent U8002A power supply (0–30 V, 0–5 A) was applied to power TE modules (TE-71-1.0-1.3). TE modules are connected in series to ensure the equal current in both of them. The heat circulates through the tested sample and heat guide.

The polymer composite substrate (PCB board) with deposited Nafion fibers was installed over two TE modules. These TE modules are mounted on the heat guide (aluminum bar). One TE module provided the cooling of the bar, while the other one was heating the bar. The layer of the filtering paper (cellulose wick) is placed between Nafion fibers and TE modules to keep the fibers wet.

Electrospun Nafion fibers deposited from the 2 wt% solution were tested “as is” (without any additional treatment). The results of this test are shown in Fig. 9. The load was matched to the impedance of the sample (170 kΩ). Therefore, the EMF (Seebeck voltage) exceeds the measured voltage twofold. As Fig. 8 shows, electrospun fibers exhibit thermoelectric voltage with Seebeck coefficients in excess of that of bismuth telluride (∼0.3 mV/K), which increases with temperature difference. The maximal achieved Seebeck coefficient (∼1.0 mV/K) is about 2.5 times lower than observed earlier with Nafion films,
TABLE I

<table>
<thead>
<tr>
<th>Content of solids, wt.%</th>
<th>Average thickness, nm</th>
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<tbody>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
</tr>
<tr>
<td>4</td>
<td>1350</td>
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</tbody>
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which was attributed to the high contact resistance of fibers with electrodes.

To improve the contact, samples of electrospun nanofibers were treated by the deposition of Nafion solution over electrodes and additional heating with pressure. The activation of samples notably (~30%) improves the thermoelectric output, as shown in Fig. 10, where measurements are carried with a load of 100 kΩ to increase the current through Nafion fibers.

The maximal performance (among three tested concentrations of solids) is achieved with medium concentration (3 wt.%), while the best results are expected at the lowest fiber diameter. This may be due to differences in contact resistance, and therefore, further improvement of the fiber/electrode contact is needed. The relatively low thermoelectric voltage may be attributed to the low volume concentration of fibers in the material layer. In fact, with the bulk of the volume being a void space between fibers, the electric conductivity of bulk water shunts the thermoelectric voltage developed in the fibers.

III. CONCLUSION

The technical feasibility of iTEGs built with Nafion nanofibers has been experimentally confirmed. Further work is directed toward the advancement of Nafion electrospinning technology and improvement of the interfaces between nanofibers and electrodes to enhance the thermoelectric power conversion efficiency. We expected to improve the TE power conversion efficiency to 50%–60% (currently 35%–40%) of the Carnot limit, which results in ~10% power conversion. Due to the ability of iTEG to work at temperatures below 400 K, where traditional TE generators convert <1% of power, the industrial application of iTEGs for conversion of concentrated solar power and recovery of waste heat is economically attractive.

REFERENCES

Matthew Salazar received the B.S. degree in physics from San Francisco State University, San Francisco, CA, USA, in 2011.

Since 2012, he has been a Research Engineer with Physical Optics Corporation, Torrance, CA. He has played key research roles in electrostatic dehumidifying, electrically supported spray and condensation technologies, production of nanofibers by electrospinning, and thermoelectric generation using a proton-conductive nanoporous polymer.

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Dr. Elabd received the U.S. National Science Foundation CAREER Award, the DuPont Science and Engineering Award, and the Army Research Office Young Investigator Award. He is a member of the American Institute of Chemical Engineers, American Chemical Society, North American Membrane Society, American Physical Society, and Electrochemical Society.

Michael Reznikov (M’99–SM’05) was born in Kiev, Ukraine, in 1948. He received the M.S.E.E. degree with a major in semiconductors and dielectrics from Kiev Polytechnic University, Kiev, in 1972 and the Ph.D. degree in physics and mathematics, majoring in solid-state physics, from the National Academy of Sciences of Ukraine, Kiev, in 1980.

At the National Academy of Sciences of Ukraine, he researched the field emissions from silicon, interfacial polarization in composites, and electrostatic coalescence of metal clusters that resulted in development of technologies for dielectric spectroscopy, nondestructive testing of thin films, and for electrostatic imaging. Since 2001 he has been a Principal Scientist with Physical Optics Corporation, Torrance, CA, USA, where he initiated and managed a number of projects in the electrostatic dehumidifying, polymer-gel-based electrolyte thermoelectric conversion, capacitive electrostatic sensing, electrically supported spray and evaporation technologies, and thermal management. He holds 12 patents, and has more than 40 publications to his credit in refereed international and national journals and proceedings of international conferences.

Dr. Reznikov received the Ukrainian State Prize for Sciences and Technology in 1986 for his research on material degradation on board of space stations. He is a member of the American Physical Society and Electrostatics Society of America.