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Flexible gel-state thermoelectrochemical materials with excellent mechanical and thermoelectric performances based on incorporating $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolyte into polymer/carbon nanotube composites†

Guangbao Wu,^b Yufeng Xue,^b Lei Wang,^a Xin Wang^{*b} and Guangming Chen^{*ac}

Thermoelectrochemical (TEC) materials are newly developed energy materials, which are promising and cost-effective in harvesting waste thermal energy based on redox electrolytes. However, liquid-state electrolytes and low thermoelectric (TE) performance seriously limit their application. Here, we report the first gel-state TEC (gel-TEC) materials based on incorporating $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes into polymer/single-wall carbon nanotube (SWCNT) composites. A porous 3D network morphology is observed, and the effect of SWCNT content on the tensile mechanical properties and TE performance is studied. Due to their large Seebeck coefficients and significantly enhanced electrical conductivities ($10.5 \pm 0.8 \text{ S m}^{-1}$), the power factor at room temperature can reach $13.5 \pm 3.0 \mu\text{W m}^{-1} \text{ K}^{-2}$, greater than those of liquid-state TEC materials and possibly the highest for gel-TEC materials. The gel-state, outstanding mechanical properties and excellent TE performance of the gel-TEC materials will speed up and widen their application in various fields such as flexible devices, wearable electronics, e-skins, etc.

Introduction

More than 90% of the energy we use is generated by thermal processes, and the primary and ultimate form of energy that we waste is heat.¹ Indeed, most of the heat generated in industrial productions and our daily lives is wasted. Thermoelectric (TE) techniques are convenient for realizing direct inter-energy conversion between heat and electricity, depending on Seebeck, Peltier and Thomson effects.^{2,3} TE devices have diverse applications, such as harvesting low-quality or waste heat, local

cooling, wearable electronics and e-skins.^{2–4} The TE materials developed so far mainly include inorganic materials (such as Bi_2Te_3 , PbSe , and BiSbTe alloys),^{5,6} small organic molecules,^{7,8} conducting polymers^{9–12} (poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPy), etc.), small organic molecule/inorganic composites,^{13–15} and polymer/inorganic composites.^{16–23} Note that typical TE materials and devices are in the solid state.

Liquid-state or gel-state thermoelectrochemical (TEC) materials are an alternative way to realize energy conversion between heat and electricity.^{24–27} Based on the chemical potential of a reversible redox reaction with temperature change, a large thermovoltage or potential gradient can be produced across the device. TEC materials have obvious advantages of low cost and intrinsic large Seebeck coefficients or thermal powers, which can reach magnitudes 1–100 orders greater than those of conventional solid TE materials.^{24,25} However, research on TEC materials is very limited, concentrating on the potassium ferricyanide/ferrocyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$) redox couple and the search for better solvents. Few other ions such as cobalt(II/III) tris(bipyridyl) and iodide/triiodide (I^-/I_3^-) redox couples have been reported.²⁸ Therefore, it still remains a great challenge to develop new redox couples to achieve high-performance TEC materials. More importantly, considering their large-scale integration and packaging for industrialization and application, flexible and leak-free gel-state TEC (gel-TEC) materials are strongly desired, which are obviously superior to the common liquid-state ones.

Here, we report the first gel-TEC materials, prepared by incorporating $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes into polymethylmethacrylate (PMMA)/single-wall carbon nanotube (SWCNT) composites. The schematic illustration is shown in Fig. 1. Black PMMA/SWCNT composite gels were prepared by polymerization and cross-linking reactions, and then immersed in a $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolyte solution to afford the gel-TEC materials. A porous 3D network morphology was observed, and the effect of SWCNT content on the tensile mechanical properties and TE performance was studied. The power factors were calculated according to $S^2\sigma$.

^aShenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, P. R. China

^bKey Laboratory of Rubber-Plastics, Ministry of Education, Shandong Provincial Key Laboratory of Rubber-Plastics, School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: wangxin@qust.edu.cn

^cInstitute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: chengm@iccas.ac.cn

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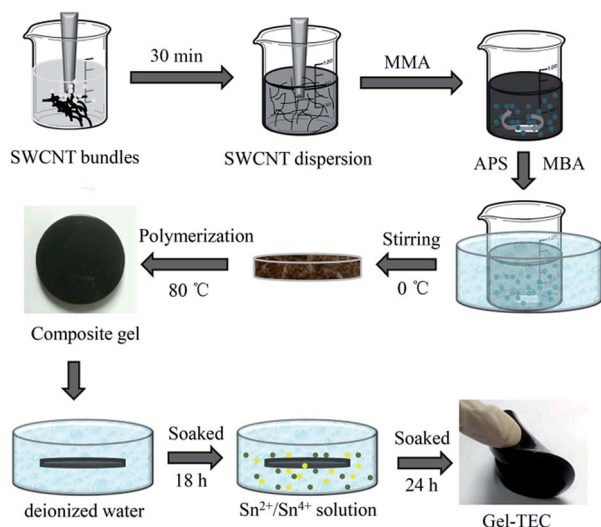


Fig. 1 Schematic illustration showing the preparation procedure for the flexible gel-TEC materials based on incorporating $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes into polymer/SWCNT composite gels.

Experimental section

Chemicals and materials

SWCNTs (diameter: < 3 nm, purity: $> 85.0\%$) were provided by Shenzhen Nanotech Port Co. Ltd, China. Methylmethacrylate (MMA) monomers (A. R. grade) were purchased from Beijing Chemical Works. Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and N,N' -methylenebisacrylamide (MBA) were provided by Shanghai Aladdin Reagent Co. Ltd. Ammonium peroxydisulfate (APS) was of analytical reagent grade (A. R.) with a purity of higher than 98.0%, and bought from Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were used as received without further purification. In all of the experiments, deionized water was used.

Preparation of gel-state thermoelectrochemical (gel-TEC) materials

The preparation procedure is schematically shown in Fig. 1. First, SWCNTs (4, 8, or 16 mg) were dispersed in 8 mL of deionized water, and treated under probe ultrasonication for 30 minutes. Then, 1.5 g of MMA monomers were poured into the well dispersed SWCNT dispersion, and stirred under magnetic stirring for 24 hours. After that, the beaker was placed in an ice-water bath, and 15 mg of MBA (cross-linking agent) and APS (initiator) were added to trigger the cross-linking reaction. Pre-polymerization took place under stirring in an ice bath for two hours. Subsequently, the reaction system was poured into a mold (Petri dish) and sealed with a plastic wrap. The polymerization reaction occurred at 80°C for 3 hours, resulting in PMMA/SWCNT composite gels. Then, the composite gel was immersed in deionized water for 18 hours to remove the crosslinking agent and the initiator, and then soaked in an $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolyte solution (0.2 mol L^{-1}) for 24 hours. Finally, after

the gel-samples were dried for ten minutes at room temperature, gel-TEC materials with solidified redox electrolytes ($\text{Sn}^{2+}/\text{Sn}^{4+}$) were obtained.

Morphological observation

The morphologies of the pure compound and the composite films were directly observed with a field-emission scanning electron microscope (HITACHI S-4800). The acceleration voltage is 15 kV.

Tensile measurements

Mechanical tensile tests were conducted using an Instron 3365 testing instrument measured at room temperature. The width and thickness of the rectangular samples were approximately 8 mm and 4 mm, respectively. The distance between the two clamps was 25 mm, and the crosshead speed was 50 mm min^{-1} .

Thermoelectric performance measurements

The Seebeck coefficients for the film samples were measured using a commercialized Seebeck coefficient measuring system, Thin-Film Thermoelectric Parameter Test System (MRS-3RT, Wuhan Joule Yacht Science & Technology Co., Ltd). During the measurements, a quasi-steady-state mode was adopted. The temperature gradient along the length of the sample (one end of the sample was heated) was determined through two thermocouples. The slope of the linear relationship between the thermoelectric voltage (ΔV) and the temperature difference ($\Delta T = 10 \text{ K}$) was then used to calculate the Seebeck coefficient ($S = -\Delta V/\Delta T$). An example of the Seebeck coefficient measurement curve is shown in Fig. S1 of the ESI.† The electrical conductivities of the composite films were measured using a Keithley 2000 multimeter (Keithley Instruments Inc., USA). At least five samples were measured, and the average value was used.

Results and discussion

Fig. 2 shows the morphological features of the dried gel-TEC materials using field-emission scanning electron microscopy (FESEM) images and the working mechanism for the $\text{Sn}^{2+}/\text{Sn}^{4+}$ gel-TEC materials. In Fig. 2a, a distinct fibrillar three-dimensional (3D) network porous structure is observed for the dried gel-TEC material using neat PMMA. The PMMA macromolecules have been cross-linked into a 3D network, and the porosity benefits the wetting behaviour and harvesting of a large amount of water molecules containing $\text{Sn}^{2+}/\text{Sn}^{4+}$. In Fig. 2b, besides the 3D network of the PMMA fibrils, a network of SWCNT bundles with distinct thin diameters is also prevalent (a FESEM image of pristine SWCNTs can be seen in Fig. 4a of our previous study).¹⁴ The hydrogen bonding between the polymer chains of PMMA and the surface functional groups of SWCNTs facilitates interfacial interaction and the stress-transfer process, which may enhance the mechanical properties. On the other hand, the 3D network of the highly electrically conducting SWCNTs is helpful for carrier transport and the improvement of the TE performance. The working mechanism of the gel-TEC materials is described in Fig. 2c. Being different from the

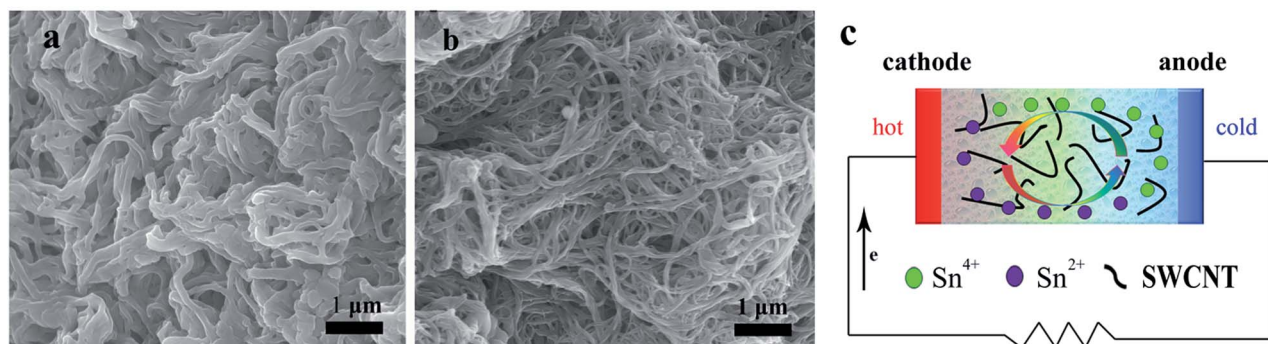


Fig. 2 FESEM images of the dried gel-TEC materials containing (a) pure PMMA and (b) the PMMA/SWCNT composite with 5.2 wt% SWCNTs. (c) Working mechanism of the $\text{Sn}^{2+}/\text{Sn}^{4+}$ gel-TEC materials.

migration carriers (electrons or holes) in solid semiconductor TE materials, charges are mainly transferred by the migration of ions through electrolytes in the gels under a temperature difference. At the hot end, Sn^{2+} ions are oxidized, providing two electrons to the anode ($\text{Sn}^{2+} - 2e^- \rightarrow \text{Sn}^{4+}$). The released electrons pass through an external load, and then are injected into the cathode by a reduction reaction ($\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$). In this work, we have introduced SWCNTs into the gel-TEC materials to increase the electrical conductivity. The mass transfer resistances are reduced by interfacial polarization under an electric field (the ions are attracted to the charged surfaces) and ion pair dissociation. Additionally, the electronic leakage can be

optimized by tuning the SWCNT concentration.²⁹ Thus, at low concentrations of SWCNTs, the TE performance can be optimized and significantly enhanced for the composite gel-TECs.

The photograph and mechanical properties of the gel-TEC composites are displayed in Fig. 3. The gel-TEC composite is black in colour due to the good dispersion of SWCNTs (Fig. 3a), and easily bent, confirming the high degree of flexibility (Fig. 3b). Further tensile measurements demonstrate that the gel-TEC composites of PMMA/SWCNTs exhibit enhanced mechanical properties compared with the corresponding gel-TEC material based on neat PMMA, as shown in Fig. 3c. The gel-TEC material based on neat PMMA reveals a low tensile fracture strength of 14.5 kPa and an elongation at break of ~60%. In contrast, the gel-TEC composites exhibit great improvements in mechanical properties. Moreover, both the tensile strength and the elongation at break increase significantly with increasing SWCNT content. For example, when the SWCNT ratio was only 5.2 wt%, the tensile strength and the elongation at break reached 31.9 kPa and 261.2%, respectively. The significant improvement of mechanical properties with increasing SWCNT loading may result from the good dispersion of low-content SWCNTs, the low crosslinking density, the long and flexible macromolecular chains between crosslinking points, and the strong intermolecular interactions (hydrogen bonding), which lead to effective stress transfer in the composites.³⁰ However, at a high SWCNT ratio of 10.3 wt%, the mechanical strength reduces, possibly due to SWCNT aggregation. Therefore, the gel-TEC materials reported here not only consist of a quasi-solid electrolyte but also display excellent mechanical properties. The quasi-solid state of the gel-TEC materials overcomes the problem of electrolyte leakage and is easily cut into various shapes and sizes, which make them much more convenient for real applications than conventional TEC materials consisting of liquid-state electrolyte. In addition, their excellent mechanical properties enable them to be applicable in complex environments.

In order to study the TE performance, the electrical conductivities (σ) and the Seebeck coefficients (S) were measured at room temperature, and the power factors ($S^2\sigma$) were calculated. Fig. 4 clearly shows that the gel-TEC material based on $\text{Sn}^{2+}/\text{Sn}^{4+}$ redox couple ions incorporated into the neat PMMA displays relatively low TE properties. The electrical conductivity, Seebeck coefficient and power factor are $6.0 \pm$

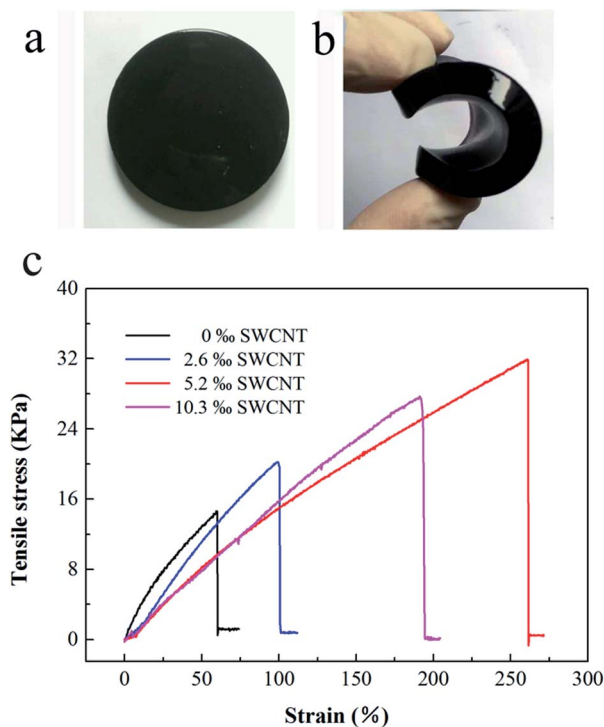


Fig. 3 Photograph of (a) the gel-TEC composite based on $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes incorporated into the PMMA/SWCNT composite with 5.2 wt% SWCNTs, and (b) the bent gel-TEC composite showing its high flexibility. (c) Stress-strain curves of tensile measurements for the $\text{Sn}^{2+}/\text{Sn}^{4+}$ gel-TEC materials.

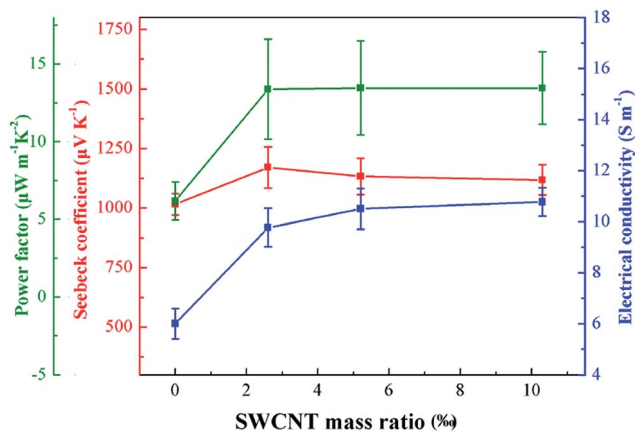


Fig. 4 Electrical conductivities, Seebeck coefficients and power factors at room temperature for the gel-TEC materials prepared by incorporating $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes into PMMA/SWCNT composites.

0.6 S m^{-1} , $1015.2 \pm 45.4 \text{ } \mu\text{V K}^{-1}$ and $6.2 \pm 1.2 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, respectively. Note that even the gel-TEC material based on neat PMMA reveals an electrical conductivity one order of magnitude higher than that of gel-TEC materials based on the $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ redox couple in a polymer matrix (around 0.6 S m^{-1}).³¹ With increasing SWCNT mass ratios, the electrical conductivity of the composite gel-TECs increases significantly first and then gradually. For example, the electrical conductivity reaches $10.5 \pm 0.8 \text{ S m}^{-1}$ at a SWCNT ratio of 5.2 wt%. The mechanism may be attributed to the formation of 3D percolation networks of well-dispersed SWCNTs with high electrical conductivity (Fig. 2b), polarization of SWCNTs under an electric field, and interfacial polarization (the ions are attracted to the charged SWCNT surfaces), thus facilitating dielectric breakdown and reducing the ohmic contact resistances even at low SWCNT concentrations.²⁹ As for the Seebeck coefficient, it firstly increases and then becomes almost independent of the SWCNT content (around $1132.4 \pm 76.3 \text{ } \mu\text{V K}^{-1}$). As a consequence, the power factor behaves in a manner similar to the Seebeck coefficient. The maximum power factor is $13.5 \pm 3.0 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, which is ~ 15.3 times higher than that of gel-TEC materials based on the $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ redox couple incorporated into a polymer matrix (deduced to be $\sim 0.88 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$).³¹ To the best of our knowledge, this is the highest power factor for quasi-solid electrolyte gel-TEC materials. Therefore, we report novel gel-TEC materials, prepared by incorporating the $\text{Sn}^{2+}/\text{Sn}^{4+}$ redox pair into polymer/SWCNT composite gels; more importantly, the gel-TEC composites display significantly enhanced electrical conductivity and power factor.

Conclusions

We report the first gel-TEC materials based on the incorporation of $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolytes into PMMA/SWCNT composites. The obtained gel-TEC materials display high flexibility, outstanding mechanical properties and excellent TE performance. At a low SWCNT ratio of 5.2 wt%, the elongation at break and tensile strength of the gel-TEC composite reach

261.2% and 31.9 kPa, respectively. A dramatically enhanced electrical conductivity of $10.5 \pm 0.8 \text{ S m}^{-1}$ and a large Seebeck coefficient of $1132.4 \pm 76.3 \text{ } \mu\text{V K}^{-1}$ are achieved. As a result, the maximum power factor reaches $13.5 \pm 3.0 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, which is much higher than that of liquid-state TECs, and may be the highest value obtained for quasi-solid-state electrolyte gel-TEC materials. The present study opens a new avenue to fabricate gel-TEC materials with both high mechanical properties and excellent TE performance, which will widen and speed up the application of TE materials in a variety of fields.

Conflicts of interest

There are no conflicts to declare.

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