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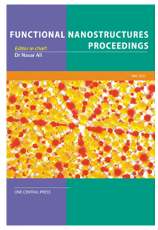

Conductive nanofilms in 3D porous structure for thermo-electric applications: theoretical and experimental study

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ABSTRACT

This work introduces the new concept of using a melamine based porous structure to act as a thermal insulator and a power generator simultaneously. We obtain randomly scattered PEDOT:PSS thin films in the scaffold by means of self-assembly conductive poly (3, 4- ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Thin film formations were found to change according to the amounts of the anionic surfactant, i.e. SDS in this study. The morphological study of the fabricated thin films was performed by scanning electron microscope, which the average thickness of the film was about 50 nm. Thermal conductivity was investigated experimentally and theoretically at different SDS contents. At the optimum condition of SDS contents of 3 wt.%, the thermal and electrical conductivities of the prepared thermoelectric porous structure were measured to be 0.0545 W/m.K and 20.7 S/cm, respectively. In theoretical part, we developed the model to predict the thermal and electrical conductivities of the hybrid thermoelectrics. The model could predict the key parameters affecting to the thermal and electrical properties, i.e., amounts of thin films, porosity, and size of foam ligaments. Together with the experimental study, it could offer a design strategy to improve the hybrid thermoelectric performance of this system.

I. INTRODUCTION

Thermal energy is one of the most interesting energy sources because around 60 percent of energy is lost in the form of waste heat [1, 2], which can be harvested by thermoelectrics to alter thermal energy into electricity. The key benefits of thermoelectric are reliable energy source, environmental friendly, long operation lifetime and applicable to ubiquitous applications [3]. Traditional thermoelectric materials are usually produced from inorganic semiconductors that are rare materials, rigid structures, and require difficult processes leading to subsequent high production costs, for example, Bi_2Te_3, Bi_2Te_2Se, and Bi_2Se_3 [4, 5]. In this work, we propose a 3D composite organic thermoelectric, consisting of organic conductive poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) films [6-8], randomly scattered in the foam's structure, to perform as an electric-generating insulators for large-scale applications. PEDOT:PSS is one of promising organic thermoelectric material due to good water processability, high flexibility and high electrical conductivity by doping co-solvents [6-8]. They are simple solution-based fabrication and use of low cost materials when compared to inorganic materials. In addition, we are interested in studying and developing models to predict thermal and electrical conductivities of the hybrid thermoelectric foams with different self- assembly PEDOT:PSS thin films in the foam's network, affected by doping anionic surfactant, sodium dodecyl sulfate (SDS) [9, 10]. The models are then validated with the experimental results of thermal and electrical conductivities at various amounts of SDS. This theoretical part could give us a basic understanding on the key parameters to improve thermoelectric properties of the hybrid foam.

II. EXPERIMENTAL METHOD

Material. The melamine foam (Basotec ®G) was purchased from BASF. PEDOT:PSS solution (Clevios™ PH 1000) and silver paste were obtained from Hereaus. Sodium dodecyl sulfate (SDS, ≥ 99%) was purchased from Sigma Aldrich. The melamine foams were cut with CO_2 laser machine into 5 × 5 × 2.5 cm^3 and 0.3 × 0.3 × 1.5 cm^3 for thermal conductivity (k) and electrical conductivity (σ) measurements, respectively. The amounts of SDS were varied in PEDOT:PSS solution from 0 to 5 wt.%. The melamine foams were then dipped into PEDOT: PSS solution. After that, they were removed and dried in a drying oven at 80°C for 3 h and 100°C for 2 h.

Characterization. The thermal property of thermoelectric foam was determined using thermal conductivity analysis (Hot Disk TCA, TPS 2500S). The electrical conductivity was measured with Seebeck coefficient/Electrical resistance measuring system (Model ZEM-3, ULVAC).

Theoretical study. Our system is derived from the geometrical model of porous metal foam consisting of solid and fluid phases, namely Boomsma-Poulikakos's model [11]. This model is widely used to describe the effective thermal conductivity of the three-dimensional tetrakaidecahedron structure, for example, open-cell metal foams (Al, Cu and Ni) filled with air and water [11-13]. The model considers a tetrakaidecahedron unit cell composed of cylindrical ligaments and contacted cubic nodes as shown in Fig. 1 (a).

In calculating thermal conductivity, it is assumed that the single rectangular unit cell is inserted in the tetrakaidecahedron structure and is divided into 4 layers (A, B, C, and D) along the heat transfer direction. The parameters, $e = r/L$ and $d = a/L$, are defined as non-dimensional variables where e is the dimensionless node length, d is the dimensionless ligament radius, r is the cubic node length, a is the ligament radius, and L is the ligament length. These structural parameters can be obtained from SEM images in Fig. 1 (b), measured and averaged from 10 ligaments. The thermal conductivity (k_{foam}) of open-cell foam is calculated from the combination of series thermal resistance (R_{th}) in each layer.

$$\kappa_{foam} = \frac{\sqrt{2}L}{2(R_{th,A} + R_{th,B} + R_{th,C} + R_{th,D})}, \tag{1}$$

Electrical conductivity of foam structure (σ_{foam}) can be calculated by using electrical resistance (R_e) in each layer of a tetrakaidecahedral unit cell written as:

$$\sigma_{foam} = \frac{\sqrt{2}L}{2(R_{e,A} + R_{e,B} + R_{e,C} + R_{e,D})}, \tag{2}$$

where R_{th} and R_e are the thermal and electrical resistances in each unit cell layer (A,B,C and D). Finally, the effective thermal (k_{eff}) and electrical conductivities (σ_{eff}) of the system are obtained by varying volume fraction (Φ_f) as follows:

$$\kappa_{eff} = (1-\phi_f)\kappa_s + \phi_f \kappa_f, \tag{3}$$

$$\sigma_{eff} = \Phi_f \sigma_f, \tag{4}$$

where k_s and k_f are thermal conductivities of the foam structure and the filling medium (i.e., thin films and air), respectively. σ_f is the electrical conductivity of the unit cell calculated from resistivity (ρf) of our single free-standing PEDOT:PSS thin film (ρf is set at 3.95 × 10-4 Ω.cm).

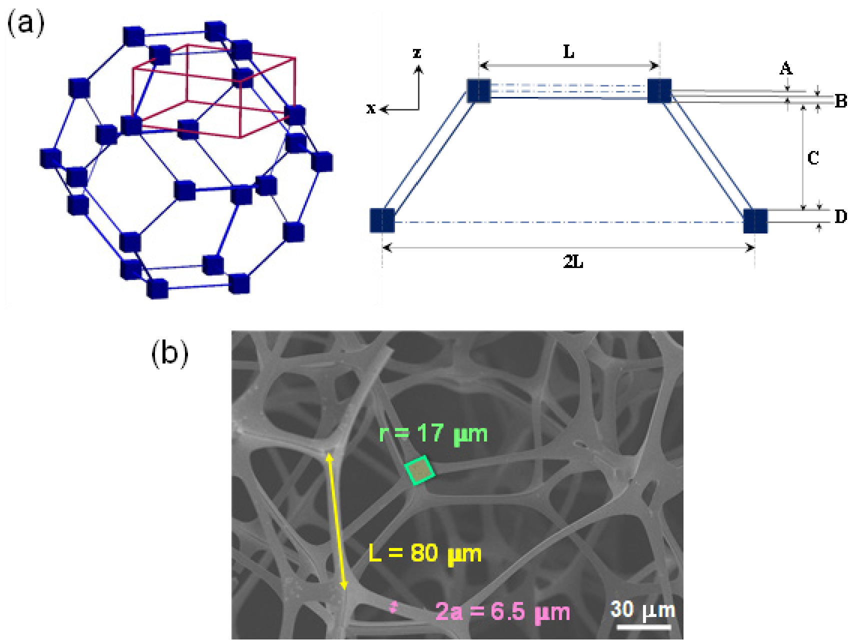

Figure 1 (a) Schematic diagram of the layered hexahedral unit cell of Boomsma-Poulikakos's model and (b) SEM image of melamine foam network.

III. RESULTS AND DISCUSSION

Figure 2 shows the dispersed PEDOT:PSS films inside the melamine foam (a) without and (b) with SDS doping. The results were observed that uniformity of thin films in the microporous scaffold foam was enhanced when PEDOT:PSS solution was doped with SDS surfactant. The highest film formation in the foam structure was achieved by SDS doping at 3 wt.%. The average thickness of PEDOT:PSS thin films in the melamine foam network was about 50 nm (data not shown).

To obtain volume fraction of the films (Φ_f), we assume equation: $\Phi_f = S.A. \times t_{\kappa,\sigma} / V_{sample}$, where *S.A.* is the surface area of films analyzed by Image J program, V_{sample} is the sample volume, and t_κ and t_σ is the fitting parameter for k and σ calculations, respectively.

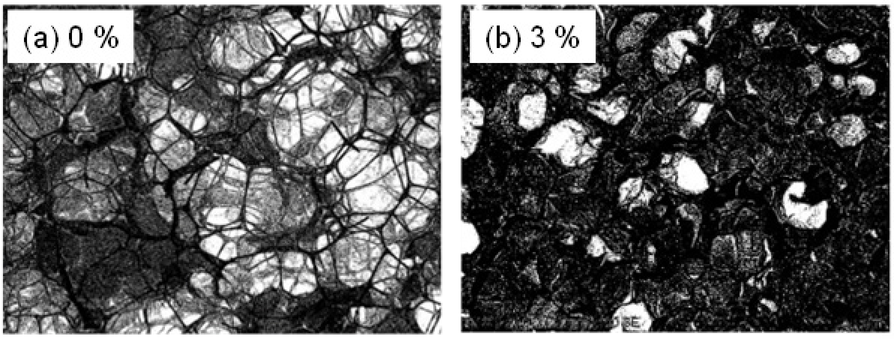

Figure 2 SEM images of PEDOT:PSS thin films fabricated in the foam network analyzed by Image J program (a) without and (b) with 3 wt.% SDS surfactant. Opaque part represents the coated thin films, while transparent part is without films.

Thermal and electrical conductivities

The experimental and modeling results in Fig. 3 (a) show an increase of thermal conductivity with SDS contents doped into PEDOT:PSS solution. The k_{eff} increases from 0.0427 W/m.K to 0.0545 W/m.K (at t_κ= 0.4) with increasing SDS contents from 0 wt.% - 3 wt.%. At 5 wt.%, k_{eff} decreases to be 0.0519 W/m.K due to the effect of residual SDS agglomerates at high SDS concentration. Both experimental data and model predictions are in good agreements.

There was a study estimated the actual electrical conductivity value of the thermoelectric aerogel to be two orders of magnitude larger than the measured experimental value due to the air portion [14]. Likely, our σ_{eff} obtained from the model was weighed by the same factor. The computed σ_{eff} from Boomsma-Poulikakos model slightly increases in the range of 15-20 S/cm at t_σ = 0.015 as shown in Fig. 3 (b), while the maximum electrical conductivity from the experiment is around 50 S/cm at 3 wt.% SDS doping corresponding to ~ 85 % of surface area of film analysed from image J program. It is obviously seen that Boomsma-Poulikakos's model is not a good model candidate to predict electrical conductivity of this system as it provides a large error. This error is caused by Boomsma-Poulikakos model that was basically derived from the network of ligaments, in which the electrical conductive path in the thermoelectric foam is mainly through the PEDOT:PSS thin films. However, there were some studies proposing the models for calculating electrical conductivity of a porous structure [15, 16], which tends to be promising for our future work.

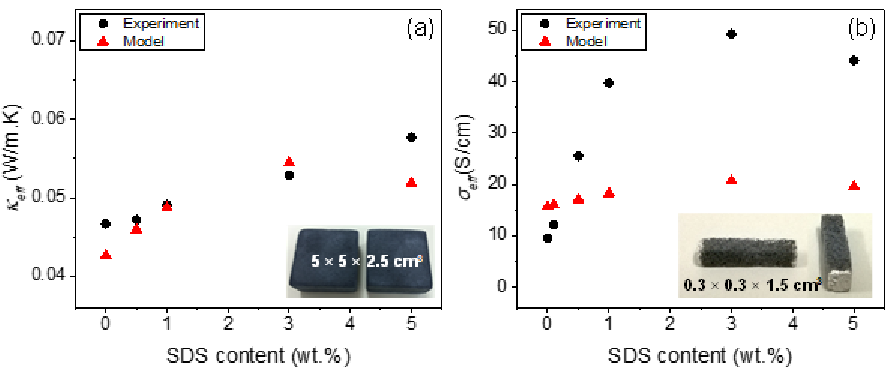

Figure 3 Modeling and experimental results of (a) k_{eff} at t_k= 0.4 (sample size: 5 × 5 × 2.5 cm³) and (b) σ_{eff} at t_σ= 0.015 (sample size: 0.3 × 0.3 × 1.5 cm³).

IV. SUMMARY

SDS surfactant has ability to reduce surface tension of aqueous PEDOT:PSS solution and also increase the film formations. The highest film growth is found at 3 wt.% SDS doping. The model suggests that the thermal conductive path is via the freestanding films and the foam ligaments, resulting in an increase of thermal conductivity as the film formation rises. In other words, it diminishes after the thin film formation drops. Although, k_{eff} increases, it is relatively low among other thermoelectric materials. For the electrical part, Boomsma-Poulikakos's model is not suitable for σ_{eff} prediction of a porous structure since it provides a high error compared with the experimental data. Moreover, t_κ is found to be substantially larger than t_σ, revealing that the preferred conductive path of the electrical conductivity is in-plane direction. This study could provide basic understandings of the roles of SDS surfactant to film formations and predict the key parameters affecting the thermal and electrical conductivities in this thermoelectric structure.

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