Development of Flexible Micro Thermo-Electrochemical Generators Based on Ionic Liquids

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Research on thermoelectrics has extended beyond conventional areas to include fields such as microtechnology and thermo-electrochemical technologies. Advances have been made to study physical properties such as the Seebeck Coefficient, electrical and thermal conductivity of ionic liquids (IL)[1]. This work presents a new design for micro thermoelectric generators based on a micro-machined electrode structure, ionic liquids as electrolytes with redox couple and a parylene sealing (SOLID technology [2]). The benefits of low temperature difference energy conversion are expected to have an important impact especially for biomedical and consumer electronic devices. The base material of the device consists of a double-sided Cu coated polyimide sheet. The copper layers are patterned with laser machining and the polyimide sheet is then etched isotropically in order to create reservoirs. The patterning allows series connection between the two sides of the sheet. The holes on one side are filled with p-type ionic liquid, while the other side contains n-type ionic liquid. The whole device is then sealed with parylene, by SOLID technology.
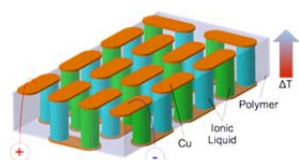

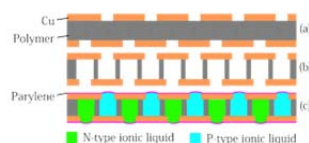Figure 1 – Principle of monolithic serial connected thermoelectric generators [3]

Figure 2 – Manufacturing of generators using liquids as thermoelectrical substances : (a) Cu/Polymer/Cu substrate is laser-patterned ; (b) caverns for the liquid are etched ; (c) after liquid loading, SOLID technology is applied for sealing.

In this paper the correlation between coefficient (α), thermal- (λ) and electrical- conductivity (σ) are studied for a large variety of ionic liquids. Using a single junction test cell (electrode / IL / electrode), the electrode distance, the redox couple concentration in the IL, and the temperature difference across the junction were varied. This set up allows determining the figure of merit ZT= $\alpha^2 \, \sigma/\lambda$ [4] as well as the conversion efficiencies of the generators. It was found in agreement with other authors that the Seebeck coefficient for e.g. 1-Butyl-3-methylimidazolium / tetrafluoroborate (BMIM / BF4) drops from 850 µV· K-1 without redox couple to 324 µV· K-1 with increasing redox concentrations (0.2 M) for LiI/I2 as redox couple. Looking at the single junction cell, surprisingly, it appears that the increase of the redox concentration tends to increase the power output despite the decrease of both conductivity and Seebeck coefficient. This is in strong contradiction to the link between the conventional figure of merit and efficiency of the thermoelectric generator. On the other side, a significant decrease in viscosity is observed for all studied IL's; for instance BMIM / BF4 has at 25°C a viscosity of 75 kg· s-1· m-1 and at 70°C of 18 kg· s-1· m-1. It is assumed that the carrier transport across the cell might be influenced by mechanical properties such as viscosity.

In a very simple model the origin of the Seebeck effect in a liquid is due to the mobility of cations and anions that create at constant heat-flow a steady state potential between hot and cold electrode. This model fits well looking at BMIM / BF4, but not at all for 1-Hexyl-3-methylimidazolium / iodide where the Seebeck potential changes sign in polarity. Apart from the experimental results, the paper aims to explain these phenomena.

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Enhanced Power Factor of PANI/GNP Nanocomposites

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Nowadays, the inorganic compounds (like Bi_2Te_3) are the best thermoelectric materials due to their suitable thermoelectric properties [1] for room temperature applications. Nevertheless, organic materials, like conjugated polymers, are becoming more important recently due to their increasing Figure of Merit (0.25-0.42)[2, 3]. Polymers generally have low thermal conductivity (©§≈ 0.1-0.5 W/m·K), flexibility, environmental stability, easily doping and de-doping, non-toxicity, potential processing advantages (e.g. printing) and straightforward preparation in comparison with inorganic semiconductors. The increase in the Power Factor of this materials, which is given by $S^2 ¥ò$, is being achieved by two mechanisms: doping the polymers [4] or blending them with different kinds of filling materials, such as carbon nanotubes, graphene nanosheets (GN) or graphene nanoplatelets [5].

Exfoliated graphene nanoplateles (GNPs)/Polyaniline (PANI) nanocomposites have been prepared by sequential processing comprising: (i) a first aniline oxidative polymerization step under acidic conditions; (ii) a mechanical blending with GNPs at different percentages. Finally, the pellets with different GNP contents have been obtained by cold pressing. The structural, morphological and thermoelectric properties have been characterized by means of elemental analysis, FTIR, SEM, electrical conductivity, Seebeck coefficient and thermal conductivity at room temperature measurements. On the one hand, a drastic increase in both the electrical conductivity and the Seebeck coefficient took place with the addition of the GNPs. The highest power factor value, 14 µW/m·K^2, is reached for a 50 wt% GNPs content which evidence a

1000-fold enhancement with respect to raw PANI polymer. On the other hand, the thermal conductivity has been measured as a function of the GNPs content so that the values range from 0.5 for pure PANI to 3.3 W/m·K for 50 wt.% GNPs content, which matches the thermal parallel resistor model for this nanocomposite.

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Organic Based Thermoelectric Materials for the Development of Flexible Heat Flux Sensors or Thermoelectric Generators

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Currently, the most efficient thermoelectric materials at room temperature are bismuth telluride-based alloys. Beside the fact that they are incompatible with the industrial scale, their scarcity and toxicity limit the range of applications. Recently, important research efforts have been focused on the development of alternative materials. Among them, organic materials based on conductive polymers are the most promising.

We synthesized fully organic and hybrid thermoelectric materials based on poly(3,4 ethylene dioxythiophene) (PEDOT). This polymer combines a high conductivity (from 100 to 3000 S/cm), a low thermal conductivity and moderate thermoelectric power (in the range 15-20 μV/K), while remaining highly versatile in terms of deposition methods, flexible and semi-transparent at low thicknesses.

We developed new routes to process PEDOT thick layers into thermoelectric devices, opening brand new possibilities. Our deposition technique consists in transferring pre-deposited polymer films through a solvation step. It is compatible with a wide range of geometries that are unreachable by usual techniques.

The thermoelectric power of the polymer was enhanced by modifying the oxidation level of the PEDOT:PSS, up to 160 μV/K. The oxidation level controls the characteristics of ionic charge carriers generated on the chains, leading to changes of the polymer properties. To this end, several reducing agents were used and their action was investigated. Thermoelectric and chemical characterizations were performed on the polymer layers. Several doping species were also tested on the PEDOT and their effects on the thermoelectric properties were discussed.

Based on these results, we fabricated a 100 % organic heat flux sensor, with a good flexibility and enhanced thermoelectric properties compared to pristine PEDOT:PSS.

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Thermoelectric Properties of Tetrathiotetracene Iodide Crystals: Modeling and Experiment

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The aim of the paper is to present a more complete physical model than has been applied so far for highly conducting organic nanostructured crystals of tetrathiotetracene iodide, TTT2I3, as a thermoelectric material. Earlier we have demonstrated that these crystals are very promising for thermoelectric applications. But the predictions were made in a simplified one-dimensional (1D) approximation. From experimental data it is known that the electrical conductivity along the molecular chains is almost by three orders of magnitude higher than in the transverse direction. Although from this fact it follows that the interchain interaction is weak, it is necessary to estimate the restrictions on the thermoelectric figure of merit ZT that this interaction will involve. We show that the elaborated more complete crystal model describes very well the temperature dependencies of electrical conductivity σ in the temperature interval between 150 K and 300 K and of Seebeck coefficient S even in a larger temperature interval from 20 K up to 300K, the highest temperature for which the measurements were made. 1D model can explain experimental dependencies only in a narrower temperature interval near 300 K. A short review of publications about the thermoelectric properties of organic materials during the last two years is also presented. Modeling in a more complete model has shown that the predictions made in 1D approximation are valid only, if the crystal purity is not very high and σ is limited up to ~ 2.5×10^6 $\Omega^{-1}m^{-1}$ and ZT ~ 4. In this case the scattering on impurities already limits the carriers' mobility. If the crystal purity is higher and, respectively, σ achieves higher values, it is necessary to take into account the interaction between the chains, because this interaction begins to limit the carriers' mobility. Reported measured values of σ, S and thermal conductivity κ at