

Room temperature synthesis of transition metal silicide-conducting polymer micro-composites for thermoelectric applications



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ABSTRACT

Organic polymer thermoelectrics (TE) as well as transition metal (TM) silicides are two thermoelectric class of materials of interest because they are composed of atomic elements of high abundance; which is a prerequisite for mass implementation of thermoelectric (TE) solutions for solar and waste heat recovery. But both materials have drawbacks when it comes to finding low-cost manufacturing. The metal silicide needs high temperature (>1000 °C) for creating TE legs in a device from solid powder, but it is easy to achieve long TE legs in this case. On the contrary, organic TEs are synthesized at low temperature from solution. However, it is difficult to form long legs or thick films because of their low solubility. In this work, we propose a novel method for the room temperature synthesis of TE composite containing the microparticles of chromium disilicide; CrSi₂ (inorganic filler) in an organic matrix of nanofibrillated cellulose- poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (NFC-PEDOT:PSS). With this method, it is easy to create long TE legs in a room temperature process. The originality of the approach is the use of conducting polymer aerogel microparticles mixed with CrSi₂ microparticles to obtain a composite solid at room temperature under pressure. We foresee that the method can be scaled up to fabricate and pattern TE modules. The composite has an electrical conductivity (σ) of 5.4 ± 0.5 S/cm and the Seebeck coefficient (α) of 88 ± 9 μ V/K, power factor ($\alpha^2\sigma$) of 4 ± 1 μ Wm⁻¹K⁻² at room temperature. At a temperature difference of 32 °C, the output power/unit area drawn across the load, with the resistance same as the internal resistance of the device is 0.6 ± 0.1 μ W/cm².

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1. Introduction

Thermoelectric (TE) energy converters are actively explored because of the global demand for renewable and affordable energy resources. Today's electricity production through heat engines and turbines waste 55% of the primary energy sources in the form of thermal energy. Waste heat and solar heat constitute an untapped energy source for our society. Thermoelectric generators (TEG) have key advantages over organic Rankine cycle, such as, no moving parts as they are solid-state electronic devices. Another area in need of autonomous energy sources is the emergence of mobile electronic devices with extended concepts such as

internet-of-thing and internet-of-everything where many sensors need to be powered in networks. Practical TEGs consist of multiple n- and p-type TE legs connected electrically in series and thermally in parallel. The maximum efficiency of a TEG is proportional to $(1 + ZT)^{1/2}$, where the dimensionless figure of merit ZT, of the material is $ZT = \alpha^2\sigma T/\kappa$ (α , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and the absolute temperature respectively). Presently the state-of-the-art TEGs are based on inorganic materials. For the low temperature $T < 250$ °C, alloys based on bismuth telluride, containing elements of moderate to high toxicity such as tellurium, antimony and lead, show ZT up to 1.2 at room temperature [1,2]. Such, bulk thermoelectric elements prepared by dicing and extrusion are traditionally assembled by pick-and-place methods, have limited cost-effective scalability. Alternative technology based on micro-fabrication involves expensive and complicated processes like

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lithography and thin-film deposition and is limited to the micro-scale regime [3–6]. Typically, 50% of the cost of a TE module comes from the material and the other half from the manufacturing process. It is thus obvious that the mass implementation of TEGs requires breakthroughs in both material science and engineering. Interesting attempts have been made to propose printing technology to create p- and n-leg with inorganic TE paste of bismuth telluride alloys [3].

One of the potential breakthroughs is related to the discovery that organic conducting polymers display promising TE properties [7,8]. In addition to their competitive properties with respect to the inorganic counterparts in the temperature below 150 °C, they are composed of naturally abundant elements and well suited for the widespread, well established solution based manufacturing facilities [9]. Among the various conducting polymers, PEDOT derivatives are being explored for their potential use in practical TE applications, due to their tunable σ and low κ [10]. PEDOT with Tosylate or PSS counter ions display interesting TE properties with the highest reported values for the power factor ($1270 \text{ W m}^{-1} \text{ K}^{-2}$) [11] and $ZT=0.25$, [8] 0.31 [12] and 0.42 [13] at room temperature.

There are however two challenges for organic TEs. The first is that the power factor is limited by the low α of these polymers; while the ratio of the electrical to the thermal conductivity is similar to Bi_2Te_3 alloys [14]. The second bottleneck is that conducting polymer TEs is today optimized as a thin film technology. The reason is that conducting polymers are formulated in inks of low solid content. Lateral architecture has been proposed to create TE modules by printing conducting polymer layers of the order of 1–2 μm thick on a thin substrate, then cutting, folding or rolling the devices (Fig. 1a). The advantage is that the temperature gradient, and thus the voltage can be large due to the long legs, but the internal resistance limits the power. To maximize power, it is preferable to keep the classical vertical architecture (Fig. 1b), and create thick vertical legs. The problem is that 10 to 100 printing/drying steps are needed to reach length of the legs of the order of 30–300 μm . This limits the throughput of the manufacturing process. Thick legs are crucial to keep a decently large temperature gradient, note that large temperature gradient also improves the conversion efficiency.

Our goal is to find a method combining mass-manufacturing by printing for patterning legs on large area, and a subsequent low temperature/high pressure treatment for sintering the legs in the

devices (Fig. 1c). So, our goal is to avoid high temperature annealing, which leads to cost increase and a dramatic CO_2 fingerprint upon manufacturing TEG. For that, we turn to composites between organic and inorganic TE materials. Inorganic nanoparticles are explored for making inks in application such as printed electronics, but again, the solid content of those inks is very low (few percent in volume) [15,16]. One other issue of nanocomposites made of inorganic nanoparticles and conducting polymers is the large numbers of inorganic-organic interfaces, at which reside an electronic energy barrier. For TEs, charges should be transported in both the organic and inorganic phases, hence it is challenging to have a pure ohmic contact between the inorganic nanoparticles and the organic conducting matrix. Instead, most of the inorganic nanoparticles possess an insulating oxide layer which leads to large contact resistance, preventing the charge carriers to actually travel in the inorganic domains.

In this work, we found a low temperature method ($<150 \text{ }^\circ\text{C}$) to prepare thick leg of a TE micro-composite (schematic shown in Fig. 2a) made of microparticles of chromium disilicide (CrSi_2) and microparticles of a conducting aerogel based on cellulose and the conducting polymer (poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate; PEDOT:PSS) at temperature below 150 °C. CrSi_2 has been chosen for the high natural abundance of its atomic elements and its resistance to oxidation [17] and high TE power factor ($\sim 1 \text{ mW m}^{-1} \text{ K}^{-2}$) [18]. Fig. 2b–d shows the chemical structure of PEDOT:PSS, crystal structure of CrSi_2 [19], and chemical structure of NFC respectively. This method avoids the high temperature sintering methods (such as spark plasma sintering or hot uniaxial pressing using induction furnace) necessary for the bulk silicides and secondly the large number of printing steps needed for achieving thick leg with polymer TEs.

2. Experimental approach

2.1. Formation of pellets, microstructural and TE characterization

The composite pellets were prepared at a pressure of 100 MPa at room temperature for 3 min and were typically 10 mm in diameter and 1 mm thick. The surface morphology of powders and pellet samples was studied using scanning electron microscope; SEM (LEO 1550 Gemini) and the elemental compositional analysis was

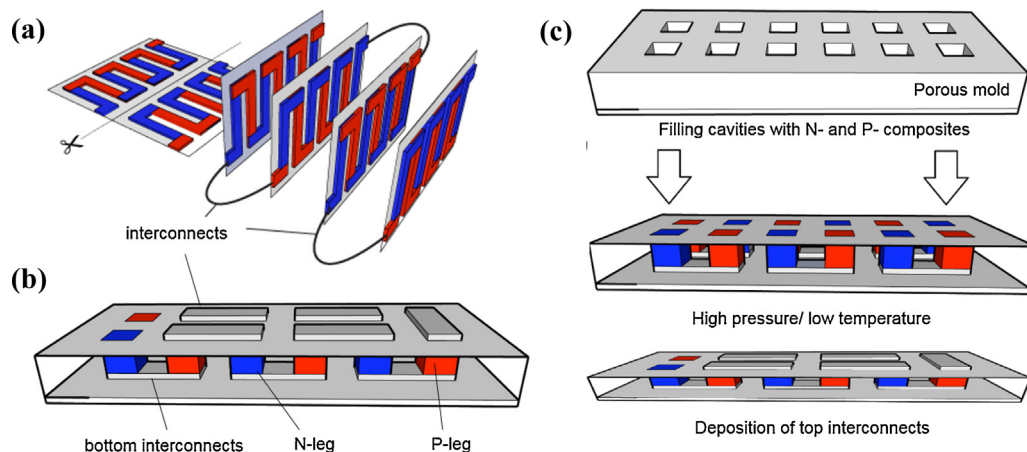


Fig. 1. Thermoelectric generators with (a) a lateral architecture, and (b) a vertical architecture. (c) The vision of combining printing technology to fill cavities with thermoelectric composite and applying pressure at low temperature to sinter the legs.

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