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Enhanced thermoelectric properties in Polypyrrole composites with silicide fillers

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Abstract

We report the design and the thermoelectric properties of organic/inorganic composites made of Poly-pyrrole (PPy) and of two silicides ($\text{Co}_{0.85}\text{Fe}_{0.15}\text{Si}$ and CrSi_2). For both composites, we find a significant enhancement of the thermoelectric properties of the PPy with increasing content of the inorganic filler. The maximum power factor of the composites were up to $0.8 \mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 50\%$ and of $2 \mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 90\%$ for $\text{Co}_{0.85}\text{Fe}_{0.15}\text{Si}$ and up to $3.37 \mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 50\%$ and of $9.7 \mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 90\%$ for CrSi_2 , more than two orders of magnitude higher than in pure PPy. This study proposed a novel and effective way to improve the thermoelectric performances of the thermoelectric polymer PPy.

Keywords: Composite materials, electrical properties, Intermetallic alloys and compounds, Polymers

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I. Introduction

The thermoelectric properties of polymers are still low compared to the state-of-the-art inorganic thermoelectric materials [1-3] however, their low cost, easy shaping for large-scale production, flexibility and light weight are strong assets to make them promising for thermoelectric applications. Their thermoelectric properties are characterized by the figure of

merit $ZT = \alpha^2 \sigma T / \lambda$ with α the Seebeck coefficient, σ the electrical conductivity, T the temperature and λ the thermal conductivity [1]. To improve their performances, one approach was to incorporate inorganic thermoelectric materials into the host organic matrix [4]. Polymer-based thermoelectric benefits from the advantages of the polymers stated above, and those of the inorganic fillers in term of performances. Several authors have studied organic/inorganic thermoelectric composites [2,4-9]. However, if some improvements of the thermoelectric properties of the polymers were observed, no significant enhancement was reported compared to state-of-the-art materials. Among them one find the intensively studied Pedot:PSS with a ZT up to 0.4 at room temperature [2,3], however their stability is low. There are also several other pi-conjugated polymers which have been investigated for thermoelectric applications such as [1,2]: Poly-aniline (PANI), Polypyrrole (PPy), Polythiophene (PT), Poly(phenylenevinylene (PPV), poly(2,7-carbazolylenevinylene). Among them PPy has attracted much interest as a promising TE candidate as it has no toxicity, it is easy to synthesize it and it has a rather good electrical conductivity and low thermal conductivity [1,2,4]. As for the inorganic load it is possible to use low toxicity materials such as silicides like CoSi-based or CrSi₂-based compounds with ZT_{max} of about 0.2-0.3 [10-14]. To date, there is only one study of organic/silicide composite namely Pedot:PSS/CrSi₂ investigated by the Ail *et al.* [9]. However, its thermoelectric performances were lower than for its components taken independently. In the present study, we have investigated the enhancement of the thermoelectric properties of *p*-type PPy with the use of *p*-type silicides fillers such as the semi-metallic Co_{0.85}Fe_{0.15}Si or the semiconductor CrSi₂ alloys.

II. Materials and methods

Powder of Polypyrrole (PPy) doped with organic acid (not specified) were purchased to Sigma Aldrich company. Co_{0.85}Fe_{0.15}Si and CrSi₂ alloys were prepared by arc melting technique using high purity Co slug (99,95%, Alfa Aesar), Cr granules (99.995%, Alfa Aesar), Fe (99.99%,

Alfa Aesar) and Si lumps (99.999%, Alfa Aesar). The drops were milled with a commercial Fritsch “Pulverisette 7” planetary micromill with silicon nitride container (45ml) and five 15 mm diameter balls with a ball to powder mass ratio fixed to 10:1 for both alloys. The speeds of the supporting disc and of the grinding ball acceleration were respectively 575 RPM and 1150 RPM. All experiments were done under argon atmosphere for 24h. The composites were made by mixing the powders of the inorganic phase (volume fraction ϕ_i) and of the PPy (volume fraction ϕ_p). We both mix and mill the powders together in a polystyrene tube filled with ZrO_2 balls with a ball to powder ratio of 10:1 by using a roller mixer at 30 rpm. The shaping of the powder was investigated by cold-pressing using a uniaxial pressure of 35 MPa applied for 5 min.

The crystal structure of the alloys was determined by XRD with $Cu K_\alpha$ wavelength and refined with Fullprof software [15] while the grain size was determined using the Williamson-Hall formula [11,14-16]. The thermoelectric properties were measured using homemade Van der Paw technic and hot probe Seebeck equipment as described in ref. [13].

III. Results and discussion

As shown in our previous studies using the same synthesis process [11-14], $CrSi_2$ and $Co_{0.85}Fe_{0.15}Si$ compounds have a nanocrystallite size about 10-20 nm (raw XRD data are given in the S. I. Figs. S2 and S3). From Figure 1 (a), increasing the content of the filler ϕ_i with $Co_{0.85}Fe_{0.15}Si$ leads, as expected, to an increase of the electrical conductivity from a percolation threshold above $\phi_i = 25\%$. The higher the content of the inorganic phase is, the larger the electrical conductivity is. Similar behavior is observed for the Seebeck coefficient. In Figure 1 (b) the electrical conductivity is normalized to its value at 60°C (chosen for better comparison), and is given as a function of the temperature. One observes that the electrical conductivity of pure PPy increases with the temperature, which is typical of a semiconductor. On the contrary, the electrical conductivity of pure $Co_{0.85}Fe_{0.15}Si$ decreases with temperature which is typical of

a metallic behavior. This is not surprising given that undoped and doped CoSi are known to have this behavior [10-12,17]. When considering the evolution of the electrical conductivity with the volume fraction of the inorganic phase, for the sample with $\phi_i = 10\%$, the electrical conductivity increases with the temperature faster than the PPy. With increasing the temperature, electrical charges from the isolated inorganic particles can be injected into the matrix PPy. The inorganic phase does not appear to strongly contribute to the electrical conductivity of the composite which is expected as it does not percolate. In contrast, for large values of $\phi_i (\geq 50 \%)$ the $\sigma/\sigma_{60^\circ C}$ decreases rapidly with temperature which is consistent with an inorganic content above the percolation limit.

In the case of the PPy/CrSi₂ composite, we have also changed the ratio between organic and inorganic phase in order to follow the evolution of the thermoelectric properties. The Seebeck coefficient (Figure 2) strongly increases with increasing ϕ_i to that of the inorganic phase. However, there is no clear trend for the electrical conductivity. Thus in the present PPy/CrSi₂ composite, one can see that the percolation threshold ϕ_i for the Seebeck coefficient is above 30%, value very similar to the case of PPy/Co_{0.85}Fe_{0.15}Si composite shown previously. Despite its semiconducting nature, CrSi₂ has metallic-like behavior close to room temperature which is due to its extrinsic transport regime [13,14].

From these data, one can determine the power factor ($\alpha^2\sigma$) (See Fig. 3) which is proportional to the ZT. In the case of the composite PPy/Co_{0.85}Fe_{0.15}Si, one finds a power factor of 0.8 $\mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 50 \%$ and of 2 $\mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 90 \%$ which is two orders higher than for the PPy. However, in the case of the PPy/CrSi₂ composite, we find a power factor of 3.37 $\mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 50 \%$ and of 9.7 $\mu\text{W}/\text{m}\cdot\text{K}^2$ for $\phi_i = 90 \%$, much larger than for PPy/Co_{0.85}Fe_{0.15}Si composite and more than two orders times larger than in PPy. These values are also respectively, about 10 times and 2 times larger than the values of the power factor found for a Pedot-PSS/CrSi₂ composite [9] despite that doped Pedot-PSS has much better

thermoelectric properties than doped PPy. The properties of these PPy-based composite are better than the best PPy-based composite from the literature which contain 2D reduced oxide graphene with power factor of $8.56 \mu\text{W}/\text{m}\cdot\text{K}^2$ [2].

III. Conclusion

In the present work, we have reported the design and thermoelectric properties of green organic/inorganic composites made of PPy and of two different silicide compounds ($\text{Co}_{0.85}\text{Fe}_{0.15}\text{Si}$ and CrSi_2). In the case of the PPy/ $\text{Co}_{0.85}\text{Fe}_{0.15}\text{Si}$ composite, both the electrical conductivity and the Seebeck coefficient increase above a percolation threshold of $\sim 25\%$. In the case of the PPy/ CrSi_2 composite, although no clear behavior has been observed on the electrical conductivity, we find that the Seebeck coefficient strongly increase above a percolation of $\sim 30\%$. We also found that the CrSi_2 /PPy composite has better thermoelectric properties than CrSi_2 /Pedot:PSS and the best PPy-based composite [2]. This can be explained by the higher power factor of CrSi_2 compared to CoSi at room temperature. Moreover, it is easy to manage for large scale applications.

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Figures

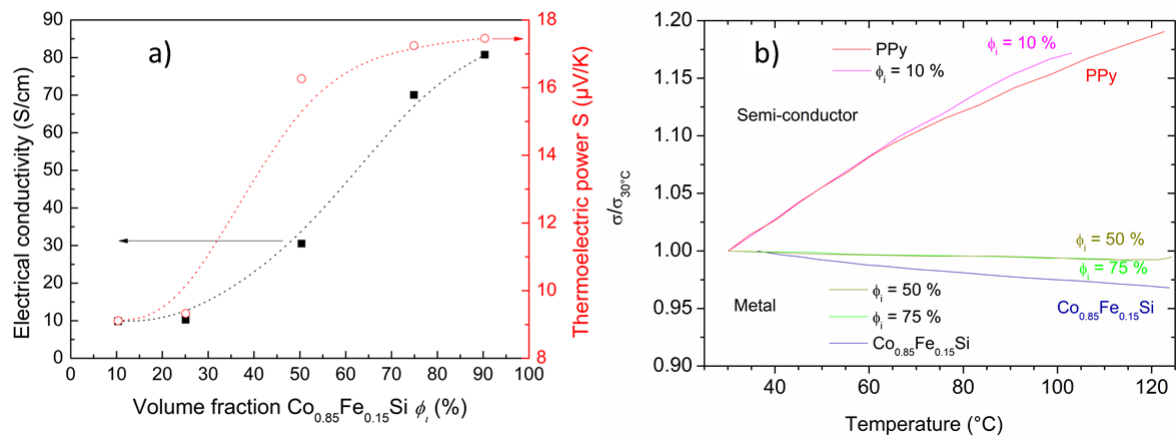


Figure 1 a) Thermoelectric properties of the composite PPy/Co_{0.85}Fe_{0.15}Si as a function of the volume fraction of Co_{0.85}Fe_{0.15}Si at room temperature. The dotted lines are guide for eyes. b) Thermal variation of the electrical conductivity for pure PPy, pure Co_{0.85}Fe_{0.15}Si and PPy/Co_{0.85}Fe_{0.15}Si composites of different volume fractions.

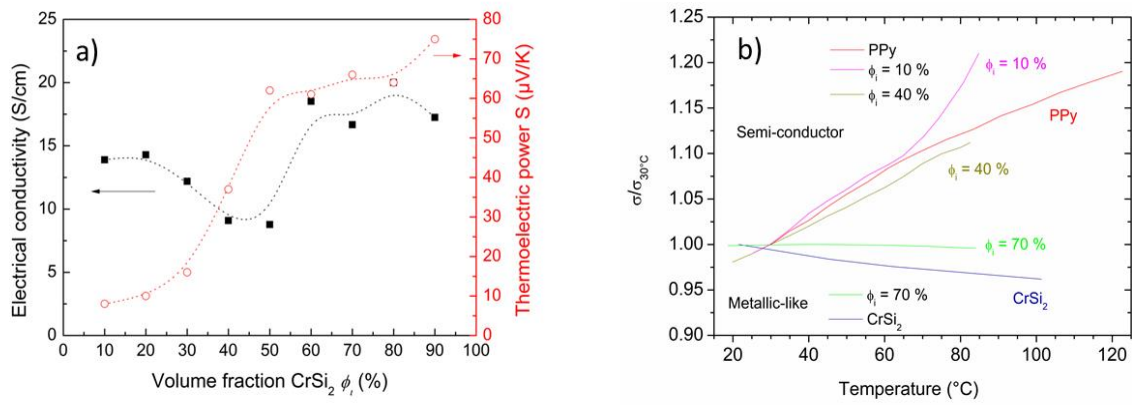


Figure 2 a) Thermoelectric properties of the composite PPy/CrSi₂ as a function of the volume fraction of CrSi₂ at room temperature. The dotted lines are guide for eyes. b) Thermal variation of the electrical conductivity for pure PPy, pure CrSi₂ and PPy/ CrSi₂ composites of different volume fraction.

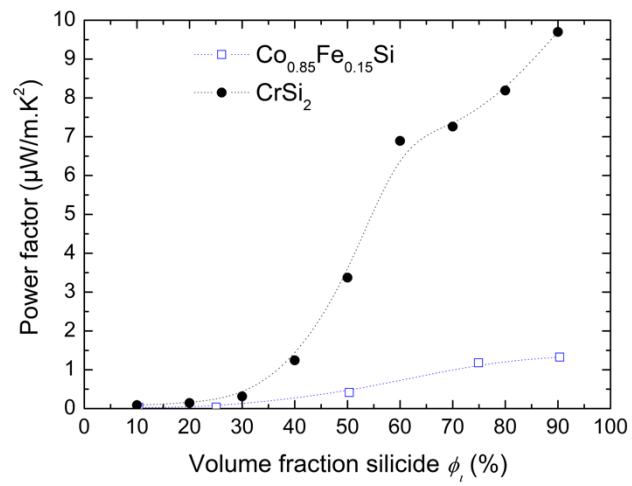


Figure 3 Evolution of the power factor ($\alpha^2\sigma$) of the composite PPy/ $\text{Co}_{0.85}\text{Fe}_{0.15}\text{Si}$ and PPy/ CrSi_2 as a function of the volume fraction of the silicide at room temperature. The dotted lines are guide for eyes.