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Thermoelectric properties and intrinsic conduction processes in DBSA and NaSIPA doped polyanilines

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ABSTRACT

Seeking to gain fundamental understanding of the thermoelectric (TE) behavior of polyanilines (PANIs), structure- property relationships of PANI nanorods, doped with dodecylbenzenesulfonic acid (DBSA) and 5-sulfoisophtalic acid sodium salt (NaSIPA), and prepared by an indirect synthetic route, are discussed in terms of the contribution of the acid concentrations on the thermoelectric properties.

The synergistic combination of high doping level and layer structure, accounts for the moderately high electrical conductivities (σ) and low constant Seebeck coefficients (α) of PANI-DBSA. Conversely, the poor doping ability of NaSIPA and low crystallinity degree explain the low electrical conductivities along with significant increases in Seebeck coefficient values. In relation to conduction mechanisms, PANI-DBSA shows a hopping behavior with a carrier concentration of $c \approx 0.49$ (hole type), while PANI-NaSIPA displays a diffusive regime, characteristic of degenerate metallic semiconductors, with an estimated charge carrier density of $n \approx 3 \times 10^{21}$ e/cm^3.

1. Introduction

The organic thermoelectric (TE) materials, as intrinsically conducting polymers (ICPs), are interesting candidates for green thermoelectric energy conversion applications, given their low cost and environmental safety [1–3]. The energy–conversion efficiency of a TE device is a function of the material's figure-of merit (ZT), average working temperature of the device and temperature difference between the hot and cold ends [4]. ZT is directly proportional to the electrical conductivity (σ) and the Seebeck coefficient (α) and inversely proportional to the thermal conductivity (ϰ) [1,2,4–6].

$$ZT = \frac{\sigma\alpha^2}{\varkappa}T \quad (1)$$

Thus, a good thermoelectrical material should have high σ and α, but poor ϰ. The three thermoelectrical parameters are interdependent in bulk materials and decoupling these parameters is definitely non-trivial [7].

Polyaniline (PANI) as one of the important ICPs has caused a lot of scientists' interests due to high stability, facile synthesis and tunable electronic properties [8]. Electrical conductivity of PANI increases with doping, which may be achieved by an acid-base reaction. As a result of the protonation of the nitrogen sites in the emeraldine base (EB), the cation radical of one nitrogen acts as a polaronic hole and these holes are charge carriers (p-type doped PANI) [9] (Fig. 1). Electrical conductivity occurs via inter-polaron hopping along and across polymer chains [10,11]. Therefore, the carrier density depends on the degree of protonation or doping level [4,12]. Furthermore, in most cases PANIs appear to be amorphous, sometimes with some degree of crystallinity, thus heterogeneous conduction is set up involving "islands" of higher conductivity regions separated by lower conductivity regions. The polaron structures are responsible for electrical conduction through the hopping mechanism in the crystalline region [9], while intergrain resonance tunnelling occurs through the strongly localized states in the amorphous media [13]. These systems are featured with low charge carrier mobility and low electrical conductivities, even at high carrier densities [14,15]. This mixture of metallic and non-metallic behaviour is a key characteristic of all ICPs, including PANI [16].

By contrast, the Seebeck coefficient is more complex and difficult to predict. The reduction of the total number of charge carriers increase the Seebeck coefficient while lowering the electrical conductivity, but because the power factor (PF) scales with α^2, a net increase in the PF

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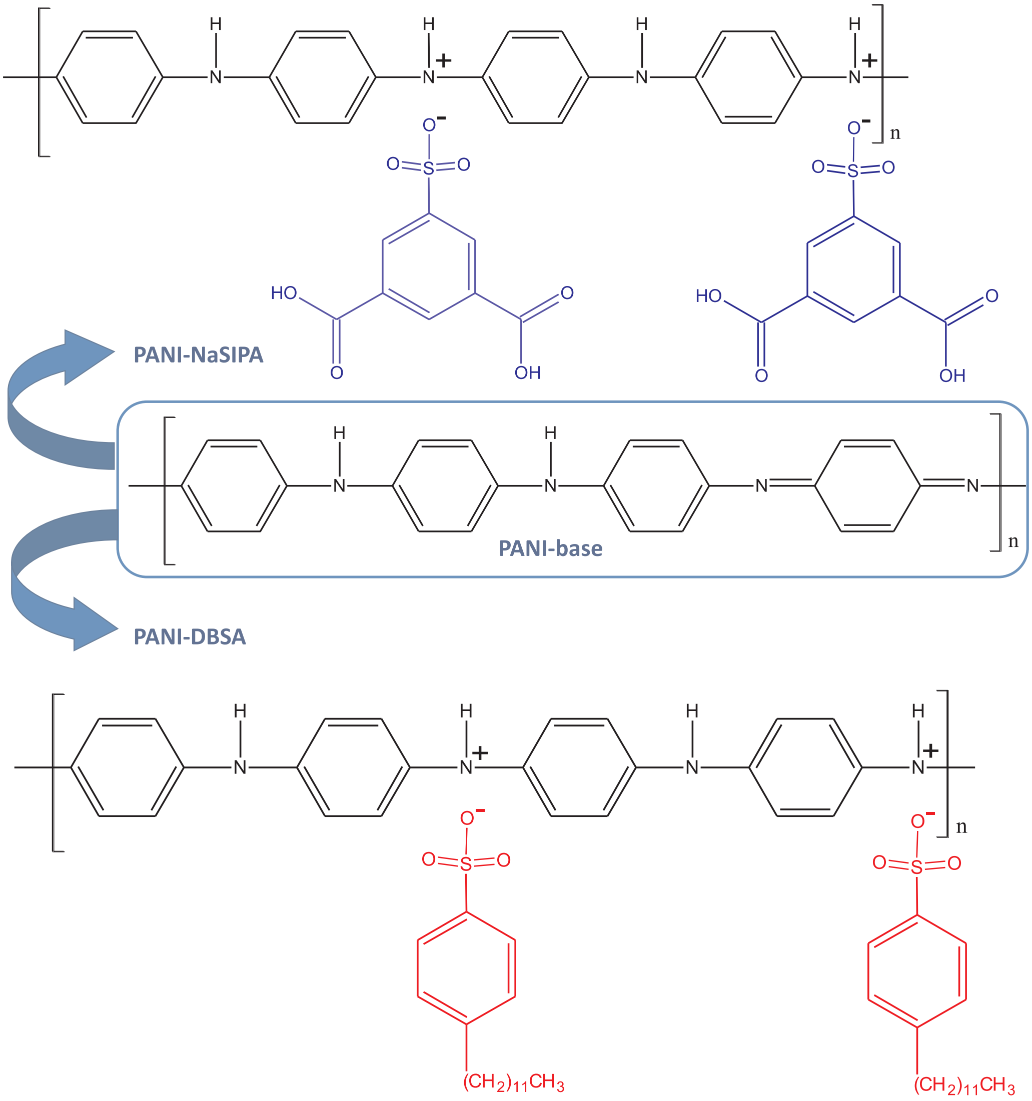

Fig. 1. Chemical structure of PANI-base and doped polyanilines, PANI-NaSIPA and PANI-DBSA.

can be achieved for certain doping ranges. The identification of conditions conducive to decouple σ and α, remains challenging [7].

In this context, the control of morphology to obtain nanostructured polymers has proved to be a successful strategy to improve the TE properties of ICPs. Previous works have shown that polyanilines synthesized with nanorod or nanofiber morphology have lower electrical resistance than those synthesized with micrometric size [17–19]. This nanostructuring strategy can increase the Seebeck coefficient, due to improved charge carrier mobility, and also reduce the thermal conductivity [8,17], resulting in an enhanced ZT.

Specifically, in a preliminary study we have introduced an eco-friendly and scalable indirect synthetic route (dedoping-redoping) [18], leading to organic doped PANIs with nanostructured morphology using either dodecylbenzensulfonic acid (DBSA) or 5-sulfoisophtalic acid sodium salt (NaSIPA) as dopants. Both bulky organosulfonic acids maintained a reasonable balance between conductivity, thermal stability and processability which are essential properties for widening industrial applications. In addition, the different chemical structures between the two dopants (rigid NaSIPA in contrast with the long alkyl flexible chains of DBSA, which in addition acts as a plasticizer) led to PANI salts with morphological and structural differences that are considered a good starting point to ascertain structure - properties relations. Since tuning the degree of doping and morphology are crucial for the optimization of thermoelectric performance of ICPs [7], the present work systematically studies the influence of the doping agent and molar acid concentration on the structure, physicochemical and TE properties of PANI-DBSA and PANI-NaSIPA, and seek to shed light on the conduction mechanisms. To the best of our knowledge, there are few studies concerning the TE performance of PANI DBSA [2] and none of PANI NaSIPA. The different nature and doping ability of the two organosulfonic acids lead to dissimilar ZT trends with molar acid concentration and different conduction mechanisms.

2. Experimental

2.1. Materials synthesis

Aniline and dodecylbenzensulfonic acid (DBSA) 70 wt.% solution in 2-propanol were purchased from Sigma-Aldrich. The 5-sulfoisophtalic acid sodium salt (NaSIPA) 95 wt% was obtained from Alfa Aesar. The potassium peroxodisulfate (APS) and acetone was obtained from Scharlau.

Two PANI samples were synthesized by indirect route involving "dedoping-redoping" steps with two organic sulfonic dopants, DBSA and NaSIPA (Fig. 1) [20]. PANI-HCl, prepared as described by Park et al. [21], was dedoped with 1 M NH_3 for 2 h in ultrasonic bath, filtered under vacuum and washed with water until neutral pH. The resultant PANI-base was redoped with increasing molar concentrations of DBSA