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Journal Name

ARTICLE

N-type Organic Thermoelectric Materials Based on Polyaniline Doped with Aprotic Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate

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The thermopower performance of polyaniline doped with the considerably reliable ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate was investigated to determine its potential as an alternative to fossil fuels. The ionic liquid, a stable ion complex, was used as the chemical dopant to confer n-type electrical properties to the polyaniline conducting polymer. The ionic liquid-doped polyaniline had an electrical conductivity, n-type Seebeck coefficient, and thermopower execution of $0.23 \text{ S}\cdot\text{m}^{-1}$, $-138.8 \text{ }\mu\text{V}\cdot\text{K}^{-1}$, and $4.43 \times 10^{-3} \text{ }\mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$, respectively as a result of the chemical doping method and thermal treatment. In addition, the ionic liquid-doped polyaniline realized stable n-type thermoelectric performance under ambient conditions for 15 days.

Introduction

Thermoelectronic materials that achieve electricity generation using temperature gradients have attracted significant interest, and numerous thermoelectric materials based on renewable resources, such as waste heat, have been investigated for various advanced applications including small heaters/coolers, short-term power generators, and human interface devices.¹⁻⁵ The most common thermoelectric materials have consisted of inorganic components, such as alloys, metallic semiconductors, and clathrates due to their excellent thermoelectric performance.⁶⁻⁸ However, inorganic thermoelectric materials have been limited to high temperature ($> 400 \text{ K}$) operation and are also expensive as a result of scarce resources, and have very rigid properties that make them difficult to process. To overcome these serious issues, many researchers have explored alternative thermoelectric materials, such as conducting polymers, organic semiconductors, organic/inorganic composites, and inorganic or organic hybrids containing carbon materials.⁹⁻¹⁷

Among these alternative thermoelectric materials, conducting polymers are emerging as influential substances. Conducting polymers have several significant advantages, such as simple processability, low-priced fabrication, high electrical conductivities, excellent Seebeck coefficients, and ease of manufacturing complexes with other materials. Above all,

polyaniline (PANI), one of the most famous conducting polymers, has readily controllable electrical conductivity due to its ability to switch the chemical salt and chemical base forms.^{18, 19} Accordingly, the polymer morphology, chemical structures, physical activities, and modification of the characteristics and electrical properties of polyaniline with other materials have been widely investigated.

Untreated polyaniline does not have high electrical conductivity because the electrical state of the polymer is neutral. Typically, acid or self-doped polyaniline materials exhibit hole-transport properties and thus behave like p-type thermoelectric components due to the electron-withdrawing characteristic of the nitrogen atom within polyaniline.^{20, 21} To obtain n-type polyaniline materials with electron-transport properties, researchers have attempted to use various dopants, such as hydrides, n-type inorganic materials, carbon materials, and self-doped components.²²⁻²⁵ F. Yakuphanoglu et al. found that n-type polyaniline composites with double wall carbon nanotubes exhibited a thermoelectric power of $-21.54 \text{ }\mu\text{V}\cdot\text{K}^{-1}$ in the initial boron-doped polyaniline state.²⁶ J. Kumar et al. reported that self-doped carboxylated polyaniline complexes with poly(diallyldimethyl ammonium chloride) also exhibited n-type electrical properties at high pH.²⁷ The thermoelectric performance of a functionalized CNT/polyaniline composite exhibited a thermoelectric power of $-58 \text{ }\mu\text{V}\cdot\text{K}^{-1}$ in a controlled environment as revealed by C. Yu et al. In order to manufacture soluble n-type materials, S-A. Chen et al. investigated n-doped polyaniline prepared using strong reductants. However, unlike acids and self-dopants within conductive polyaniline, n-type dopants are very unstable and readily oxidized in air. Therefore, there is a significant need for the development of robust, stable n-type dopants for polyaniline.

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In the present study, a simple manufacturing process and the remarkable n-type thermoelectric (TE) performance of polyaniline materials doped with the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate were investigated. Ionic liquid-doped polyaniline (PANI-IL) exhibited extremely stable thermoelectric performance in ambient conditions over an extended period of time. The thermoelectric power and electrical conductivity of PANI-IL were $-138.8 \mu\text{V}\cdot\text{K}^{-1}$ and $0.23 \text{ S}\cdot\text{m}^{-1}$, respectively; these values are higher than those of other treated polyaniline materials. In addition, the chemical structure, surface morphology, and doping states of the stable IL-doped polyaniline were confirmed, and its application as an organic thermoelectronic material was demonstrated.

Experimental

Materials

Aniline monomer ($\text{C}_6\text{H}_5\text{NH}_2$, $\geq 99.5\%$), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\geq 98.0\%$), hydrochloric acid (HCl, 37%), ammonium hydroxide solution (NH_4OH , 28.0 – 30.0%), and m-cresol ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, 99%) were purchased from Sigma-Aldrich Co. LLC. These reagents were used without further purification. The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ($\text{C}_8\text{H}_{16}\text{N}_2\text{O}_4\text{S}$, $\geq 95\%$), which was used as the chemical dopant, was also obtained from Sigma-Aldrich Co. LLC. but subjected to vacuum distillation. All other solvents and chemicals were employed as supplied.

Synthesis of The Polyaniline Emeraldine Base

In order to synthesize polyaniline via chemical oxidative polymerization, ammonium persulfate (APS, 23 g) and aniline monomer (40 ml) were dissolved in 400 mL and 600 mL of 1 M HCl medium, respectively.²⁸ These dispersions were cooled to 276 – 280 K, and then the APS dispersion in HCl was slowly added to the aniline/HCl dispersion with stirring. The polymerization of polyaniline was allowed to proceed with cooling for 5 h, after which time the polyaniline precipitated from solution over 1 h. The polymer was washed using 1 M HCl and the deionized (DI) water using a vacuum filtration method. The color of the polyaniline was light green. The product was then re-dissolved in 0.1 M NH_4OH (250 mL) overnight. Next, this suspension was filtered and the collected product was repeatedly washed using DI water. Finally, the polymer was dried in a vacuum oven for 24 h. At this point, the polyaniline emeraldine base was a deep, dark blue.

Fabrication of The 1-Ethyl-3-methylimidazolium Ethyl Sulfate Doped Polyaniline (PANI-IL) Film

The deep dark blue polyaniline (0.2 g) was dissolved in m-cresol (10 mL), and then 1-ethyl-3-methylimidazolium ethyl sulfate (2 mL) was slowly added to the solution. The polyaniline/ionic liquid/m-cresol mixture was stirred for one week at a constant speed, and the color slowly changed from blue to green. Prior to deposition of a conductive ionic liquid-doped polyaniline (PANI-IL) film, 10 mm $\times$ 10 mm glass

substrates were washed in sequence with acetone, DI water, and methanol for 10 min each in order to remove any glass impurities and then dried in a convection oven at 373 K for more than 1 hour. Subsequently, the bare glass substrates were treated with an oxygen plasma for 5 min in order to augment the adhesion between the glass surface and the polymer. The prepared PANI-IL material was then filtered using a syringe filter (PTFE membrane with a 5.0- μm pore size) and deposited on the base glass substrate via drop casting of 70 μL from a micropipette. Finally, the PANI-IL film on the glass substrate was annealed in a 150 $^\circ\text{C}$ for 30 min.

Determination of The Thermoelectric Properties

A home-made instrument was used to determine the TE properties of the doped polyaniline film, including its electrical conductivity and Seebeck coefficient. The apparatus consisted of four gold probes, two Peltier devices, a thermocouple, a source/meter, and a voltammetry system. The Peltier devices were attached to an aluminum heat sink and provided appropriate temperature gradients. The current/voltage was controlled using a Keithley 2400 source/meter, which provided a starting temperature gradient of ten degrees. The electrical conductivity was calculated from the thickness of the film (confirmed using an Alpha step 500 surface profiler) and the sheet resistance, which was determined using the Van der Pauw method.

Results and discussion

PANI as a conducting polymer was synthesized via oxidative polymerization using ammonium persulfate (APS) in an organic solvent (e.g., m-cresol). The chemical structure of the prepared polyaniline was that of an emeraldine base, and thus the conductivity of the polymer could be adjusted through the addition of dopants. Depending on the choice of dopant type (i.e., oxidants or reductants), polyaniline can act as an n-type or p-type conductive material, respectively.^{20, 25} To obtain n-type conductive materials, polyaniline must be doped with strong reductants, such as metal hydrides.²² However, metal

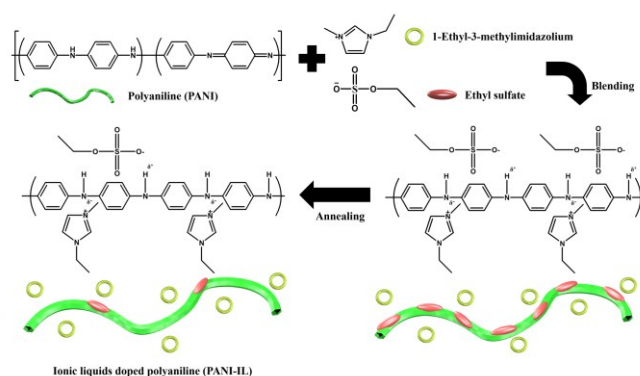


Fig. 1 Scheme of the chemical structure and illustration of 1-ethyl-3-methylimidazolium ethyl sulfate doped n-type polyaniline (PANI-IL)

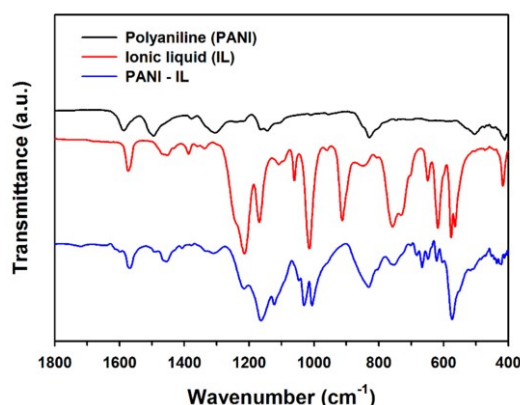


Fig 2. ATR-FTIR spectra of polyaniline (PANI), ionic liquid (IL), and n-type polyaniline-ionic liquids (PANI-IL)

hydride reductants are readily oxidizable and thus extremely unstable when exposed to moisture; therefore, it is difficult for polyaniline doped with hydride reductants to retain n-type properties. Ionic liquids, which are salts composed of both anions and cations, are electrically charged pairs that are stable under ambient conditions. Figure 1 presents a schematic illustration of n-type polyaniline doped with 1-ethyl-3-methylimidazolium ethyl sulfate. This ionic liquid has a high decomposition temperature and excellent thermal stability under atmospheric conditions.²⁹ When doped with the ionic liquid, the chemical structure of the emeraldine base form of polyaniline changed due to the presence of the anions and cations in the IL resulting in the creation of a charge potential. Consequently, the ionic liquid-doped polyaniline (PANI-IL) exhibited electrical conductivity. In addition, the PANI-IL was stable under ambient condition and functioned as a thermoelectric material.

The chemical structures of the polyaniline (PANI), 1-ethyl-3-methylimidazolium ethyl sulfate, and PANI-IL were determined using Fourier transform infrared (FT-IR) spectroscopy, as shown in Figure 2. The spectra were obtained over the range from 1800 cm^{-1} to 400 cm^{-1} . Peaks attributed to the C=C stretching mode of the aromatic rings in PANI and PANI-IL were observed at 1564 cm^{-1} and 1484 cm^{-1} , respectively. The C-N stretching modes at 1310 cm^{-1} and 1180 cm^{-1} for PANI and PANI-IL were due to benzoid and quinoid structures, respectively. The peak at 810 cm^{-1} was due to C-H stretching in the aromatic rings in PANI and PANI-IL.^{30,31} The FT-IR peaks for the 1-ethyl-3-methylimidazolium cations of the IL appeared at 1574 cm^{-1} and 1169 cm^{-1} and corresponded to the in-plane C-N stretching mode and in-plane C-C, N-CH₂, and N-CH₃ stretching modes, respectively. Peaks for the IL anion component were observed at 1215 cm^{-1} , 1014 cm^{-1} , and 912 cm^{-1} , and were assigned to C-O-SO₃ symmetric and asymmetric stretching modes.³² In addition, the peaks for PANI-IL are shifted to lower wavenumbers. Its result shows a variation of FT-IR peaks by doping process.^{33,34} After annealing of the PANI-IL film, these peaks for the anion disappeared in the FT-IR spectrum of the polymer due to partially degradation of ethyl sulfate molecules. These results indicate that the

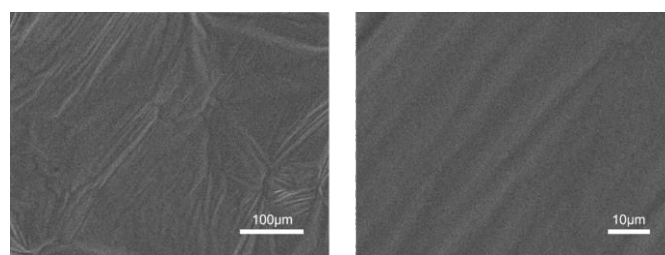


Fig 3. SEM images of n-type polyaniline-ionic liquids film (PANI-ILs)

conductive PANI-IL film exhibited the necessary structure for an organic thermoelectric material with n-type properties.

The scanning electron microscopy (SEM) images in Figure 3 show the surface morphology of the PANI-IL film. Patchy, creased conformations could be seen on the surface of the conducting PANI-IL, and these surface creases all formed in a single direction on the glass substrate. Thus, the surface structure of the PANI-IL film consisted of sympathetic formations suitable for electrical charge transport.

Next, the Raman spectra of PANI and PANI-IL films were analyzed to evaluate the effect of the ionic liquid, and the results are presented in Figure 4. The chemical structures of conductive materials significantly influence the intensities of their Raman peaks. Thus, in the spectrum of the PANI film, a peak for the C=N stretching vibration mode of a quinoid diimine structure appeared at 1485 cm^{-1} . In the Raman spectrum of the PANI-IL film, on the other hand, this peak was shadowy due to the doped state of the PANI structure following addition of the ionic liquid. The peak appearing at 1608 cm^{-1} in the PANI-IL spectrum was associated with the C-C benzoid structure. In addition, a peak at 1235 cm^{-1} corresponding to C-N bonding vibrations of benzoid groups, also appeared. These peaks were attributed to the IL-doped polyaniline structure. Furthermore, the Raman peak at 1159 cm^{-1} in the spectrum for PANI was shifted to 1171 cm^{-1} in the

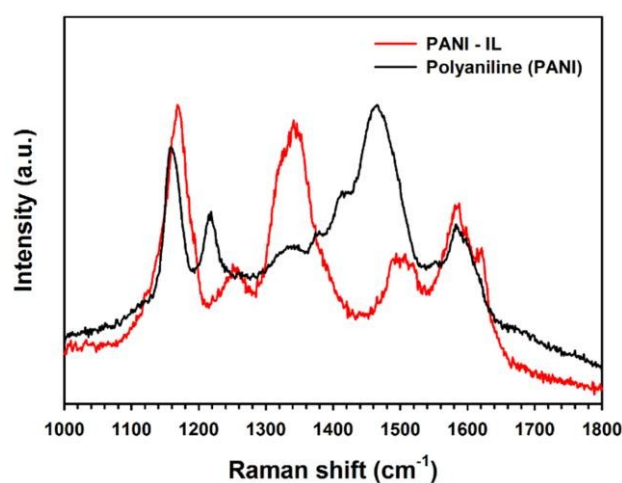


Fig 4. RAMAN spectra of polyaniline (PANI) and n-type polyaniline-ionic liquids (PANI-ILs)

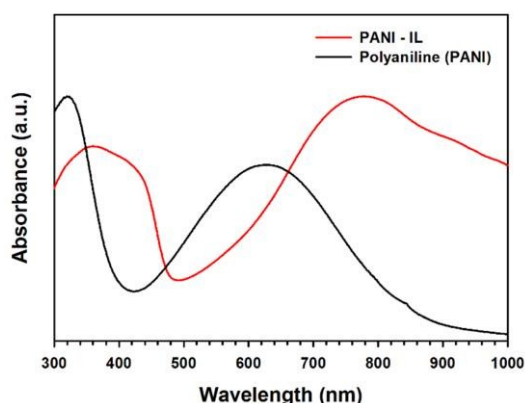


Fig 5. UV-Vis-NIR spectra of polyaniline (PANI) and n-type polyaniline-ionic liquids film (PANI-ILs)

PANI-IL spectrum due to the presence of the benzoid mode in the doped state. In addition, as a result of this shift, a C-N stretching peak due to doping was revealed in the spectrum of the PANI-IL film at 1339 cm^{-1} .³⁵⁻³⁷ These results also indicate that the PANI-IL film exhibited conductive properties in the doped state as an n-type thermoelectric material.

To further confirm the chemical structures of the undoped PANI state and n-type doped PANI-IL state, ultraviolet-visible-near-infrared (UV-Vis-NIR) spectra were obtained and are shown in Figure 5. Absorption peaks for the undoped PANI appeared at 320 and 620 nm and were attributed to the transition state of the benzoid structure and excitonic absorption from the benzoid state to the quinoid state, respectively. Absorption peaks for the doped PANI-IL emerged near 400 and 800 nm and were assigned to $\pi - \pi^*$ electron transition and a π electron-polaron excitation states. Moreover, the intensities of the peaks at 320 and 620 nm observed in the spectrum for the undoped PANI were slightly reduced for PANI-IL.³⁸ The absorption peaks for the doped polymer indicated that PANI-IL consisted of an effective carrier-transfer structure and was an electrically n-type

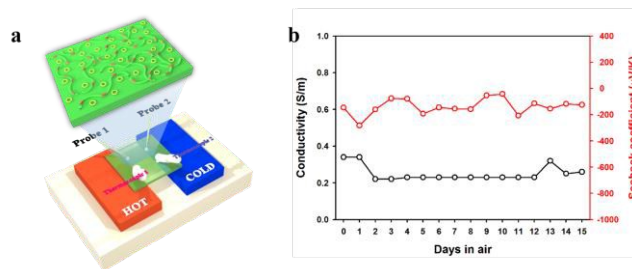


Fig 7. (a) Schematic diagram of thermoelectric measurement setup and polyaniline-ionic liquids (PANI-IL) film coated on glass and (b) conductivity, Seebeck coefficient, and stability data of ionic liquid doped n-type polyaniline (PANI-IL) film in air at 15 days

conductive polymer.

Also, To demonstrate the n-type doped state of polyaniline-ionic liquid film, we analyzed the work function of undoped PANI and n-type doped PANI-IL coated on ITO glass by using ultraviolet photoelectron spectroscopy (UPS) equipped with a He I source (21.22 eV). The The work function was calculated given by this formula :

$$\Phi = h\nu - |E_{\text{cutoff}} - E_F|$$

where Φ , $h\nu$, E_{cutoff} and E_F are the work function, photon energy, kinetic energy cutoff and fermi energy, respectively. The UPS spectra of PANI and PANI-IL was shown the Figure 6. As shown this figure, fermi energy both PANI and PANI-IL films was regarded as zero point. Kinetic energy cutoff (E_{cutoff}) of initial PANI and n-type PANI-IL film exhibited 16.39 and 16.68 eV, respectively. According to the above formula, the work function of PANI was obtained a 4.83 eV. The n-type PANI-IL work function was slightly shifted lower at 4.54 eV than that of initial polyaniline film.³⁹ As a result, ionic liquid doped polyaniline (PANI-IL) film exhibited the n-type semiconductor behavior.

Next, to evaluate the thermoelectric characteristics of the organic n-type PANI-IL film, an analytical instrument for

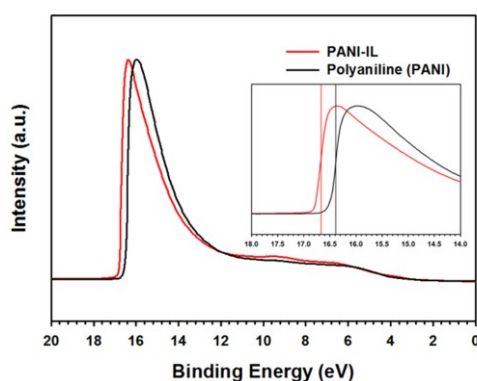


Fig 6. UPS spectra of polyaniline (PANI) and n-type polyaniline-ionic liquid (PANI-ILs)

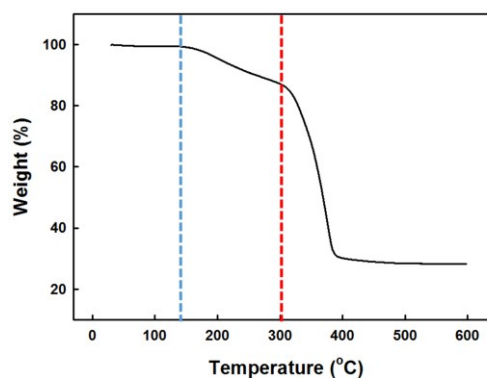


Fig 8. TGA curve of n-type polyaniline-ionic liquids film (PANI-ILs) in N_2

Sample	Electrical conductivity ($\text{S}\cdot\text{m}^{-1}$)	Seebeck coefficient ($\mu\text{V}\cdot\text{K}^{-1}$)	Carrier concentration (cm^{-3})	Carrier mobility ($\text{cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$)	Power factor ($\mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$)	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$)	ZT
PANI-IL	0.23	-138.8 ^a	2.262×10^{14}	2.492×10^0	4.43×10^{-3}	0.22	6.04×10^{-6}
PANI-B	0.01	-21.54	/	/	5.57×10^{-6}	/	/
PANI-HCl	525	8.5	/	/	3.79×10^{-2}	0.276	0.4×10^{-4}

^a mean value of measured Seebeck coefficient

Table 1. Thermoelectric properties, carrier concentration, and carrier mobility of PANI-ILs film, PANI-B²⁶ and PANI-HCl²¹

determination of the thermoelectronic properties of polymer films was developed using Peltier devices, as shown for the PANI-IL film in Figure 7(a). The n-type PANI-IL film was coated via drop casting on a glass substrate pre-cleaned using O_2 plasma. The PANI-IL film was then gradually baked to 150 °C over 30 min in order to evaporate any residual solvent and degrade the sulfonate groups in the anionic portions of the PANI-IL. This annealing process induced the selective elimination of the negatively-charged ethyl sulfate groups, rather than dissipation of the imidazolium groups from the PANI-IL film. This phenomenon was attributed to the different thermal stabilities of the ethyl sulfate and imidazolium groups in the ionic liquid. The decomposition of ethyl sulfate occurs at 120 °C, whereas that of imidazolium takes place at 275 °C, as shown in Fig 8.²⁹ It is thus proposed that following elimination of the ethyl sulfate groups, a large quantity of imidazolium cations remained, resulting in an electrical charge imbalance in the PANI-IL film. To counteract this unstable charge imbalance, the PANI polymer then provided negative charges. Therefore, PANI-IL was assumed to have positively charged, doped electrical properties, or in other words, be an n-type thermoelectric material. The electrical properties and thermoelectric performance of PANI-IL are summarized in Table 1. The untreated PANI film did not exhibit electrical properties or thermoelectric performance. The electrical conductivity of PANI-IL was determined to be $0.23 \text{ S}\cdot\text{m}^{-1}$. Which was lower than that of others p-type PANI emeraldine salts because PANI-IL was in the quasi-doped state and an unstable compound compared to fully doped, p-type PANI materials. Causatively, the PANI-IL film exhibited a low-rise charge carrier concentration of $2.262 \times 10^{14} \text{ cm}^{-3}$.⁴⁰ On the other hand, the PANI-IL material exhibited an excellent charge carrier mobility of $2.492 \times 10^0 \text{ cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$, which was higher than those of other doped PANI polymers.⁴¹ Moreover, the carrier mobility of PANI-IL was much higher than those of other materials, such as pentacene, PCBM, and perylene derivatives.⁴²⁻⁴⁴ Given the high carrier mobility and low carrier concentration after annealing, the PANI-IL film also had a very high n-type Seebeck coefficient with an average value of $-138.8 \mu\text{V}\cdot\text{K}^{-1}$. In addition, the power factor and thermal conductivity of the n-type PANI-IL material were $4.43 \times 10^{-3} \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ and $0.22 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$, respectively, as determined using the laser flash apparatus (LFA) method. Due to these excellent thermoelectric properties, the figure of merit (ZT)

value for the ionic liquid-doped polyaniline film was 6.04×10^{-6} , which is a relatively high value for n-type organic thermoelectric materials. Furthermore, the thermoelectric performance of the PANI-IL film was highly stable under ambient conditions, as shown in Figure 7(b). The thermoelectric properties and electrical conductivity of the n-type PANI-IL film remained unchanged over 15 days in a thermoelectric setup-box. Therefore, the PANI-IL film prepared using an imidazolium-based ionic liquid as a robust dopant exhibited durable, n-type thermoelectric performance under ambient conditions. Further work using other ionic liquids as dopants is required to refine the approach because protic ionic liquids also have air stability and electrical conductivity in this study was relatively low.⁴⁵⁻⁴⁷

Conclusions

The chemical structure, surface morphology, doping state, and electrical conductivity of ionic liquid-doped polyaniline (PANI-IL) were scrutinized in detail. Polyaniline as a conducting polymer was converted into a stable n-type thermoelectric material using the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate as the dopant. When the PANI-IL film was baked at a suitable temperature, the ethyl sulfate anions in the IL were selectively decomposed, leaving a large quantity of imidazolium cations in the PANI-IL film. Consequently, the PANI-IL film exhibited n-type thermoelectric performance under ambient conditions due to maintenance of the electrical charge balance.

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