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Highly-conductive porous poly(ether ether ketone) electrolyte membranes for flexible electrochromic devices with variable infrared emittance

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Abstract

Electrolytes with superior ion conductivity are highly demanded for variable infrared emittance devices (IR-VEDs) to realize fast response time and good IR emittance modulation ability. Herein, a poly(ether ether ketone) (PEEK) membrane featured by well-connected pore structure and high porosity is proposed for the first time as the electrolyte material for the IR-VEDs. In contrast to the conventionally used gel electrolytes, the newly designed porous PEEK membrane is capable of obtaining high liquid electrolyte loading while maintaining good membrane integrity, resulting in high conductivity ($6.8 \times 10^{-3} \text{ S cm}^{-1}$) and simple device assembly process. Flexible IR-VEDs have been fabricated by employing polyaniline films deposited on porous
Au electrode as the IR regulation layer. By controlling the loading of liquid electrolyte in porous electrode, continuously high-speed ion transfer channels could be constructed between the PEEK electrolyte membrane and the Au electrode in the devices taking advantage of their porous structure. The resultant IR-VED exhibits an excellent overall performance integrating superior IR emittance adjustment ability (the emittance change in the wavelength range of 2.5-25 µm is 0.47), fast switching time (< 10 s) and good cycling stability, indicating promising applications in dynamic thermal control fields.

**Keywords:** variable infrared emittance; polyaniline; porous; poly(ether ether ketone) electrolyte; ion transfer channel
1. Introduction

Electrochromic devices with tunable mid-infrared (mid-IR) radiation have drawn increasing attention due to their great potential applications in dynamic military camouflage, spacecraft thermal control and energy-saving equipment [1-3]. So far, several categories of EC materials, such as tungsten oxides (WO$_3$) [4,5], polythiophene (PTh) [6,7], and polyaniline (PANI) [8-11], have been studied for the fabrication of IR variable emittance devices (IR-VEDs). Among these EC materials, PANI is the most widely investigated one due to its high coloration efficiency, excellent environmental stability, good processability, high flexibility, light weight and low cost. For example, Chandrasekhar et al. reported an IR-VED based on a copolymer film of aniline and diphenyl amine (PANI-PDPA) using polymeric materials as dopant. This IR-VED showed an emittance variation ($\Delta \varepsilon$) of 0.3-0.4 in the wavelength range of 2.5-45 µm [11]. Topart et al. studied a multilayer IR-VED which employed a camphor sulfonic acid-doped PANI film as the IR active layer. It showed a variable emittance from 0.35 to 0.8 at 12 µm [12]. Li et al. reported an IR-VED based on sulfuric acid-doped PANI film, which exhibited an average $\Delta \varepsilon$ of 0.24 in 8-12 µm region [13]. Although these investigations of IR active layers have indeed contributed to the development of IR-VEDs, further improving the comprehensive performance, including emittance tunability, switching time, cycling durability, and simplifying the manufacturing process of the devices remains significant challenges in their various applications.

Electrolyte is an essential component in EC-based IR-VEDs, and its properties
directly affect the electrochemical response of the devices. Compared with the conventional liquid electrolytes which are not suitable for flexible device applications, and the all-solid electrolytes which show low conductivity, gel polymer electrolytes (GPEs) have attracted increasing attention because of relatively high conductivity and good electrolyte stability [14-16]. The GPEs are usually composed of a polymer, e.g. poly(methyl methacrylate) (PMMA), poly (ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly (ethylene glycol) (PEG), poly(vinylidene fluoride) (PVDF) and its copolymer poly (vinylidene fluoride-hexa-fluoropropylene) (PVDF-HFP), etc., as the matrix, and a liquid electrolyte, e.g. tetrabutylammonium tetrafluoroborate/acetonitrile, lithium perchlorate (LiClO$_4$)/propylene carbonate (PC), acids and ionic liquids, etc., as the plasticizer and ion-conducting media [6, 8, 9, 11-13, 17-20]. Generally, high liquid electrolyte loading is highly necessary for the GPEs to achieve high conductivity and consequently fast response time of the IR-VED, but it always results in poor membrane forming ability of the GPEs, thus complicating the fabrication process of the IR-VEDs. To maintain good mechanical integrity, GPEs with relatively low electrolyte loading (~200 wt%) and moderate ion conducting ability (~10^{-4} S·cm^{-1} at RT) were usually prepared for device assembly, leading to unsatisfactory performance [21-23].

In our previous work, a series of 4-dodecylbenzene sulfonate acid-doped PANI films were synthesized on porous flexible Au electrodes by electrochemical deposition. An IR-VED based on this PANI film was fabricated using a PVDF/PMMA blend membrane, which contained 20 wt% LiClO$_4$/PC solutions and
had a conductivity of $1.42 \times 10^{-5}$ S⋅cm$^{-1}$, as the electrolyte. The corresponding IR-VED exhibited a $\Delta \varepsilon$ value of 0.32 [9]. In the present work, as a further effort to enhance the performance of IR-VE
ds from the perspective of electrolyte design, a flexible porous poly(ether ether ketone) (PEEK) membrane with high porosity was prepared to enhance the loading of liquid electrolyte (i.e. improve ion conductivity) while maintaining good membrane integrity to simplify the manufacturing process of the devices. Importantly, in the devices, continuous ion transfer channels could be constructed between the porous electrolyte membrane and the porous Au electrode, thereby reducing their interface resistances and facilitating ion diffusion. The porous PEEK membranes could be fabricated by a convenient and scalable phase inversion procedure which is beneficial for practical applications. To the best of our knowledge, PEEK has been widely used as the electrolytes in fuel cells and capacitors [24-26], however, this is the first time it has been applied to IR-VE
ds. And the resulting devices have an excellent combination of significantly enhanced IR adjustment ability, fast switching time, good cycling stability, high flexibility and simple fabrication process, indicating that this newly designed porous PEEK membrane is a promising electrolyte candidate for IR-VE
ds.

2. Experimental section

2.1 Materials

Bisphenol A (BPA, 99%), 4,4-difluorobenzophenone (DFBP, 99%), 4-dodecylbenzene sulfonate acid (DBSA), 2,3,4,5-tetrahydrothiophene-1,1-dioxide (THTD) and $N,N$-dimethylacetamide (DMAc) were purchased from Aladdin Reagent.
used as received without purification. Aniline (99.5%) was obtained from Acros and distilled under reduced pressure before use. PC and LiClO$_4$ were received from Alfa Aesar. Potassium carbonate ($\text{K}_2\text{CO}_3$), ethanol and toluene were obtained from Beijing Chemical Reagent, China. The porous gold electrode was prepared by depositing Au (~200 nm thick) onto a microporous substrate of nylon 66 (p-NL) with a pore size from 0.5 to 2 µm (Au/p-NL) by thermal evaporation.

2.2 Preparation of porous PEEK electrolyte membrane

PEEK with a molecular weight of $M_n$=55 kDa was synthesized according to a typical reaction route as follows [27,28]: BPA (0.02 mol), DFBP (0.02 mol), $\text{K}_2\text{CO}_3$ (0.022 mol), THTD (25 mL) and toluene (15 mL) were added into a three-necked flask with a mechanical stirrer, a nitrogen inlet and a condensation. The mixture was kept at 140 °C for 2 h to remove the produced water by azeotropic distillation with toluene, and then kept at 160-170 °C for 4-6 h for the polycondensation reaction. The high viscosity mixture was coagulated into deionized water with stirring. The resulting fibrous polymer was pulverized into powder and then washed several times with boiling ethanol and water and dried in a vacuum oven. The porous PEEK membrane was prepared by a phase inversion method. The PEEK powder was dissolved in DMAc at a concentration of 10 wt% by stirring under 50 °C for 6-8 h. The homogenous and viscous PEEK/DMAc solution without air bubbles was casted on a clean glass plate by a tubular casting knife and subsequently immersed in deionized water at RT for 3-5 h to complete the phase inversion. The obtained free standing membrane was dried at 70 °C for 24 h. The electrolyte membrane was
received by immersing the porous PEEK membrane in LiClO$_4$/PC solution (1 M) at 60 °C for 48 h, and termed as PEEK-LiClO$_4$/PC.

2.3 Preparation of DBSA-doped PANI films and assembly of IR-VEDs

The DBSA-doped PANI films were prepared by electrochemical depositing aniline onto the Au/p-NL electrodes with active areas of $2 \times 2$ cm$^2$[9]. The deposition was conducted using a galvanostatic method with a current density of 0.1 mA cm$^{-2}$ and a polymerization charge of 1.5 C in an aqueous solution of 0.01 M aniline monomer and 0.1 M DBSA. Ag/AgCl and Pt foil were used as the reference electrode and counter electrode, respectively. The IR-VEDs were assembled by sandwiching the PEEK-LiClO$_4$/PC electrolyte membrane between two pieces of DBSA-doped PANI films which acted as the IR active layer and the ion storage layer, respectively, and then hot-pressing at 170 °C by two rollers. An IR-transparent polyethylene (PE) membrane was employed as the encapsulation layers for the devices. Here, three IR active layers with different LiClO$_4$/PC loading in the p-NL substrates, i.e. 0.005, 0.007 and 0.009 g/cm$^2$, were prepared for device assembly to construct ion diffusion electrodes between the PANI films and the PEEK electrolyte membranes. The resulting devices were termed as IR-VED1, IR-VED2, and IR-VED3, respectively.

2.4 Measurements

The gel permeation chromatographic (GPC) analysis of PEEK was carried out with a PL-GPC220 instrument with DMF as eluent and polystyrene as standard. The morphologies of the porous PEEK membrane, the Au/p-NL electrode and the PANI film were observed on a field-emission scanning electron microscope (FEI Helios
The porosity of the PEEK membrane was measured by dipping the membrane samples into deionized water for 48 h. The weight differences of the samples before and after water adsorption were recorded. The porosity (P%) can be calculated from the following equation (1):

\[
P\% = \frac{V_p}{V_{PEEK} + V_p} \times 100\%
\]

(1)

where \( V_p \) is the volume of pore and \( V_{PEEK} \) is the compacted volume of PEEK membrane. \( V_p \) was measured by immersing porous the PEEK membrane in PC solution for saturated adsorption. And the \( V_p \) value can be calculated according to the adsorption mass of PC and its density. Thereafter, compacting the corresponding porous PEEK membrane, and \( V_{PEEK} \) was determined by an Electronic Densimeter MH-300 A.

The electrolyte uptake (wt%) of porous PEEK membrane was measured by weighing the membrane before and after LiClO\(_4\)/PC adsorption. The ion conductivity of the porous PEEK electrolyte membrane was evaluated on a Princeton Applied Research Model PMC-200 Potentiostat by electrochemical impedance spectroscopy (EIS) method from 0.1 Hz to 10\(^5\) Hz. The membranes were sandwiched between two Au electrodes and the measurement was conducted at RT. The conductivity \( \sigma \) (S·cm\(^{-1}\)) was calculated according to equation (2):

\[
\sigma = \frac{L}{RA}
\]

(2)

where \( R \) (\( \Omega \)), \( L \) (cm) and \( A \) (cm\(^2\)) are the membrane resistance, the distance between the two electrodes, and the area of the membranes, respectively.
The electrochromic performances of the IR-VEDs were evaluated on an electrochemical workstation (CHI760D, Shanghai Chenhua Instruments, China). Spectral emittance (2.5-25 µm) of the devices was measured ex-situ and in-situ via reflection method on a VERTEX 70 (Bruker) FT-IR spectrometer with an A562 integrating sphere. The value of \( \varepsilon \) can be calculated by weighting \( (1-R(\lambda)) \) (namely spectral emittance) with the black body spectrum according to the following two equations (3) and (4)[29,30]:

\[
B(\lambda) = \frac{c_1 \lambda^{-5}}{\exp \left[ \frac{c_2}{\lambda T} \right] - 1} \tag{3}
\]

\[
\varepsilon = \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} (1 - R(\lambda))B(\lambda)d(\lambda)}{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} B(\lambda)d(\lambda)} \tag{4}
\]

where \( c_1 \) is the first radiation constant \((3.7418 \times 10^8 \text{ W } \mu \text{m}^4 \text{m}^{-2})\), \( c_2 \) is the second radiation constant \((1.4388 \times 10^4 \text{ m K})\), \( \lambda \) is the wavelength, and \( T \) is the temperature.

3. Results and discussions

3.1 Morphologies of the porous PEEK membrane, Au electrode and PANI film

In this work, porous PEEK membranes were constructed for the electrolyte layer in the IR-VEDs by a simple phase inversion procedure to enhance the liquid electrolyte loading without sacrificing membrane integrity, thus improving the ion conductivity of electrolyte membrane and the response sensitivity of the devices, and simultaneously simplifying the device assembly process. PANI films prepared by the same method as reported in our previous work were employed as the IR adjustment layers [9]. Figure 1a-c illustrates the surface images of the Au/p-NL electrode, the PANI film and the porous PEEK membrane determined by SEM. A homogenous
distribution of pores with the diameter of ~1 μm is observed for the Au/p-NL electrode (Figure 1a). After electrochemical depositing, a dense PANI film is formed on the porous electrode (Figure 1b). The PEEK membrane shows isolated spherical pores on the surface with a diameter range of 0.5-2 μm (Figure 1c), which matches well with the pore size of the Au/p-NL electrode. The porosity of the PEEK membrane is as high as 81%, implying the existence of large amount of reservoirs in the membrane for the liquid electrolyte. Furthermore, the cross-sectional SEM image of the PEEK membrane, as shown in Figure 1d, displays a vertically connected pore structure that will further provide high-speed channels for ion transport. Figure 2a and b show the photographs of the prepared PANI film (green) and porous PEEK membrane (white). As observed, they are all uniform, indicating good processability.

**Figure 1**

### 3.2 Conductivity and mechanical properties of the PEEK electrolyte membranes

The PEEK-LiClO$_4$/PC electrolyte membranes were prepared by a LiClO$_4$/PC solution adsorption procedure. For the PEEK membranes, a moderate thickness of 100-200 μm is preferred. Because the membranes in this thickness range have sufficient pore volume to achieve high absolute loading of liquid electrolyte which is beneficial to provide a sufficient number of demanded ions for the redox reactions of the PANI films, while ensuring that the corresponding IR-VEDs are light, thin and flexible. In this work, the selected thickness of the porous PEEK membrane is ~100 μm. After immersing the membrane in LiClO$_4$/PC solution (1 M) at 60 °C for 48 h, a saturated electrolyte loading of ~580 wt% was obtained, which was about 29 times
higher than that (~20 wt%) of our previously used P(VDF-HFP)-LiClO$_4$/PC electrolyte membrane. As a consequence, a high ion conductivity of $6.8 \times 10^{-3}$ S cm$^{-1}$ at RT was achieved by this PEEK-LiClO$_4$/PC membrane, which was two orders of magnitude higher than that ($\sim 1.42 \times 10^{-5}$ S cm$^{-1}$) of P(VDF-HFP)-LiClO$_4$/PC membrane [9]. Here, it should be mentioned that, the well-connected pore structure of PEEK membrane (Figure 1d) will also facilitate the rapid transport of ions, thereby significantly enhancing the ion conductivity. In addition, this highly conductive PEEK-LiClO$_4$/PC membrane had good mechanical properties. The tensile stress, strain and modulus were 1.17 MPa, 62.0% and 19.46 MPa, respectively.

3.3 CV and IR reflectance test of the IR-VEDs

Figure 2d shows the CV curves between -1.5 V and 0.8 V of the IR-VEDs with different LiClO$_4$/PC loading in the p-NL substrates scanned at 50 mV/s in 2-electrode mode. All the CV curves exhibit a pair of redox peaks at around 0 V and -1.0 V, respectively, attributed to the transformation of PANI between an emeraldine salt (ES) state and a leucoemeraldine base (LB) state accompanied by ion transport [8]. As observed, the oxidation peaks of the IR-VED2 and IR-VED3 shift negatively and their reduction peaks shift positively compared with the IR-VED1. This may be because the internal resistances of the devices and interfacial resistances of PEEK electrolyte membrane and electrode decrease with the increase of LiClO$_4$/PC loading in the p-NL substrates, resulting in easier ion insertion into or extraction from PANI films. The EIS measurements of the devices were performed before cycling. The results show that the internal resistances of IR-VED1, IR-VED2 and IR-VED3 are
18.64 Ω, 16.30 Ω and 15.39 Ω, respectively, and the interface resistances of IR-VED1, IR-VED2 and IR-VED3 are 1.04 Ω, 0.45 Ω and 0.26 Ω, respectively.

Figure 2i illustrates the corresponding IR reflectance changes of the IR-VED1 at different voltages. The intense IR absorptions at 3.5 µm, 6.8 µm and 14 µm are attributed to the absorbance of protection layer PE. When the applied voltage is -0.8 V, the reduced PANI (LB) exhibits high IR transmittance, and therefore a high reflectance is achieved by the device ascribed to high IR reflectance of the Au electrode under the PANI film. Increasing the voltage to -1.0 V, higher IR reflectance is obtained due to the further reduction of PANI. At the voltage of -1.2 V, the device show similar reflectance curve to that at -1.0 V, indicating that PANI is in its completely reduced and IR-transparent state at -1.0 V [31]. When reverse voltages (i.e. 0.2 V, 0.5 V and 0.6 V) are applied, the device exhibits low IR reflectance due to the high IR-absorption characteristic of PANI at conductive ES form (bipolaronic state). The reflectance curves of device at 0.5 V and 0.6 V are similar, which are slightly lower than that at 0.2 V. However, with increasing the voltage to 0.8 V, a rising IR reflectance curve is obtained. This is because the further oxidation of PANI causes it to transform into a nonconductive pernigraniline form, at which the PANI is substantially IR-transparent again [11]. Thus, to obtain high optical modulation capability, the potentials of 0.5 V and -1.0 V are chosen as the actuating voltages to evaluate the performance of the IR-VED. Figure 2e and f display a very uniform and highly contrasting color variation of the device at 0.5 V (green) and -1.0 V (yellow). Furthermore, the device could maintain this excellent color change ability in the case
of bending, as shown in Figure 2g and h, demonstrating excellent flexibility.

**Figure 2**

### 3.4 IR emittance and response time of the IR-VEDs

The IR emittance adjustment capability is one of crucial parameters for evaluating IR-VED performance. Figure 3a-c shows the $\Delta \varepsilon$ value variations of the IR-VEDs in the wavelength ranges of 2.5-25 µm, 3-5 µm and 8-14 µm after 0 to 200 cycles at the voltages of 0.5 V and -1.0 V. All the devices show the maximum $\Delta \varepsilon$ values after 100 cycles, indicating full activation. Figure 3d-f shows the corresponding emittance curves of the IR-VEDs at 0 and 100 cycles. After 100 cycles, the high emission curves remain substantially unchanged, but the low ones move to lower compared with that before cycling, resulting in enhanced $\Delta \varepsilon$. Obviously, IR-VED3 has higher $\Delta \varepsilon$ values, i.e. 0.47, 0.25 and 0.48 in the wavelength ranges of 2.5-25 µm, 3-5 µm and 8-14 µm, respectively, than those of IR-VED1 and IR-VED2 (Figure 3a-c and Table 1). The IR-VED3 also exhibits significantly improved IR emittance ability than those of our previously prepared device with $\Delta \varepsilon$ of 0.32, 0.18 and 0.39 in 2.5-25 µm, 3-5 µm and 8-12 µm regions, using PVDF/PMMA membrane containing 20 wt% LiClO$_4$/PC solutions as the electrolyte. This is primarily because the highly conductive PEEK membrane with high LiClO$_4$/PC loading, and the small interface resistances between PEEK membrane and porous electrode make the redox reactions of PANI easier and more complete. More importantly, IR-VED3 exhibits comparable or even much improved IR emittance adjustment capability than many other noted PANI-based IR-VEDs as discussed in the Introduction. The insets of
Figure 2g and f are the IR thermal images of the IR-VED at 0.5 V and -1.0 V, respectively. It can blend well with both high and low emission backgrounds endowing it great potential to be used in dynamic IR camouflage.

Fast response speed is desired for the IR-VEDs in practical applications. Herein, the response times of the devices were studied via the I-t curves by applying step voltages of 0.5 V and -1.0 V. The results are shown in Figure 3g-i. As expected, IR-VED3 has faster response times, that are 8.9 s switching from LB to ES and 9.3 s switching from ES to LB, compared with that of the IR-VED1 and IR-VED2 (Figure 3g-i) due to its higher LiClO$_4$/PC loading in the p-NL substrates. This could prone to the formation of continuous ion-conducting channels between the porous Au/p-NL electrode and the porous PEEK electrolyte membrane in the device as shown in Figure 2c, and thus enhancing the ion conductivity. As is evident from the above discussions, the increase of the loading the LiClO$_4$/PC in the p-NL substrates is beneficial to the improvement of the IR emittance modulation ability and the response speed of the IR-VEDs, but not as much as possible. Because the excessive liquid electrolyte would penetrate the surface of the active PANI front electrode, reducing the IR regulation range [11].

**Figure 3**

3.5 Cyclability of the IR-VEDs

The cycling stability, as a significant performance evaluation metric for the IR-VEDs, was measured here by monitoring the changes in $\Delta \varepsilon$ and current of the device after different cycles by applying continuous step voltages between 0.5 V and
-1.0 V with the step time of 50 s. Figure 4a shows the emittance curves of the IR-VED3 after 100, 300, 500, 800 and 1000 cycles. As observed, the low-emission curves have almost no changes, and the high ones show slight decreases after different cycles (Figure 4a and Table 1). As shown in Figure 4b, the device exhibits noticeable decreases of $\Delta \varepsilon$ (in 2.5-25 $\mu$m, 3-5 $\mu$m and 8-14 $\mu$m regions) from 100 to 300 cycles. However, relatively stable $\Delta \varepsilon$ values in 3-5 $\mu$m and 8-14 $\mu$m regions and a slight decline in $\Delta \varepsilon$ in 2.5-25 $\mu$m are observed in the subsequent 300-1000 cycles. After 1000 cycles, the IR-VED3 had the $\Delta \varepsilon$ as high as 0.45 and 0.38 in the wavelength ranges of 8-14 $\mu$m and 2.5-25 $\mu$m, respectively (Table 1), indicating an outstanding cycling stability of the device. In addition, the IR-VED could maintain good current stability after 1000 cycles at RT (Figure 4c), 0 °C (Figure 4c1), and 60 °C (Figure 4c2) conditions. This good cycling stability demonstrates that the present IR-VED has feasibility for practical applications.

### Table 1 The changes in $\varepsilon$ and $\Delta \varepsilon$ values of the IR-VED3 after different cycles.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>0</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{0.5V(2.5-25\mu m)}$</td>
<td>0.85</td>
<td>0.83</td>
<td>0.82</td>
<td>0.80</td>
<td>0.79</td>
<td>0.79</td>
<td>0.78</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>$\varepsilon_{-1.0V(2.5-25\mu m)}$</td>
<td>0.44</td>
<td>0.36</td>
<td>0.38</td>
<td>0.39</td>
<td>0.38</td>
<td>0.39</td>
<td>0.38</td>
<td>0.38</td>
<td>0.39</td>
</tr>
<tr>
<td>$\Delta \varepsilon_{(2.5-25\mu m)}$</td>
<td>0.41</td>
<td>0.47</td>
<td>0.44</td>
<td>0.41</td>
<td>0.41</td>
<td>0.40</td>
<td>0.39</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>$\varepsilon_{0.5V(3-5\mu m)}$</td>
<td>0.87</td>
<td>0.87</td>
<td>0.87</td>
<td>0.87</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.89</td>
</tr>
<tr>
<td>$\varepsilon_{-1.0V(3-5\mu m)}$</td>
<td>0.71</td>
<td>0.62</td>
<td>0.64</td>
<td>0.74</td>
<td>0.75</td>
<td>0.74</td>
<td>0.76</td>
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<td>0.76</td>
</tr>
<tr>
<td>$\Delta \varepsilon_{(3-5\mu m)}$</td>
<td>0.16</td>
<td>0.25</td>
<td>0.23</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
</tr>
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</table>
4. Conclusions

In this work, to enhance the IR emittance modulation ability, switching speed and cycling stability, as well as simply the fabrication process of the PANI-based IR-VEDs, a new porous PEEK membrane with high porosity has been prepared for the electrolyte layer by a convenient and scalable phase inversion method. The PEEK membrane has a well-connected pore structure which could provide a large number of reservoirs for liquid electrolyte. The resulting PEEK electrolyte membrane exhibits high ion conductivity ($6.8 \times 10^{-3} \text{ S cm}^{-1}$ at RT) and good membrane integrity. By controlling the loading of liquid electrolyte in porous electrode, continuous ion transfer channels could be constructed between the porous PEEK electrolyte membrane and the porous Au electrode in the devices. The resultant flexible IR-VED exhibits significantly improved $\Delta \varepsilon$, i.e. 0.47, 0.25 and 0.48 in the wavelength ranges of 2.5-25 µm, 3-5 µm and 8-14 µm, respectively, superior to previously reported IR-VEDs. The excellent IR emittance adjustment ability, fast switching time and superior cycling stability indicate good feasibility of the present IR-VED in practical applications.

<table>
<thead>
<tr>
<th>$\varepsilon_{0.5V(8-14\mu m)}$</th>
<th>0.90</th>
<th>0.89</th>
<th>0.90</th>
<th>0.90</th>
<th>0.90</th>
<th>0.89</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{1.0V(8-14\mu m)}$</td>
<td>0.49</td>
<td>0.41</td>
<td>0.44</td>
<td>0.45</td>
<td>0.44</td>
<td>0.43</td>
<td>0.44</td>
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</tr>
<tr>
<td>$\Delta \varepsilon_{(8-14\mu m)}$</td>
<td>0.41</td>
<td>0.48</td>
<td>0.46</td>
<td>0.45</td>
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<td>0.46</td>
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[27] Y. Zhao, J. Yin, Synthesis and properties of poly(ether ether


Figure 1. SEM images of the Au/p-NL electrode (a), the PANI film (b), the porous PEEK membrane (c), and the cross-sectional morphology of the porous PEEK membrane (d). The inset of (b) is the magnified image of PANI film.
Figure 2. Digital photographs of the PANI film (a) and porous PEEK membrane (b); schematic diagram of the IR-VED (c); CV curves of the IR-VEDs (d); the color change of the IR-VED at 0.5 V (e and g) and -1.0 V (f and h); the insets of (g) and (f) are the IR thermal images of the IR-VED at 0.5 V and -1.0 V, respectively; the IR reflectance curves of the IR-VED at different applied voltages (i).
Figure 3. Δε value variations of the IR-VEDs in the wavelength ranges of 2.5-25 μm (a), 3-5 μm (b) and 8-14 μm (c) after 0 to 200 cycles; emittance curves of the IR-VEDs at 0 and 100 cycles (d-f); I-t curves of the IR-VEDs by applying step voltages of 0.5 V and -1.0 V (g-i).
Figure 4. The emittance curves of IR-VED3 in 2.5-25 µm after 100, 300, 500, 800 and 1000 cycles (a); the changes in \( \Delta \varepsilon \) values of IR-VED3 in 2.5-25 µm, 3-5 µm and 8-14 µm regions after different cycles (b); the current stability test of the IR-VED after 1000 cycles at RT (c), 0 °C (c1), and 60 °C (c2).
Declaration of Interest Statement

All the authors declare no competing financial interest.
Highlights

(1) A PEEK membrane with high porosity was proposed as the electrolyte for IR-VEDs.

(2) The highly conductive PEEK membrane exhibited good membrane integrity.

(3) The flexible IR-VEDs exhibited superior IR adjustment ability and excellent cycling stability.