

Conducting Polymeric Electrochromic Device for Smart Thermal Management

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Abstract In order to develop a smart variable emittance thermal control coating, we here report on a flexible solid-state electrochromic device (ECD) based on soluble polyaniline by simple fabrication process. Devices were assembled in sandwich configuration of electrochromic materials on flexible PET substrate and a Li⁺ doped polyacrylonitrile as a solid polymer electrolyte. The initial surface emissivity characteristics related to oxidation states, doping concentration, doping agent and thickness were discussed. The smart thermal management of this ECD was characterized by its emittance in view of the thickness of active layer and the applied voltage. The emittance of our ECD can be tuned from 0.46 to 0.75 without any fine optimization, which is similar to that of other solid-state ECDs. The major advantage of this work is that the electrochromic variable emittance coating can be prepared by using simple process, such as spin coating and spray coatings. These methods do not require any special equipments and vacuum working conditions, and are easily applied for large area process as well. This study may open new avenues in the development of flexible electrochromic devices for spacecraft thermal control.

Key words Electrochromic, All-polymeric, Variable emittance coating, Smart thermal control

导电高分子电致变色智能热控器件

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文 摘 采用简单的旋涂、喷涂等方法, 制备了一种由可溶性聚苯胺为主体电致变色智能热控器件。该器件的基底为聚酯, 固体电解质为锂盐/聚丙烯腈。通过电切换调控, 该器件发射率能够在 0.46–0.75 内调控, 且红外光谱反射率变化大于 38%。研究了厚度、预掺杂酸种类、浓度等对聚苯胺活性层发射特性的影响; 考察了导电高分子聚苯胺层厚度、电切换电压等因素对涂层体系发射率调控的影响。结果表明发射率的调控范围与电化学还原的深度密切相关, 通过调节材料厚度、掺杂酸种类等可有效提高发射率调控范围。该导电高分子电致变色智能热控涂层在航天器热控制方面展示了良好的应用前景。

关键词 电致变色, 导电高分子, 变发射率, 智能热控

0 Introduction

In space, spacecrafts or satellites are exposed to significant thermal variations where the temperature of environment could change from -100°C to $+400^{\circ}\text{C}$. There-

fore, some thermal control procedure and systems are needed, which dissipates excess heat from both internal equipment and the absorption of solar radiation into deep space with radiators in order to keep the temperature of

all the elements of a spacecraft within the allowable limits for all mission phase. Traditionally, thermal control is accomplished through radiative surface-coating, internal heaters, heat pipes and mechanical louvers. For all but the radiative surface coatings, many approaches always require more mass or power than is available, so they are appropriate neither for antenna nor for new generation small satellites which have restricted payload weight, volume and power requirements. Correspondingly, the radiative surface coatings have many advantages, such as light weight, ease of processing, low cost and flexibility. However, the radiative surface coatings are most often passive, they are unable to actively adjust their functions in response to variation in the thermal load and environmental conditions. For example, their emittance can meet the requirements of thermal management systems either for heat retention in sun eclipse or for heat discharge in sunshine, and cannot for both. Thus, the simplest way to overcome the bottleneck is to develop a new flexible radiator coating, which can vary its emissive properties according to the thermal condition for the ideal operation of the spacecraft at a given temperature. Several devices following such strategy, such as microelectromechanical surface, thermochromic device and electrochromic devices (ECDs), have been developed^[1-2].

In recent years, as an actively thermal control coating, electrochromic devices (ECDs) have attracted much attention due to their reversible and persistent emittance-modulation properties, fast switching time, high contrast ratios, and wide application potential. Presently, polyaniline and tungsten oxide (WO_3) based solid states ECDs have been intensively studied and regarded as the most promising candidate for variable emittance coatings^[3-4]. The optimal emittance modulation of these devices is up to 0.4 over the 2.5 to 40 μm spectral range, these values may be compared with ca. 0.16 to 0.56 obtained for the mechanical louvers, the current spacecraft thermal control technology. From NASA's reports, the ECDs have pass through the first spaceflight on NASA-Goddard's ST5 mission^[5]. Compared with other thermal control techniques, these ECDs can effectively save 90% electronic power and reduce 75% weight. This thermal control technique can be applied to a wide variety of spacecraft, from microspacecraft (< 25 kg) where it may be the only practical thermal control technology, to space based radars and inter-

planetary missions. While most previous work with ECDs relative to thermal control coatings are focused primarily on the best experiment data reports or structure designs, there is few reports related to conducting polymer initial surface emissivity control, processing simplifying and factors which influence the emissivity modulation^[6-7].

In order to develop a smart thermal control coating, we have reported on a flexible solid-state electrochromic device based on soluble polyaniline by a simple fabrication process. Devices were assembled in sandwich configuration of electrochromic materials on flexible PET (PE) substrate and a Li^+ doped polyacrylonitrile as a solid polymer electrolyte. The initial surface emissivity characteristics related to oxidation states, doping concentration, doping agent and thickness were discussed. Furthermore, the optic-electrochemical performance of this ECD was also discussed in view of the thickness of active layer and voltage applied. The emittance of our ECD can be tuned from 0.46 to 0.75, and reflectivity modulation can be up to 0.4 without any fine optimization, which is similar with that of some other solid state ECDs. However, it should be mentioned that spin coating or spray coating methods were adopted for the construction of the devices. These fabricating techniques are not only more easily than sputtering or electro-deposition reported, but do not require any special equipment and vacuum working conditions. As an added advantage these devices have a symmetrical configuration with only three different types of materials.

1 Experimental

1.1 Preparation of EC device

The pre-oxidized polyaniline solution was prepared by chemical doping. Briefly, the synthesized neutral polyaniline was firstly dispersed homogenously with different concentration acid by boil milling, and then dissolved in metacresol. The acids include CSA, PSSA and H_2SO_4 . The electrolyte was polyacrylonitrile containing 0.1 M LiClO_4 and 1 mM hydeoperchlorate acid (HClO_4) dehydrated before using. The ECD was fabricated following structure shown in Fig. 1. The film thickness was controlled by spin rate and spray dose. To inhibit circuits, the electrode was separated implanted upon the soft substrate (PET/PE) or underneath the protective layer. All fabricating processes were performed by spinning and spraying technique.

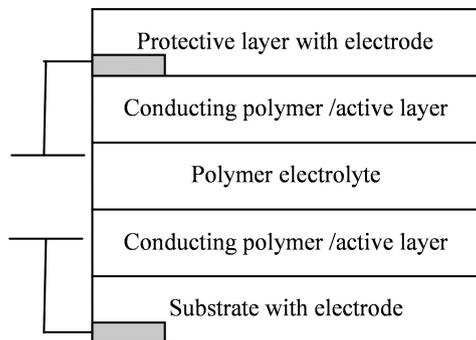


Fig. 1 Structure of electrochromic device

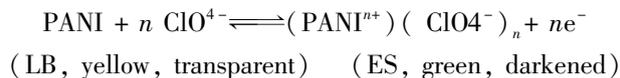
1.2 Electrochemical and optical measurement

The initial electrochromic performance was investigated with a three-electrode cell by using polyaniline film as working electrode, a platinum wire as the counter electrode, and a standard Ag/AgCl in saturated KCl as the reference electrode. The supporting electrolyte was 0.1 M LiClO₄ with 1mM hydeoperchlorate acid (HClO₄). The work potential was applied by a Keithley source (Keithley 2 400 and Keithley 2 000). Electrochemical properties were carried out on a CHI 660 electrochemistry station. The emittance was carried out on an A-E emissometer. UV-vis-NIR spectra of ECD were measured with a P-E model Lambda 950. UV-vis spectrophotometer. IR spectra of ECD were in situ measured with BIO-RAD Model FTS-3000 FTIR spectrometer.

2 Results and discussion

2.1 Emissivity modulation of polyaniline film

In order to further understand electrochromic mechanism of polyaniline, electro-optical response was firstly measured on half devices, consisting of either substrate/electrochromic layer, or substrate/electrode/electrochromic layer. In this work, the active layer was chosen as polyaniline, which had three main stable oxidation states; the fully reduced leucoemeraldine form, the 50% oxidized emeraldine form and the fully oxidized pernigraniline form. Polyaniline film is polychromic, i. e., transparent yellow for leucoemeraldine form (LB), green for the emeraldine salt form (ES), blue for the emeraldine base form (EB), and black for the pernigraniline form. The self-synthesized polyaniline film is pre-doped to conducting state with green color. After applying a small positive potential, the polyaniline film is de-doped upon reduction to compensate for the charge, transiting its state from emeraldine salt to leucoemeraldine base. Thus, the film changes its color from green to transparent yellow. This color change process can be represented by the following simplified reaction [8-9]:



Unfortunately, the leucoemeraldine form (LB) can be easily oxidized into emeraldine base form (EB) (d) by oxygen. Thus, the performance of the electrochromic devices thereafter depends heavily on their exposure to air. Contrarily, when the potential is switched again to negative, the anions diffuse into the polyaniline resulting in oxidation, or p-doping, resulting in visible color changes from transparent yellow to green aspect and to black finally. Combined with visual color change, the optical properties (refractive index n , extinction coefficient k) of polyaniline film also reversibly change with the insertion or extraction of protons. Correspondingly, the emittance can be modulated obviously with applying a small positive/negative potential by electrochemical method. Tab. 1 demonstrates the dependence of emissivity changes on the thickness of polymer film for variable states.

Tab. 1 Dependence of emittance on oxidation states for different polyaniline thickness

thickness / μm	emittance(ε)			emittance changes ($\Delta\varepsilon$)
	conduction state	reduced state	oxidized state	
0.5	0.58	0.89	0.88	0.4
1	0.42	0.89	0.86	0.44
2	0.43	0.88	0.86	0.43
3	0.44	0.85	0.85	0.41
5	0.43	0.84	0.82	0.39

When thickness is lower than 1 μm , the thinner films exhibit a slight increase in emittance changes; however, up to 2 μm , the emittance change decreases with increasing film thickness. We interpret the dependence as being due to the amount of the film that is doped for a given operating voltage and working time. For a thin film less than 1 μm , the film is easily reduced, and can be easily oxidized by atmosphere, the film is only partially doped. Therefore in thinner films the atmosphere results in higher volume of re-doped material, and thus lower emittance changes. For thicker films ($\geq 2 \mu\text{m}$), the comparatively lower field strength for the same operating voltage results in lower volume of doped materials, and thus lower emittance changes. It also can be seen that polyaniline can modulate its emittance from 0.42 to 0.89 combined with its states transfer. Another phenomenon should be mentioned that the emittance of different thick-

ness polyaniline is constant in fully reduced state or in fully oxidized state. This result indicates that the polyaniline can easily be realized high emittance modulation only if it was fully reduced or oxidized.

Experiments were performed in order to further understand the dependence of the electrochromic materials on acid type and acid concentration. Tab. 2 demonstrates the dependence of emissivity modulation on the dopant type. The data show that the initial emissivity of the polyaniline is distinctly different for PSSA, H_2SO_4 and for CSA. The emittance changes of the three dopants, however, are slight lower than that of initial emissivity. To our surprise, the initial emittance of electrochromic film depends severely on the acid type. The organic acid may be more effective at doping polymer film than the inorganic acid, possibly due to greater solubility of the organic acid in the polymer matrix. Thus, the initial emissivity performance of polyaniline can be obtained by selecting doping acid for variable thermal control environment.

Tab. 2 Dependence of polyaniline film emittance on dopant type

No.	doping acid type	emittance(ϵ)		emittance changes($\Delta\epsilon$)
		initial state	reduced state	
1	PSSA	0.80	0.05	0.75
2	H_2SO_4	0.65	0.18	0.47
3	CSA	0.73	0.08	0.65

The dependence on pre-doping acid concentration was examined on Au substrate. Tab. 3 shows the dependence of the initial emissivity performance and emittance changes on the pre-doping acid concentration in the polyaniline preparation for sufficient voltage application periods to achieve complete doping. At lower pre-doping concentration, the polymer film has lower initial emittance, which is similar to the emittance of Au substrate. While at higher pre-doping concentration, the polymer shows higher initial emittance, which is similar to the emittance of the ES state polyaniline. Only at medial pre-doping concentration, the polymer shows higher emittance change. Compared data with Tab. 1, there is a decrease in emittance on Au substrate. These results indicate that the initial emissivity performance and emittance change of polyaniline can be modulated by film thickness, substrate, doping acid type and doping concentration.

Tab. 3 Dependence of emittance on doping concentration (doping acid was CSA)

No.	thickness / μm	pre-doping concentration	emittance		emittance changes
			initial state	reduced state	
1	1	1:1	0.45	0.39	0.06
2	1	1:0.25	0.38	0.14	0.24
3	1	1:0.05	0.05	0.08	0.03

2.2 Emissivity performance of electrochromic devices

The electrochromic devices were assembled with structure shown in Fig. 1. Just like single polyaniline film, the devices change their color from dark green to transparent yellow after applying a small positive potential. Once the potential is switched to negative, the device recovers its original green aspect proving that it works satisfactorily. Responding to visual color change, the device can be reversibly modulated its emittance from 0.46 to 0.75 at the most. Tab. 4 summarized the emittance changes with different active layer thickness. From the Tab. 4, the initial emittance of the ECD decreases with increasing the polymer thickness. When a positive potential is applied, the emittance increases obviously with the active layer reducing from oxidized state. Interestingly, the transmittance of oxidized state increases largely with increasing the polymer thickness, while the transmittance of reduced state does not depend much on the thickness of polyaniline. Thus, it can be envisaged that the emittance variation between oxidation and reduction incurred by positive potential is not simply caused by intrinsic optical change of the signal layer, i. e. polyaniline, but a composite film, especially for substrate film. Selecting other substrate, the emittance change can be obviously enhanced, seen the optimized results.

Tab. 4 Electrochromic performance with ECDs with different active layer thickness

No.	thickness / μm	emittance(ϵ)		$\Delta\epsilon$	applied potential/V	response time/s
		initial	reduced			
1	10	0.61/0.46 ¹⁾	0.82/0.75 ¹⁾	0.21/0.29 ¹⁾	100	14
2	5	0.62	0.81	0.19/0.24 ¹⁾	50	670
3	3	0.61	0.78	0.17	50	254
4	2	0.61	0.84	0.23	50	210
5	1	0.66	0.84	0.18	50	77
6	0.75	0.73	0.89	0.16	50	64

Explanant;1) optimized results.

Fig. 2 shows the emittance change as a function of polyaniline thickness. The emittance change of ECDs

increases obviously with the increase of polymer thickness till to 2 μm . When it is thicker than 2 μm , the emittance change does not vary much with increasing the thickness of polyaniline. The emittance change varies from 0.16 to 0.23, indicating that polyaniline thickness is not the crucial factor influencing on the modulation. However, the polyaniline thickness has some effects on response time. With the thickness increasing, the response time becomes longer. This probably is caused by a slower charge movement in the reduction reaction due to migration length increase.

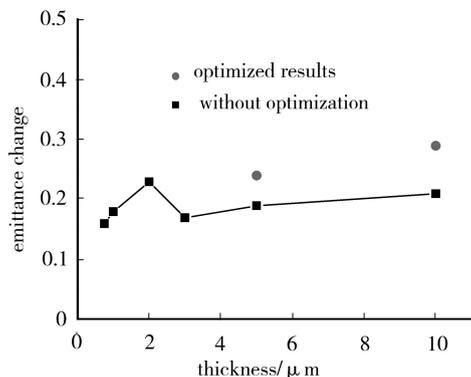


Fig. 2 Emittance change as function of polyaniline thickness, dot data is optimized result

Next, the electrochromic behavior of the device was measured on different positive potential. The polyaniline film was selected as 3 μm for weakening optical interference in the measurement. Tab. 5 summaries the emittance of ECDs dependence on working voltage for a given devices, including their response time.

Tab. 5 Electrochromic performance of ECDs as function of applying potential

No.	emittance(ε)		$\Delta\varepsilon$	applied potential /V	response time/s
	initial	reduced			
7	0.45	0.71	0.26	10	1820
8	0.45	0.71	0.26	50	420
9	0.46	0.67	0.21	75	156
10	0.43	0.68	0.25	100	60
11	0.46	0.67	0.21	200	16

The emittance change as a function of working voltage is illuminated in Fig. 3. When a positive potential is applied, the emittance of ECD increases with the color changing from dark green to transparent. To our surprise, the device shows relatively high emittance when a low voltage (10 V) is used. From Fig. 3, it can be seen

that the working voltage does not influence emittance change much. This means that for practical purposes the device would not need high working voltage for maintaining its function. Because the cyclability of electrochromic device can be effectively improved by lowering the working voltage, this result makes the design of low power smart thermal control system possible.

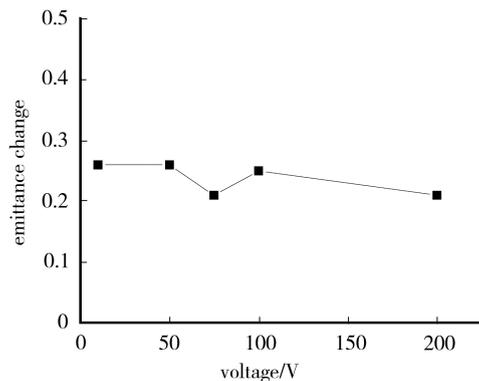


Fig. 3 Emittance change as function of working voltage

2.3 Feasibility analysis for variable thermal management

To determine the feasibility of using these ECD coatings mentioned above for smart thermal management in space, a thermal calculation was performed. Considering a rigid flat thermally conductive plate as a typical structure in the space environment, this variable emittance ECD is covered at side of the plate facing the sun, and the other side is shaded from the sunlight. Neglecting albedo and IR radiation flux from the earth, the steady-state temperature of this system can follow below equation [10-11]:

$$T = \left[\frac{S}{\sigma\pi} \right]^{\frac{1}{4}} \left[\frac{\alpha + \frac{w}{S}}{\varepsilon_f + \varepsilon} \right]^{\frac{1}{4}}$$

Where S is the solar flux, nominally 1 353 W/m^2 , σ is the Stefan-Boltzman constant, α is the solar absorption, ε_f is a fixed normal total emittance, w is an internal heat generation power normalized on a radiative surface area. Assuming $w = 500 \text{ W}/\text{m}^2$ and solar absorption is fixed at 0.1, the steady-state temperature of this ECD system can be crudely calculated as 240 K and 280 K respectively. Considering the solar absorption is a variance value, the temperature modulation would be amplified by further sophisticated deduction. These results indicate that this ECD coating could be actively used as thermal management.

Another important parameter of electrochromic de-

vices for space thermal control is reflectivity. For a typical device, the integrated reflectance change is more than 38% in the infrared spectral region. At last, it is worthy noting that there exists optical memory effect for this electrochromic devices. As observed, the device can retains its transparent color under open circuit condition for a long time, then slowly darken its coloration and recovering its original dark green state. This optical memory effect could be properly utilized according to space environment shifts, especially for sun eclipse or sunshine, which would save a large amount of power.

3 Conclusion

In conclusion, in this work, we demonstrated an all-polymeric flexible electrochromic device for space thermal management using simply process techniques, such as spin and spray coatings. The initial emissivity performance and emittance change of polyaniline could be modulated by film thickness, substrate, doping acid type and doping concentration for variable thermal control environment. The emissivity of the devices could be effectively modulated by optimizing the substrate and polyaniline thickness. Furthermore, the electrochromic performance and mechanism was discussed in the view of application on spacecraft thermal. Although the environment performance of this device under atom oxygen, UV radiation, and so on, need to be explored further for highly demanding applications, this study may open new avenues in the development of flexible electrochromic devices for spacecraft thermal control.

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