Supporting Information

A novel self-healing electrochromic film based on triphyelamine cross-linked polymer

Rongzong Zheng,^a Jiaqiang Zhang,^b Chunyang Jia,*^a Zhongquan Wan,^a Yaru Fan,^a Xiaolong Weng,^a Jianliang Xie,^a Longjiang Deng^a

 ^aState Key Laboratory of Electronic Thin Films and Integrated Devices, National Engineering Research Center of Electromagnetic Radiation Control Materials, School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, PR China
^bBeijing Spacecrafts, China Academy of Space Technology, Beijing 100190, PR China

1.Cyclic voltammogram

The cyclic voltammogram curve of the polymer film changed obviously at initial cycles, which could be called the ion activation of DATPFMA film (**Fig. S1**). With the Li⁺ ions insertion and extraction, the spike potential of the cyclic voltammogram curve was improved, and the corresponding area of the cyclic voltammogram curve was also increased at the initial cycles, the rational interpretation of the phenomenon was the oxidation of DATPFMA film turn to be completely sufficient at initial cycles.



Fig. S1 The initial several cyclic voltammogram cycles of polymer DATPFMA film at 100 mV/s in 0.1M LiClO₄/CH₃CN solution.

The morphology of DATPFMA film coated on ITO glass substrate was investigated by SEM (**Fig. S2**). As the polymer mixture is flowable to get a homogeneous and compact film during the dry process at 110°C, which has smooth and uniform thickness of about 8-10 μ m (**Fig. S2a, b**). Many different size pores appear on the surface of the polymer film after several cyclic voltammetry circles (**Fig. S2c-d**), which can be attributed to the Li⁺ ions insertion/extraction and changed the surface morphology.



Fig. S2 SEM images of DATPFMA film: (a) the cross-section image, (b) the initial morphology of the film, (c) and (d) the morphology of the film after several cyclic voltammetry circles.

The spike potential differences was increased in the first several cyclic voltammogram circles, which can be attributed to the increased porosity in specific surface area. Meanwhile, the triphenylamine units of DATPFMA are easily oxidized to hold more positive charges, which remarkably enhanced the charge storing capacity of the polymer film at initial ion activation process.

The charge storing capacitity became saturated and the cyclic curves became reversible after the activation process because the morphology of the DATPFMA film gained steady state gradually and simultaneously triphenylamine units of polymer DATPFMA oxidized sufficiently. Therefore, the spike potential and the charge storing capacity of the polymer film was reversible and saturated.

In order to find out the correlation between the pores appeared on the surface of polymer film and its electrochemical properties, electrochemical impedance spectroscopy (EIS) was performed. The EIS provided a strong evidence to investigate and verify bulk and interfacial electrical properties^[1] of the polymer film under specific experimental conditions. EIS analysis of the polymer film was performed by employing an AC signal of small amplitude that is 5 mV when the corresponding frequency changed from 100 KHz to 0.01 Hz, which activated the initial state of DATPFMA films at 0.7 V, 0.45 V and 0 V, respectively and corresponding Nyquist plot is shown in **Fig. S3**. The equivalent circuit of the process is shown in **Fig. S4**, which were fitted by ZSimpWin software, and the fitting errors for each component is less than 10%.





All the EIS curves have two arcs, and the circular arcs in high frequency region are similar, while the second arcs in low frequency region has shown considerable variations. The high frequency circular arcs are similar, which indicates that the same electrolyte resistance (R_s) and polarization resistance (R_p) of the electrod [2]. The low frequency circular arcs on the nyquist polts curves show remarkable difference which is principally related to the charging process^[3], the bulk membrane coating capacitance C_c , the charge-transfe resistance (R_c) and the warburg impendance (Z_w) are shown in equivalent circuit. For equivalent circuit of the initial film under 0.7 V, 0.45 V and 0 V (**Fig. S4c**), the impedance is consisted of bulk resistance (R_b), bulk membrane capacitance (Q), contact resistance (R_f) and double-layer capacitance (C_{dl}) because the polymer film was so smooth and compact that the ions could not pierce into the film surface to insert/extract^[4]. For the impedances of the activated films (**Fig. S4a-b**), the decreased R_b and Q values can be attributed to the appearance of holes, which improved the ions insertion/extraction process.



Fig. S4 The equivalent circuit of DATPFMA film at different voltages: (a)The activated film under 0.7 V, 0.45 V. (b)The activated film under 0 V. (c)The initial film under 0.7 V, 0.45 V, 0 V.



Fig. S5 The procedure of testing thermal property of polymer DATPFMA via DSC.

Notes and references

- [1] C. Fernández-Sánchez, C. J. McNeil and K. Rawson, *TrAC Trends Anal. Chem.*, 2005, 24, 37-48.
- [2] L. F. Marchesi, S. C. Jacumasso, R. C. Quintanilha, H. Winnischofer and M. Vidotti, *Electrochim. Acta*, 2015, **174**, 864-870.
- [3] B. A. Yezer, A. S. Khair, P. J. Sides and D. C. Prieve, J. Colloid Interf. Sci., 2015, 449, 2-12.
- [4] A. C. Nwanya, C. I. Amaechi, A. E. Udounwa, R. U. Osuji, M. Maaza, F. I. Ezema, *Appl. Phys. A*, 2015, **119**, 387-396.