

Vapor Phase Polymerization Deposition Conducting Polymer Nanocomposites on Porous Dielectric Surface as High Performance Electrode Materials

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Abstract: We report chemical vapor phase polymerization (VPP) deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) and PEDOT/graphene on porous dielectric tantalum pentoxide (Ta_2O_5) surface as cathode films for solid tantalum electrolyte capacitors. The modified oxidant/oxidant-graphene films were first deposited on Ta_2O_5 by dip-coating, and VPP process was subsequently utilized to transfer oxidant/oxidant-graphene into PEDOT/PEDOT-graphene films. The SEM images showed PEDOT/PEDOT-graphene films was successfully constructed on porous Ta_2O_5 surface through VPP deposition, and a solid tantalum electrolyte capacitor with conducting polymer-graphene nano-composites as cathode films was constructed. The high conductivity nature of PEDOT-graphene leads to resistance decrease of cathode films and lower contact resistance between PEDOT/graphene and carbon paste. This nano-composite cathode films based capacitor showed ultralow equivalent series resistance (ESR) ca. 12 m Ω and exhibited excellent capacitance-frequency performance, which can keep 82% of initial capacitance at 500 KHz. The investigation on leakage current revealed that the device encapsulation process has no influence on capacitor leakage current, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene films. This high conductivity and mechanical strength of graphene-based polymer films shows promising future for electrode materials such as capacitors, organic solar cells and electrochemical energy storage devices.

Keywords: Vapor-phase polymerization; Conducting polymers; Graphene; Nanocomposites; Solid tantalum electrolyte capacitor

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Introduction

Conducting polymers (CPs) and its nanostructures has been a subject of growing interest in recent years for their promising application in microelectronics, capacitor, sensor, solar cell, et al [1-4]. As for capacitor and solar cell, it can offer high conductivity and optical

transparence for the application of electrode materials, and optimized device performance has been reported after construction of CPs and its nanostructure for electrode materials and electrode surface modifying [5-7].

Solid tantalum electrolyte capacitors (STEC) based on sintered tantalum powder structure makes them volumetrically efficient, which has compact porous con-

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struction and large capacitance. CPs, such as poly(3,4-ethylenedioxythiophene) (PEDOT) has been used as STEC cathode films due to its higher conductivity and reliability, which produces high performance STEC with low equivalent series resistance (ESR) [8]. However, one of the drawbacks for PEDOT as STEC electrodes is their brittleness and low mechanical strengths. Coupling CPs to carbon nanomaterials has been shown to be an effective approach to improving the mechanical strengths and conductive performance of the CPs.

Most of conducting polymers are insoluble and infusible due to the stiffness of their all-conjugated aromatic backbone structures and processing uniform conducting polymer and its nanostructures on special substrate, especially on a porous structure, to build electrode films has always represented a challenge [9-13]. The common deposition process of CPs cathode films on porous tantalum pentoxide to fabricate STEC is based on an in situ polymerization method, which is a solution based deposition process. However, this deposition process represents challenge with the decrease of tantalum particle size, which can afford larger capacitance with smaller size. With decrease of tantalum particle size, the solution based deposition method is getting difficult and uncontrollable to prepare uniform CPs films onto the tantalum pentoxide surface containing micro/nano porous structure.

Among the different techniques used to obtain micro/nano structure CPs, the vapor-phase polymerization (VPP) has attracted more attention because of its simplicity and controllability [14,15]. VPP process is a solvent-free process and polymers are synthesized by delivering monomers to a surface through the vapor phase. VPP method can also form chemically well-defined films directly on the different morphology surface or template, and represents a facile way to prepare conducting polymer and its nanocomposites on special substrate, such as porous structure substrate [16]. In the VPP process, the oxidant is thought to play a templating role that leads to particularly ordered polymers and sometimes crystalline ones, which would result in formation of polymer nanostructures with significantly higher charge conductivities because of better interchain π - π stacking in the obtained polymers. This conducting polymer nanocomposites with excellent electrical and thermal stability would be suitable as high performance capacitor electrode materials. Moreover, the simple and controllable preparation method of VPP would also give a convenience to fabricate high performance capacitors and nanocapacitors [17,18].

VPP self-assembly deposition of PEDOT has been reported by some research teams, and these VPP conducting polymer films show promising applications in solar cells and supercapacitors [19,20]. However, to our best knowledge, there is a lack of reported work to build PEDOT and PEDOT nanocompos-

ites as SETC electrode films through VPP process. In this work, we report VPP deposition of PEDOT and PEDOT-graphene on porous Ta_2O_5 as tantalum electrolyte capacitor cathode films. In the first step, oxidant and oxidant-graphene nanocomposite for polymerization were successively prepared on porous tantalum pentoxide surface by dip-coating. In the second step, the exposure of oxidant films on 3,4-ethylenedioxythiophene (EDOT) monomer vapor was used to convert the oxidant/oxidant-graphene films into PEDOT/PEDOT-graphene composite films. The inner PEDOT layer constructed on Ta_2O_5 is for entire capacitance extraction, and the outer PEDOT-graphene layer constructed on PEDOT is for improving conductive ability and mechanical strength of cathode films. A VPP film based Ta/ Ta_2O_5 /PEDOT/PEDOT-graphene/carbon/Ag electrolyte capacitor is constructed, and electrical performance of this capacitor is measured.

Experiment

Materials

A solution of oxidant iron (III) p-toluenesulfonate (FeTos) 40 wt% in butanol and 3, 4-ethylenedioxythiophene (EDOT) were obtained from HC Starck (under the respective trade names Clevios CB40 and Clevios M). Graphene dispersion and other reagents were purchased from Sigma-Aldrich and used without further purification. A porous tantalum sintering pellet (tantalum powder specific volume=100000 $\mu\text{f} \cdot \text{V}$) for capacitor construction was purchased from Xinyun electronic company.

Construction of tantalum capacitor

$\text{Ta}/\text{Ta}_2\text{O}_5$ anodes of 68 μF used in the experiments were regular anodes, sintered in vacuo and subsequently anodized in 2.5% (wt%) phosphoric acid at 65°C. Then the Ta_2O_5 covered porous anodes pellet was dipped in FeTos solution and the FeTos solution was dip-coated on Ta_2O_5 surface. This process was carried out in KSV dip-coating instrument with a 0.5 mm/min dipping speed, which can ensure a well soaking of oxidant solution into the porous Ta_2O_5 structure. Then, the FeTos covered pellet was put in a 60°C vacuum oven for solvent evaporation. Oxidant layer was increased by a repeated dip-coating and drying process. After the construction of FeTos layer as inner layer, a FeTos/graphene outer layer was introduced on FeTos films by dip-coating and drying process. The thickness of this outer layer was also increased by repeated process. Following the construction of FeTos and FeTos/graphene films, tantalum sintering pellet was transferred into a small vial full of EDOT monomer vapor. The FeTos and

FeTos/graphene films were exposed on EDOT monomer vapor for 1 h to ensure complete polymerization. After the polymerization, the PEDOT/PEDOT-graphene films were then soaked in ethanol for 10-15 min and dried under vacuum oven at 40°C for 30 min. For a complete tantalum capacitor construction, graphite and Ag pastes were deposited on PEDOT/graphene in sequence to form the electrical contact. The schematic VPP deposition and capacitor structure are shown in Fig. 1.

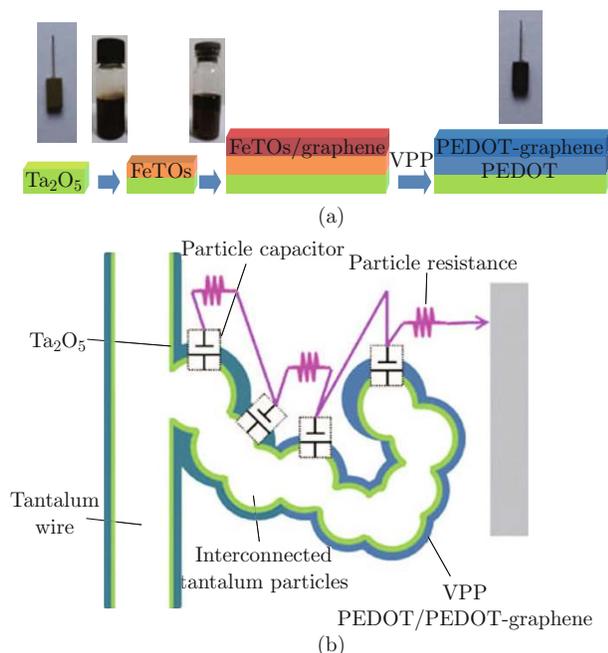


Fig. 1 Schematic of (a) VPP deposition of PEDOT/PEDOT-graphene on Ta_2O_5 as cathode films and (b) structure of VPP film based capacitor.

Characterization

XRD patterns were recorded on Bruker AXS D8 using scanning speed of $0.02^\circ/s$ and an accelerating voltage of 40 kV. Film surface morphology was investigated by using scanning electron microscopy (SEM) model S-2400 from Hitachi. The conductivity of VPP PEDOT and PEDOT/graphene was characterized by a homemade four-point probe instrument. The characterization of the capacitors was carried out using an HP 4263A LCR meter measuring capacitance, dissipation factor (DF), and equivalent series resistance (ESR). The leakage current (LC) was measured by using Tonghui LC testing instrument with model TH4321.

Results and discussion

One key issue in manufacturing vacuum sintered anodes based solid tantalum electrolyte capacitors is to build up a robust cathode layer to protect dielectric layer from possible mechanical damage. We find out the

drawback of the Ta/ Ta_2O_5 /PEDOT capacitors made using the VPP process is the fragility of the parts due to the powdery nature of chemically synthesized PEDOT. In order to overcome this problem, we develop a VPP deposited PEDOT/graphene outer layer to improve the mechanical strength of the whole cathode films. This PEDOT/graphene outer layer can not only improve the mechanical strength ability of the whole cathode, but also reduce the cathode resistance due to the high conductive ability of graphene. The PEDOT/graphene may also result in lower contact resistance between PEDOT/graphene and latter formed carbon paste due to its suitable conductivity, and therefore, further reduces the capacitor's ESR effectively.

Figure 2(a) shows typical sintered anode Ta porous structure, and this body shows high specific surface for the fabrication of capacitors with large capacitance. Figure 2(b) shows porous sintered anode covered by a continuous tantalum pentoxide dielectric layer. The extremely porous nature of the pellet structure requires that the cathode plate is prepared with some type of liquid or vapor preparation process. These processes will allow penetration into the depths of the structure to facilitate the deposition of cathode films through the pore structure, covering the entire surface area of the dielectric Ta_2O_5 . It is essential that the solid electrolyte, in this case PEDOT, covers the whole dielectric layer in order to achieve full capacitance. It should be noted that low dipping and raising speed for sintered anode body from the FeTos solution is critical to achieve full capacitance, which will ensure a complete coverage of FeTos films on tantalum pentoxide surface. After the exposure of FeTos and FeTos/graphene covered sintered anode body in EDOT vapor, the anode body changes from yellow (shown in Fig. 2(b)) to deep violet (as shown in Fig. 2(d)) corresponding to the polymerization of EDOT into PEDOT. It should be noted that sufficient polymerization time is required for this VPP process because of the low EDOT vapor pressure in the reactor, and the enough time for EDOT vapor to pervade into films and be adsorbed on oxidant spot is needed. A reaction time at least 30-60 min appeared to be necessary to reach complete EDOT polymerization under ambient temperature or shorter at higher temperature. Figure 2(c) shows close package of VPP PEDOT on tantalum pentoxide, and it also presents particle morphology due to coverage of ultrathin PEDOT layer. After the VPP deposition of PEDOT/graphene, the particle morphology disappears and the entire tantalum pentoxide surface was covered by PEDOT/PEDOT-graphene films (as shown in Fig. 2(d)). However, we did not introduce the FeTos/graphene as inner layer in order to avoid the blocking of graphene on pore structure, which may result in incomplete coverage of PEDOT/graphene on Ta_2O_5 and incomplete capacitance extraction.

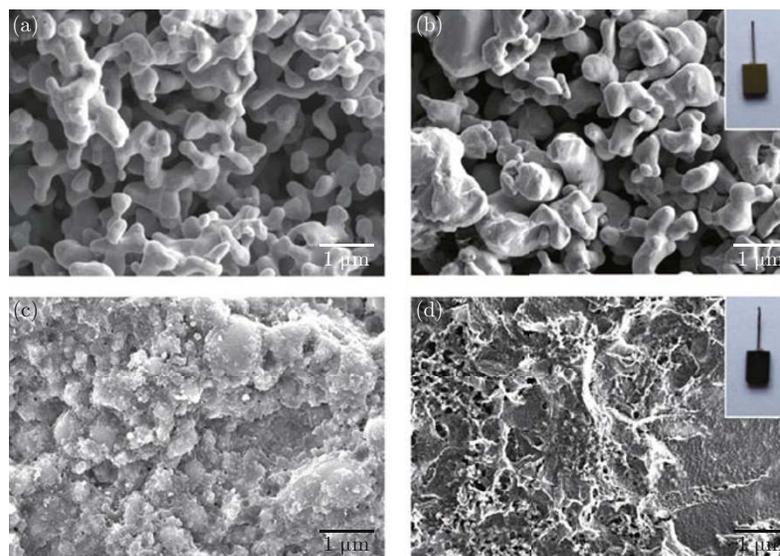


Fig. 2 SEM images of (a) high specific surface area sinter anode tantalum body, (b) Ta_2O_5 covered anode, (c) PEDOT covered tantalum body and (d) PEDOT/graphene covered tantalum body.

The VPP PEDOT films deposited on Ta_2O_5 exhibits a better uniform molecular structure because of the template effect, which results from self-assembly of EDOT in crystalline FeTos films. The XRD analysis (as shown in Fig. 3) presents diffraction peaks at $2\theta = 10.8^\circ$, 12.3° , 16.5° , and 23.7° , and these peaks have been attributed to the crystalline lattice of PEDOT chains doped by tosylate anions [21]. The XRD spectrum of PEDOT/graphene almost exhibits same diffraction peaks with relative weak peak intensity, indicating the close package of PEDOT on graphene also results in formation crystalline PEDOT structure in nanocomposites.

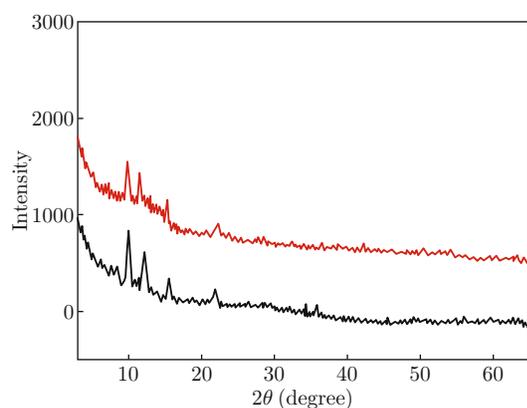


Fig. 3 XRD analysis of VPP PEDOT/graphene (red line) and VPP PEDOT (black line) deposited on sintered tantalum anode body.

The VPP deposition of PEDOT films on tantalum pentoxide is time dependent on deposition process, enough polymerization time is needed to ensure the complete coverage of PEDOT on dielectric layer to achieve full capacitance. Figure 4 shows capacitance

evolution of capacitor with increasing polymerization time. The PEDOT/PEDOT-graphene device shows satisfactory capacitance with extraction at 1 h, which is attributed to making homogeneous PEDOT coating inside the tantalum oxide pores. However, the PEDOT-graphene device shows inferior capacitance extraction performance. As we mentioned above, due to the larger size of graphene, the FeTos/graphene solution may block the pore structure, and prevent the latter oxidant solution from soaking into pore structure to form a complete coverage on inside tantalum pentoxide.

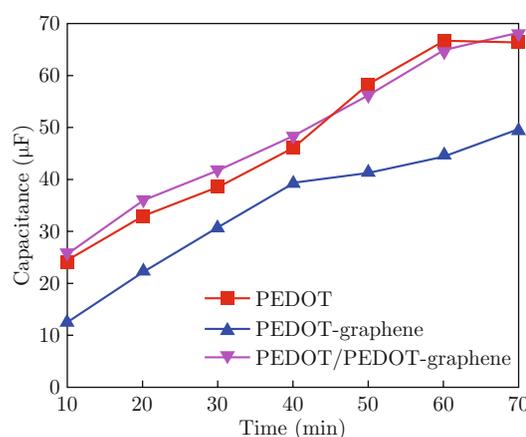


Fig. 4 Capacitance dependence of capacitor on polymerization time of VPP process.

For the conductive performance investigation, the VPP PEDOT and PEDOT/graphene deposited on SiO_2 substrate show conductivity ca. 250 ± 20 and 320 ± 20 s/cm respectively, measured by four probe method. The VPP PEDOT/PEDOT-graphene nanocomposite shows conductivity ca. 310 ± 20 s/cm,

which exhibits higher conductivity than pure VPP PEDOT. The higher conductivity leads to lower resistance of cathode films and ESR of capacitors. Figure 5 shows ESR-frequency characteristics of capacitors with different VPP films as cathode films. The PEDOT/PEDOT-graphene based capacitor exhibits ultralow ESR about 12 m Ω and excellent ESR-frequency performance. Although the PEDOT-graphene films exhibits highest conductivity, the capacitor with pure PEDOT-graphene as cathode films shows high ESR. We conclude that graphene may block the pore structure during FeTos/graphene dip-coating process and latter FeTos/graphene solution cannot penetrate into the depths of the pore structure to facilitate the deposition of PEDOT onto the inside Ta₂O₅. Incomplete coverage of PEDOT on Ta₂O₅ would lead to extremely enhancement of contact resistance between dielectric layer and carbon paste, which would also result in higher ESR of capacitor.

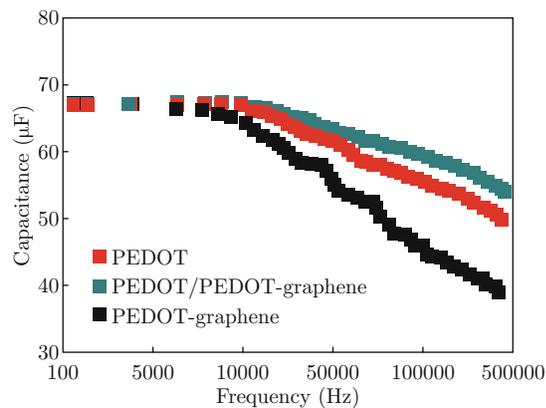


Fig. 5 ESR versus frequency performance of tantalum capacitor with different VPP films as cathode films.

The advantage of lower ESR of tantalum capacitor means the device may exhibit excellent capacitance-frequency characteristic. Tantalum electrolyte capacitor based on sintered porous structure likes a parallel connection structure of abundant particle capacitors (as shown in Fig. 1(b)). There is additional resistance added to the capacitor element from its location to the termination points of the capacitor. With the increase of working frequency, the deep particle capacitor will show up as decaying capacitance with increasing frequency, which results in a “roll-off” effect of capacitance. As shown in Fig. 6, all VPP films based capacitor show decaying capacitance with increasing frequency, and higher ESR would lead to an enhancement of decaying capacitance. The PEDOT/PEDOT-graphene based capacitor exhibits best capacitance-frequency performance, and it can keep 82% of initial capacitance at 500 KHz. The higher ESR of PEDOT-graphene based capacitor display a serious capacitance loss with increasing frequency and almost 50% ca-

pacitance was lost at 500 KHz. These results indicate that the PEDOT/PEDOT-graphene nanocomposite layer constructed on Ta₂O₅ lead to substantial decrease of capacitor ESR, and is suitable as ultralow ESR tantalum capacitor cathode films.

As practical electrical applications, the tantalum electrolyte capacitors need to be encapsulated, and this encapsulation process gives a mechanical force on anode Ta₂O₅ films, which would result in leakage current resulted performance degradation of devices. In this

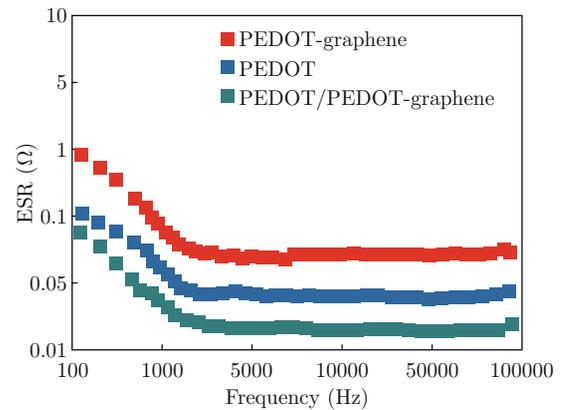


Fig. 6 Capacitance versus frequency performance of different VPP film based tantalum capacitors.

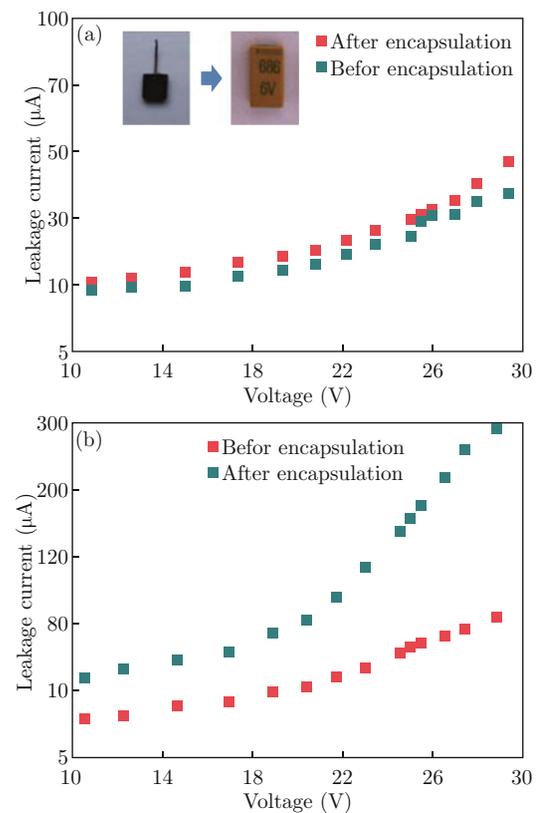


Fig. 7 Influence of device encapsulation process on leakage current of VPP (a) PEDOT/PEDOT-graphene films and (b) PEDOT films based capacitor.

Table 1 Performance comparison of capacitors with PEDOT/graphene and PPy as cathode electrode materials (capacitor model 16 V68 μF)

Electrode materials	Capacitance (μF)	Loss (%)	ESR ($\text{m}\Omega$)	Leakage current (μA)	
				20°C	65°C
PEDOT/graphene	67.3	1.7	12	6.8	7.2
PPy	67.1	2.5	35	7.1	20.3

work, the advantage to introduce PEDOT/graphene into cathode films is not only to improve the conductive ability of cathode films, but also to improve the mechanical strength of cathode films to protect dielectric layer from possible mechanical force damage. Figure 7 shows the leakage current performance comparison of VPP films based capacitors before and after encapsulation. As shown in Fig. 7(a), the encapsulation process shows no influence on leakage current of PEDOT/PEDOT-graphene based capacitor, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene to protect Ta_2O_5 dielectric layer. However, an obvious leakage current enhancement is observed in VPP PEDOT based capacitors (as shown in Fig. 7(b)). We conclude the fragile nature of PEDOT can not form an effective buffer layer to absorb or reduce the mechanical force during the encapsulation, which lead to mechanical destroy of Ta_2O_5 and the increase of leakage current. In addition, we did not found any influence of encapsulation process on other parameters of PEDOT/PEDOT-graphene based capacitor, and this capacitor shows stable electrical performance for practical electronic applications. We also give a capacitor performance comparison between our work and the polypyrrole (PPy) based tantalum capacitor, which is shown in Table 1. It can be seen that PEDOT/graphene based capacitor exhibit lower ESR and better leakage current-temperature characteristic, indicating high performance of this nanocomposite as electrode materials. Furthermore, comparing with noxious PPy, the innocuous characteristics of PEDOT/graphene also gives it promising future as environment-friendly electrode materials.

Conclusions

We developed PEDOT/PEDOT-graphene nanocomposite films as cathode films for solid tantalum electrolyte capacitor. The PEDOT inner layer and PEDOT-graphene outer layer were constructed on porous Ta_2O_5 anode surface through VPP process. The incorporation of graphene into PEDOT resulted in an enhancement of conductivity and mechanical strength than pure PEDOT films, and the high conductivity of PEDOT-graphene also resulted in lower contact resistance between PEDOT and carbon paste. The VPP PEDOT/PEDOT-graphene based tantalum capacitor

showed ultralow ESR ca. 12 $\text{m}\Omega$ and exhibited excellent capacitance vs frequency characteristic. The device encapsulation process showed no influence on leakage current of PEDOT/PEDOT-graphene based capacitor, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene's protecting the Ta_2O_5 dielectric film from being destroyed during encapsulation. In conclusion, this highly conductive and mechanically strong graphene-based polymer films shows promising future for high performance electrode materials such as capacitors, organic solar cells and energy storage device applications.

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