



# Electro-polymerisation of 3,4-ethylenedioxythiophene on reticulated vitreous carbon in imidazolium-based chloroaluminate ionic liquid as energy storage material

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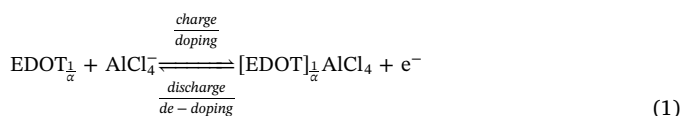
## ABSTRACT

This work shows the electro-polymerisation of thin film poly(3,4-ethylenedioxythiophene) on three-dimensional reticulated vitreous carbon substrates by cyclic voltammetry and pulsed polymerisation methods from a Lewis neutral chloroaluminate ionic liquid containing 3,4-ethylenedioxythiophene monomer. The polymer composite is attractive as an energy storage electrode for sustainable and high-performance technologies due to its unique properties of battery and capacitor in one system, *i.e.*, the redox reaction occurring simultaneously with the anion doping/de-doping of the conductive polymer with  $\text{AlCl}_4^-$  ionic species contained in the ionic liquid. The structure of the polymer films, their doping/de-doping mechanism and the stability in the ionic liquid were characterised by scanning electron microscopy and cyclic voltammetry and compared with films electro-polymerised on planar vitreous carbon. The typical granular and nano/micro-porous polymer structure observed on planar vitreous carbon was successfully replicated on the macro-porous reticulated vitreous carbon surface. The polymer films show approximately 45% higher capacity than films on planar substrates and similar efficient redox behaviour, proving that the material has hybrid battery-capacitor properties enhanced by the higher area per unit volume of reticulated vitreous carbon.

## 1. Introduction

The drive towards sustainable energy, especially electro-mobility, requires energy storage technologies, which combine high specific energy and power like a battery and capacitor in one system. Conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) have the unique characteristic to undergo a redox reaction like a battery (Eq. (1)), generating positive charged centres (sulphur or carbon) in the polymer structure during the oxidation (charge reaction). When the polymer is reduced (discharge reaction), the charged sites return to their neutral state. In parallel to this redox reaction, the generated charged (neutral) centres are compensated/doped (decompensated/de-doped) by anions from the electrolyte and incorporated into the nano/micro-porous polymer structure as electrical charges like in a capacitor. Because of these two properties, such conductive polymers can be classified as hybrid battery-capacitors [1,2]. In contrast with other conductive polymers such as polypyrrole and polythiophene, PEDOT has the ability to form doping/de-doping sites at high potentials, making it suitable for energy storage applications.

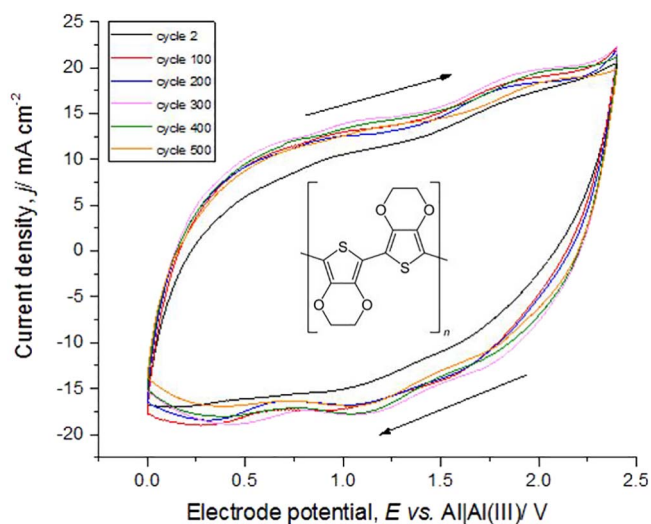
The amount of doped charges per monomer unit is determined by the generated and accessible charged centres in the polymer, increasing with the doping potential and the degree of doping ( $\alpha$ ,  $\alpha = 0$  to 1) [3–5].



The formation of the doping/de-doping sites depends on the polymer structure, which is predetermined by the electro-polymerisation method, the applied potential and the doping anion of the electrolyte [5]. In contrast to PEDOT polymerised in aqueous solution, PEDOT films obtained in an imidazolium-based chloroaluminate ionic liquid EMIm- $\text{AlCl}_3$  have different morphology which influences the charge/discharge cycles (doping/de-doping) process. Since the nucleophilicity of the ionic liquid is very low, the polymer is very stable during the cycling and the formation of doping/de-doping active sites improves at high electrode potentials, leading to better battery

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**Fig. 1.** Cyclic voltammogram of a PEDOT (inset: structural formula) film on a 0.8 cm<sup>2</sup> area vitreous carbon disc, from 0 V to 2.4 V vs. Al|Al(III) at 100 mV s<sup>-1</sup>. Cycles: 2nd (black line), 100th (red line), 200th (blue line), 300th (violet line), 400th (green line) and 500th (orange line) cycle in monomer-free Lewis neutral EMImCl-AlCl<sub>3</sub>. The PEDOT film was previously polymerised in Lewis neutral EMImCl-AlCl<sub>3</sub> containing 0.1 mol dm<sup>-3</sup> EDOT from -0.5 V to 2.6 V vs. Al|Al(III) at 100 mV s<sup>-1</sup>, during 20 cycles and 25 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

performance [5–7].

The formation of a nano/micro-porous thin film structure of the conductive polymer on a high surface area three-dimensional conductive substrate allows more active material (“footprint-area” [8]) to be accessible. Thus, the high area per unit volume of reticulated vitreous carbon (RVC) could result in higher energy per active electrode material [8–10].

## 2. Experimental

The monomer EDOT was electro-polymerised on both planar vitreous carbon (VC; Micro-to-Nano, 0.8 cm<sup>2</sup>) and on reticulated vitreous carbon (RVC; Duocel, ERG Aerospace, 1.4 cm<sup>2</sup>) working electrodes. The experiments were carried out in a PTFE-cell fitted with an identical planar vitreous carbon disc and an aluminum wire (Alfa Aesar, Puratronic, 99.999% metal basis, diameter 2 mm) counter and reference electrodes, respectively.

A Lewis neutral imidazolium based ionic liquid

( $\chi(\text{EMImCl}):\chi(\text{AlCl}_3) = 50 \text{ mol-}\%:50 \text{ mol-}\%$ ) was prepared using 1-ethyl-3-methylimidazolium chloride (EMImCl; Merck, purity  $\geq 98\%$ , water  $\leq 1.0\%$ ) and aluminum chloride (AlCl<sub>3</sub>; Alfa Aesar, anhydrous, ultra-dry, packed in glass ampule under argon gas, metal basis 99.99%) [5,11]. The ionic liquid containing 0.1 mol dm<sup>-3</sup> EDOT (EDOT; Alfa Aesar, purity 97%), was used as polymerisation solution.

EDOT was polymerised by three methods: cyclic voltammetry (CV) from -0.5 to 2.6 V vs. Al|Al(III) at 100 mV s<sup>-1</sup>, differential pulse amperometry (DPA) and increasing pulse potentials (reverse normal pulse voltammetry; RNPV) from 0 V to 2.5 V vs. Al|Al(III) with a pulse length of 1 s and 200 pulses. A glove box with nitrogen atmosphere ( $< 0.5 \text{ ppm}$  water and  $< 0.5 \text{ ppm}$  oxygen) at  $\sim 25 \text{ }^\circ\text{C}$  was used.

The morphology of PEDOT films was investigated by scanning electron microscopy (SEM; LEO 1450VP and JEOL JSM 6500F). The samples were rinsed with dimethyl carbonate after the electro-polymerisation and dried in vacuum for at least 1 h.

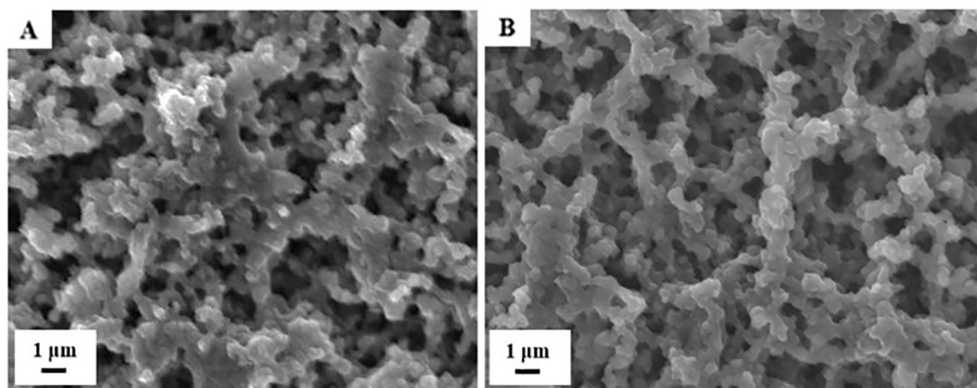
## 3. Results and discussion

### 3.1. PEDOT electro-polymerised on planar vitreous carbon

The PEDOT film electro-polymerised by cyclic voltammetry on planar high purity vitreous carbon (Fig. 1) shows anion doping sites at around 1 V and 2 V and de-doping sites at around 1.8 V, 1.3 V and 0.5 V vs. Al|Al(III). These doping sites are characteristic for PEDOT films in a Lewis neutral EMImCl-AlCl<sub>3</sub> ionic liquid with AlCl<sub>4</sub><sup>-</sup> as the predominant anion. In a neutral ionic liquid, the AlCl<sub>4</sub><sup>-</sup> anion has a wider potential stability window, making more doping/de-doping sites available, which is important for battery applications. The doping/de-doping sites were already predefined during the electro-polymerisation and play an important role in terms of the electrode performance [5]. For instance, de-doping sites at high potentials are related to high specific energy and power. The reversibility of the doping and de-doping and the redox-reaction of the polymer reaction ( $Q_c/Q_a$ ) reaches a minimum coulombic efficiency of 97% within 500 cycles, considering the overall cathodic and anodic transferred charges. This high reversibility demonstrates that the doping anion AlCl<sub>4</sub><sup>-</sup> does not remain trapped into the conductive polymer, proving that there is a good accessibility to the doping positions in the polymer during doping (charge) and de-doping (discharge) processes.

The current density between the 2nd and 500th cycle fluctuates  $\pm 5 \text{ mA cm}^{-2}$  around the maximum value. This is caused by the typical expansion and contraction of the polymer film [2,12] during the doping and de-doping processes, providing a varying number of accessible doping positions, which are related to the polymer capacity.

The typical porous structure of PEDOT consists of agglomerated



**Fig. 2.** SEM images of PEDOT on a 0.8 cm<sup>2</sup> area planar vitreous carbon after (A) electro-polymerisation by cyclic voltammetry in Lewis neutral EMImCl-AlCl<sub>3</sub> containing 0.1 mol dm<sup>-3</sup> EDOT and (B) after 500 cycles in monomer-free Lewis neutral EMImCl-AlCl<sub>3</sub>.

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