

## ELECTROCHEMICAL STABILITY OF PEDOT/DBS CONDUCTING POLYMER FILMS

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### Introduction

Conducting polymers have been shown to be good materials for use in energy storage devices, chemical sensors, optoelectronic devices and artificial muscles<sup>1,2</sup>. The stability of any conducting polymer in both reduced and oxidized states is an important parameter for technological applications. The main factor that determines the lifetime of a conducting polymer is the chemical stability of the matrix itself. In the case of PEDOT, chemical attack at positions 3 and 4 were excluded as the origin of the degradation since these positions are blocked by the ethylenedioxiide substituent. However, other reasons cannot be ruled out. This paper reports the study of electrochemical stability of PEDOT/DBS conducting polymer films. The investigations were carried out using cyclic voltammetric technique.

### Methodology

EDOT monomer (Aldrich 98%) was used without any further purification. Other chemicals, sodium dodecyl benzenesulfonate (NaDBS) (Aldrich) and NaCl (Merck) were used as received. 0.05M SDBS aqueous electrolyte containing 0.02 M EDOT was used for the synthesis of PEDOT/DBS films. PEDOT/DBS films were formed on Pt electrode (10-mm length, 0.5 mm diameter) using the galvanostatic electropolymerization technique. The redox behaviour of the films up to 1000 cycles in 1 M NaCl at constant scan rate of 100 mV s<sup>-1</sup> in the a potential range of -0.9 to 0.5 V was investigated using cyclic voltammetric technique. Nickel foil and Ag/AgCl were used as counter and reference electrodes respectively. The cycling electrolyte (NaCl) was purged with nitrogen gas to reduce the oxygen concentration.

### Discussion and Conclusion

The electrochemical stability of the PEDOT/DBS film was tested using cyclic voltammetry. 1000 continuous cycles were carried out in electrolytes having 1 M NaCl at constant scan rate of 100 mV s<sup>-1</sup> in the a potential range of -0.9 to 0.5 V and the cyclic voltammograms (CVs) obtained are shown in figure 1. The CVs exhibit a capacitive with a considerable current at the beginning (at potential 0.5 V) of the potential scanning. The first cycle exhibits a strong reduction peak at -0.6 V and a oxidation peak at around -0.3. Then, the voltammogram stabilizes after a few repeated electrochemical cycles and it reaches a rectangle-like shape. During this stabilization, while the reduction peak current decreases continuously, the oxidation peak at a -0.6 V grows steadily until the film become stable. Furthermore, only very little shifts in the peak potentials (anodic and cathodic) are observed during this process. Thus, the film evidently underwent some rearrangement of the structure due to motion of ions and solvent during the first reduction.

During each cycle, the film undergoes reduction and oxidation. For an ideal, reversible redox reaction, the cyclic voltammetry curves will remain invariant no matter how many cycles have been performed. But in practice, they are found to change with the number of

sweeps, providing information about corresponding changes in the microstructure and composition of the films. In this regard, the cyclic voltammograms were found to be almost unchanged after first few cycles (around 20 cycles) up to 1000 cycles.

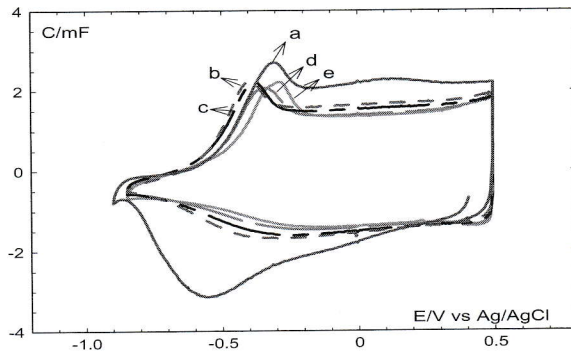


Fig. 1 Cyclic voltammograms of a PEDOT/DBS film cycled in 1 M NaCl aqueous electrolyte; (a) 1<sup>st</sup>, (b) 20<sup>th</sup>, (c) 100<sup>th</sup>, (d) 500<sup>th</sup> and (e) 1000<sup>th</sup> cycle. Scan rate: 100  $\text{mV s}^{-1}$ .

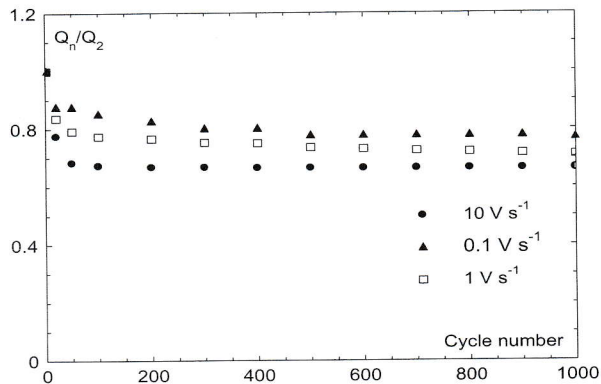


Fig. 2 Electrochemical activity of PEDOT/DBS films as a function of cycle number at different scan rates. Cycling electrolyte: 1 M NaCl

Figure 2 shows the charge variation of the cyclic voltammograms obtained as a function of cycle numbers. For easy comparison of the variations, the ratio of  $Q_n/Q_2$  (also defined as residual electrochemical activity)<sup>3</sup> versus cycle number are shown in figure 2, here  $Q_n$  and  $Q_2$  corresponds to the charges of the  $n^{\text{th}}$  and 2<sup>nd</sup> cyclic voltammograms respectively. Accordingly, there is a loss of 12% in activity until 20<sup>th</sup> cycle due to some rearrangement of the structure. Then, about 75% of the electrochemical activity remained up to 1000 cycles. Furthermore, similar tests were carried out at a two faster scan rates (1, 10  $\text{V s}^{-1}$ ) and the results are also shown in the same figure 2. The results clearly indicate that the PEDOT/DBS films have better electrochemical stability over a large number of cycles.

Interestingly, the degradation of the PEDOT/DBS films under normal environmental conditions was also investigated. Films electrodeposited on a Ptelectrode were stored in air

at room temperature for different period of times. Figure 3 shows the cyclic voltammogram of fresh, 1.5 hours, 1 day and 1 week old films. Accordingly, cyclic voltammetric behaviour seems to be unchanged and the electrochemical activity is retained even after storing for a long time after the film is formed. This is an evidence for non degradation of the film on storage under normal environmental conditions. It should be noted that R. Kiebooms et al. have reported that the doped PEDOT is stable up to a temperature of 150 °C and beyond that temperature a continuous degradation taking place until a major decomposition occurs (Kieboomset. al, 1997).

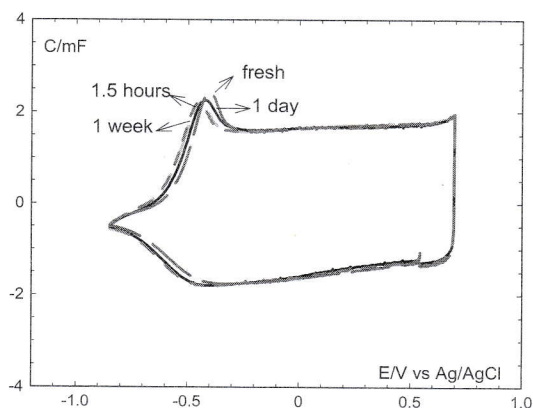


Fig. 3. Cyclic voltammograms of identical PEDOT/DBS films obtained at different aging of the film, cycled in 1 M NaCl electrolyte. Scan rate: 100  $\text{mV s}^{-1}$ .

Furthermore, the stabilized PEDOT/DBS films were kept for about 16 hours at two selected potentials (0.4 and 0.2 V) of oxidized state, and it was observed that there are no significant changes in the cyclic voltammograms obtained before and after this time interval. This reveals that this system shows a strong stability in the oxidized state.

During the first cycle a large water movement is observed. On continuous cycling the shape of the cyclic voltammograms remains unchanged indicating PEDOT/DBS films have stable cycle life. The charge variation of the cyclic voltammograms obtained shows that the electrochemical activity remains for a large number of cycles. The electrochemical activity is retained even after storing for a long time after the film is formed. This shows non degradation of the film on storage under normal environmental conditions.

## References

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