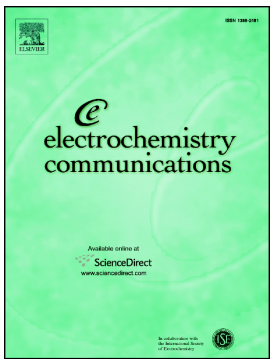

Bridging electrode gaps with conducting polymers around the electrical percolation threshold

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Bridging electrode gaps with conducting polymers around the electrical percolation threshold

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Abstract

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is grown electrochemically using cyclic voltammetry between the gaps of interdigitated Au electrodes with separations of 10, 20, and 50 μm. Three electrical conductivity regimes are identified through resistance measurements and SEM imaging. The first is the insulating region where there are no complete conducting pathways between the electrodes. The second is the percolation region where a few localised conducting polymer bridges have formed. The third is the thin film region where a continuous conducting polymer film connects the electrodes. The demonstration of the ability to reliably generate conducting polymer electrical percolation networks is important for their future use in high sensitivity devices.

Keywords

Cyclic voltammetry

Conducting polymer

Percolation network

1. Introduction

Conducting polymers (CPs) are increasingly used in technologically advanced devices such as supercapacitors, LEDs, MEMs and chemical sensors [1-4]. Various chemical and physical deposition methods are used to deposit conducting polymers onto substrates. Of these processes electrochemical methods offer significant benefits including accurate control of the amount of polymer deposited and stability of the polymers. Electrochemical deposition also allows the polymer to be grown *in situ* and has proved to be a particularly good deposition technique for conductometric sensors, also known as chemiresistors [3,5]. CPs are an attractive sensing material in chemiresistors because they can be easily functionalised to interact with particular analytes and they operate at room temperature [6]. In these devices CPs are usually deposited as a thin film [6], but the sensitivity of the device can be increased by creating a percolation network of polymers [7,8]. In the percolation region the change in electrical conductivity as a function of the amount of polymer deposited is significantly greater than in the thin film region. Fig. 1 shows an idealised graph of three distinct conductance regions between two electrodes as a function of the amount of polymer between the electrodes. For low polymer amounts there is no conduction because there is insufficient polymer to allow even a single electrical connection to be formed between the electrodes, thus this is referred to as the insulating region. As a small number of isolated contacts are formed the percolation threshold is reached, which marks the beginning of the percolation region. In electrical percolation, electrical connectivity is created in randomly distributed systems of discrete elements [9]. The percolation region is characterised by the non-linear relationship between the amount of polymer between the electrodes and the conductivity across the electrodes. As more polymer is deposited the thin film region is reached, where film thickness is the major factor that controls film conductivity. The detailed shape of the graph in Fig. 1 will depend on numerous experimental parameters, but the general shape will

be common to all systems of this type, and can be described as an initial flat insulating region, followed by a steep increase in conductivity due to electrical percolation, followed by a constant gradient thin film region.

The experimental study of electrical percolation networks is a field where there are only a few published studies. Sauerwald et al. reported on the behaviour of metal oxides operating in the percolation region [8]. Wang et al. created a carbon nanotube/polythiophene sensor that makes use of the percolation region [10]. Bruck et al. demonstrated how a percolation network of single walled carbon nanotubes immobilised on an insulating poly(methyl methacrylate) substrate can act as a sensor [9].

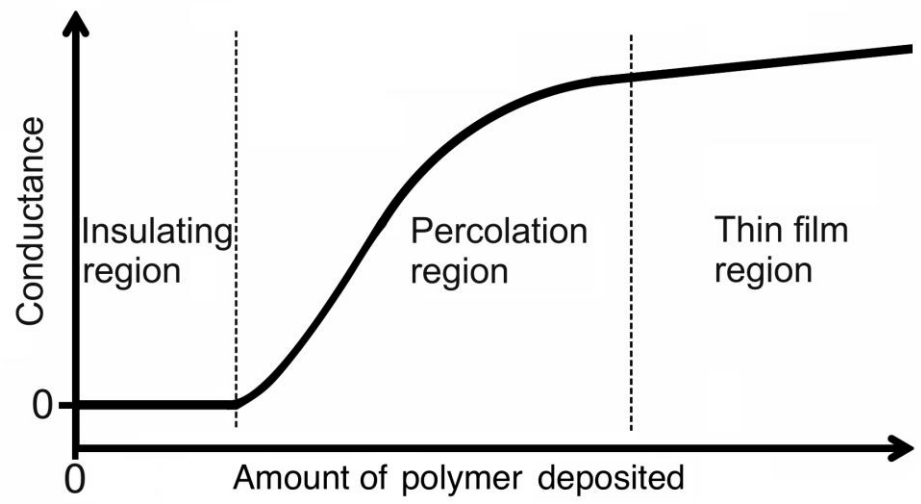

Fig. 1. Conceptual graph showing the change in conductance between two electrodes as a function of the amount of conducting polymer deposited between the electrodes. Three distinct conductance regions can be identified. The insulating region is where there are no continuous electrical connections between the electrodes. The percolation region is where isolated conducting pathways or networks have formed. The thin film region is where a continuous conducting film connects the electrodes.

In the work reported here we use interdigitated electrodes (IDEs) to study the onset of the percolation region of PEDOT for a variety of electrode gap sizes. PEDOT was chosen for its excellent stability, processability, and high conductivity [11]. IDEs are electrodes where two opposing interlocking comb-structured metal electrodes are patterned onto an insulating substrate. We have found that the most reliable method for CP deposition is to electrochemically grow the polymer onto the IDE from a monomer solution. Bartlett et al. [5] reported how a film of CPs can be grown electrochemically on an insulting substrate. In our work we use a similar method to that of Bartlett et al. [5] to grow the CPs between the gaps of the fingers of the IDEs. There have been extensive reports [12-19] concerning the electrochemical deposition of CPs onto electrodes, however a detailed study of the relationship between the amount of CP deposited as a function of resistance has so far not been performed.

2. Materials and methods

IDEs (NanoSPR Devices, USA) with three different gap widths of 10, 20 and 50 μm were used for our study. The IDEs consisted of Au electrodes on an insulating glass support. The Au fingers themselves had a width of 20 μm and length of 1 mm for all IDEs, with 20 fingers per electrode. PEDOT was electrochemically grown using a potentiostat (Metrohm Autolab PGSTAT204) on the Au IDEs from a solution of acetonitrile containing 0.01 M monomer 3,4-ethylenedioxythiophene (EDOT) and 0.1 M lithium perchlorate salt (Sigma-Aldrich, UK) [20,21]. Cyclic voltammetry (CV) was used to grow the CPs, where the potential between the working and reference electrodes was swept between a low and high value, and the current between the working electrode and the counter electrode was monitored. The three-electrode cell used a Pt coil (BASi, USA) as the counter electrode and an Ag/AgCl (CH Instruments, USA) as the reference electrode. When sufficiently high potentials are reached, EDOT from

the solution will be oxidised by the electrode surface resulting in the formation of the conducting polymer PEDOT [22]. The expectation was that for larger gap widths the onset of the percolation region would require more CV cycles because the polymer would have further to grow to bridge the gap. In our experimental setup we electrically short circuit the two IDE combs and treat them as a single working electrode.

Scanning electron microscopy (SEM) was carried out using secondary electrons for imaging on a Zeiss Merlin employing a 3 kV accelerating voltage.

3. Results and discussion

CV scans were performed from -1.0 V to +1.4 V and back to -1.0 V as shown in Fig. 2. The first two CV scans for the electrochemical polymerisation of EDOT on a 20 µm gapped IDE are shown in Fig. 2a. In the first scan (black CV trace, the nucleation loop) there is a crossover at around +1.1 V (I in the figure), which is indicative of a homogeneous comproportionation reaction between an oligomeric follow-up product and the starting monomer [22,23]. The peak at around -0.8 V (II in the figure) is due to the reduction of the polymer that is formed on the surface as a result of process I. On the second CV scan (red trace) a further peak appears at around +0.4 V (III in the figure). This peak is due to the oxidation of the polymer, which was not present until after polymer formation occurred during the first CV scan (black). It can also be seen that peak II increases in intensity on the second scan which is due to more PEDOT having been deposited on the IDE. Fig. 2b shows the growth of PEDOT on IDEs with 5 CV scans. It can be seen that for every subsequent scan after the first scan (black trace) the currents for all three peaks increase, which indicates that more polymer is being deposited with every scan. These CV results agree with previously

reported experiments involving the electrochemical growth of PEDOT from a solution of EDOT in $LiClO_4$/acetonitrile [22,24].

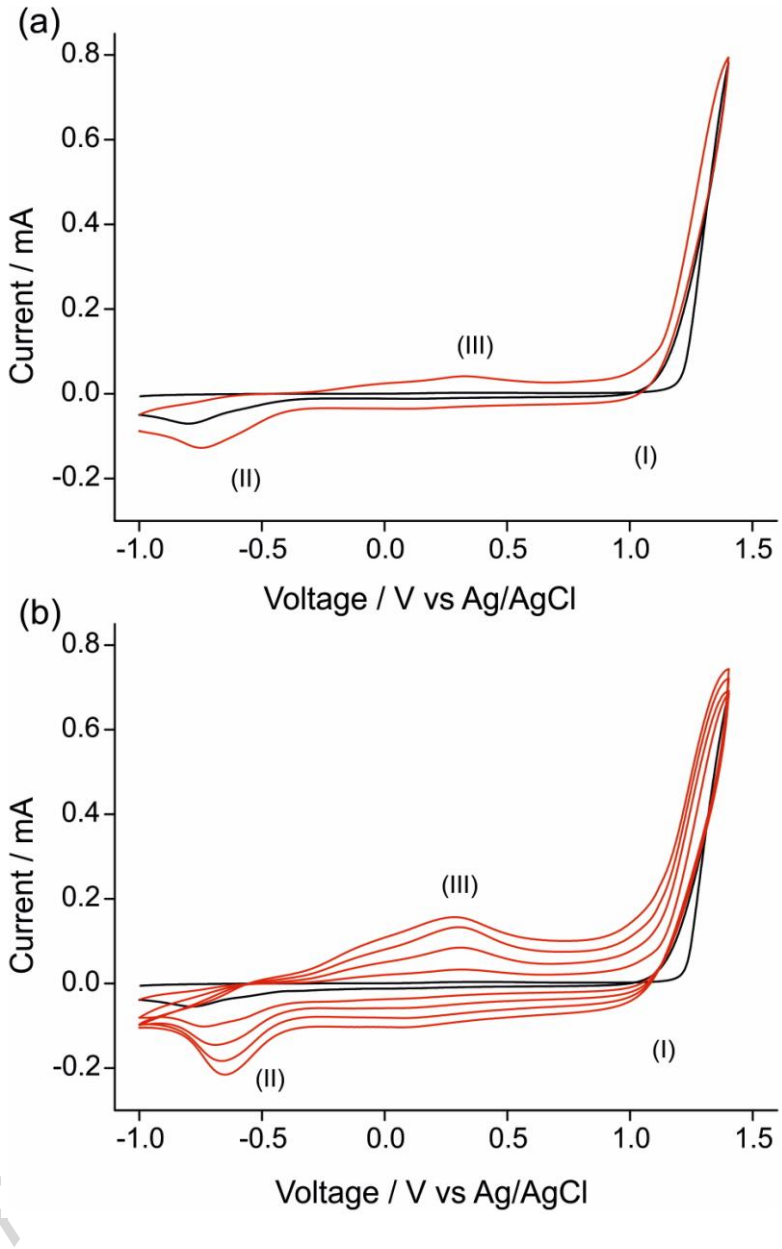

FIG. 2. Cyclic voltammetry at a scan rate of 0.1 V/s for the growth of PEDOT from a solution of 0.01M EDOT in 0.1M $LiClO_4$/acetonitrile on a 20 µm Au IDE for a) 2 cycles and b) 5 cycles. The black line is the first scan. The red lines are the subsequent scans. The cross-over of scans at (I) is due to the growth of PEDOT, the peaks at (II) and (III) are due to reduction and oxidation of PEDOT, respectively.

CV initially causes PEDOT to nucleate on the gold IDE fingers. After the first sweep a very thin conducting polymer film forms on the gold, but this does not extend significantly beyond the metallic parts of the IDEs. With subsequent CV scans more PEDOT is grown as shown by the increase in the peak intensities due to reduction (peak II) and oxidation (peak III) in Fig. 2b. During this process the polymer starts to grow outwards from the fingers onto the insulating glass substrate. These conducting polymer strands can continue to grow through electropolymerization on the insulating glass substrate because they are electrically connected to a gold IDE. As growth proceeds the polymers may meet their counterparts that nucleated on the opposing IDE finger, and this results in isolated conducting polymer strands forming connecting bridges between the IDE fingers. With further CV scans more polymer bridges are created, resulting in increased electrical conductance across the IDEs.

Fig. 3 shows a graph of conductance versus number of CV scans for the three different gap sizes. After the CV scans were completed, and before conductance measurements were carried out, the IDEs were taken out of the solution and washed with acetonitrile and allowed to dry in air. The electrodes were then put back in monomer-less solution (0.1 M $LiClO_4$/acetonitrile) and held at 1.4 V for 30 s to p-dope PEDOT for increased stability and conductivity [25]. After p-doping, the electrodes were taken out of solution, washed with acetonitrile and allowed to dry in air before resistance measurements were made between the two IDE combs. A DC potential of 1 V was applied and the resulting current was measured allowing a resistance value to be calculated. The reciprocal of the resistance (conductance) values are plotted in Fig. 3. For each resistance measurement a fresh IDE was used and the average conductance values of three separate experiments are plotted. It can be seen that initially the conductance is zero (within measurement constraints) for all three electrode gaps. For the 10 µm gap IDE (Fig. 3a) there is a small increase in conductance following the first

CV scan, and then a dramatic further increase following the second scan. For the third and subsequent scans the conductance does not change significantly. For the data plotted in Fig. 3a we would say that the percolation region lies between the first and second CV scan. For the 20 µm gap IDE (Fig. 3b) the significant increase in the conductance occurs following the third CV scan. The three different regions of CP concentration (Fig. 1) can be clearly identified in Fig. 3b. Between zero and two scans is the insulating region, between two and four scans is the percolation region, and above four scans is the thin film region. For the 50 µm gap IDE (Fig. 3c) there is no significant increase in the conductance until five CV scans are performed, which is consistent with the larger gap sizes. It is also worth noting that the units for the y-axis for the 50 µm gap IDE are around a factor of 20 times smaller than for the plots of the 10 and 20 µm IDEs. The trends of our results are as expected, in that the percolation threshold is a function of IDE gap width and number of CV scans. It is further worth noting that the number of CV cycles that are required to reach the percolation threshold also depends on the monomer concentration. A higher monomer concentration will cause the percolation threshold to form sooner, as more monomer is available for oxidation.

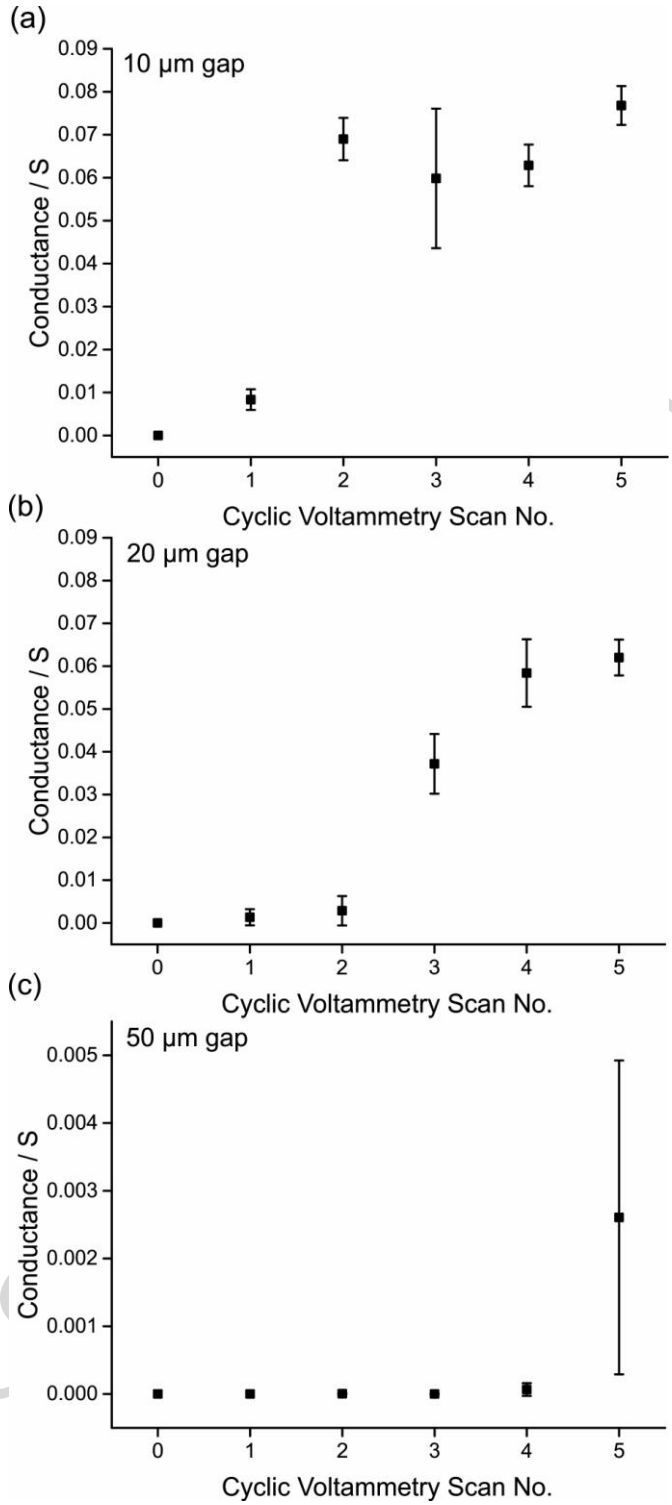

FIG. 3. Conductance vs CV scans for IDEs with gap widths of a) 10 µm, b) 20 µm and c) 50 µm. Error bars are obtained from the standard deviation of the conductance values of three electrode measurements for each CV scan. Thus the data in this figure is the result of 45 separate experiments, each using a fresh IDE.

Fig. 4 shows SEM images of PEDOT grown on 20 µm gap IDEs for every subsequent scan from one to five CV cycles (Fig. 4a to e). It can be seen that the polymer nucleates on the gold fingers and completely covers them before growing out onto the glass substrate and eventually forming electrically conducting bridges between the electrodes. CV has previously been shown to yield rod-like fibrous structures for the growth of PEDOT [26]. It is also visible that the growth is random and covers only a small area of the glass substrate. There are no visible bridges in the first and second CV cycle, which agrees with the resistance measurements in Fig. 3b where the IDE is still in the insulating region. After three CV cycles the CP can be seen to extend to the middle of the IDE, but no obvious bridges are seen, however we know from the conductance measurements that some bridges must have formed at this stage. In the images following the fourth and fifth CV cycles (Figs. 4d and e) parts of the glass substrates can be seen to have continuous CP connections.

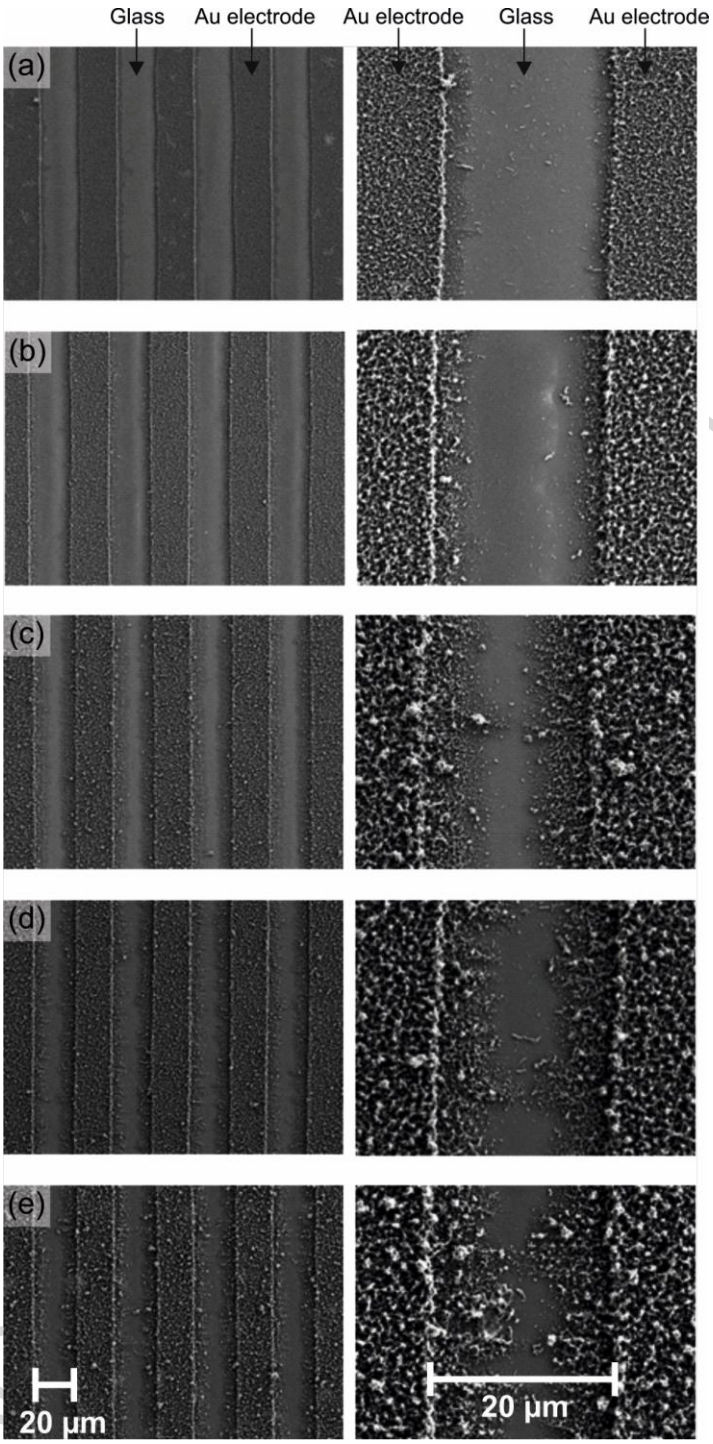

FIG. 4. Scanning electron micrographs of a 20 µm gap Au IDEs with a) 1, b) 2, c) 3, d) 4, and e) 5 CV scans. The left column is at low magnification showing 5 Au electrode strips and the right at higher magnification showing individual glass gaps between the electrodes. The amount of PEDOT between the electrodes increases as a function of the number of CV scans.

4. Conclusions

We have shown how an electrical percolation network of PEDOT can be electrochemically grown between IDEs on an insulating glass substrate. The trend of the resistance measurements was supported through SEM imaging of polymer bridging. Our results support the shape of the conceptual graph shown in Fig. 1. In this figure it can be seen that for a chemiresistor-based sensor there will be an increased proportional conductance change if an adsorbed analyte changes the resistance of the network when the sensor is operating in the percolation region as opposed to the thin film region. Our work forms the experimental basis for the development of CP-based devices that exploit the high sensitivity offered by electrical percolations networks. We are currently expanding our research in this area by investigating percolation networks of a range of CPs beside PEDOT. We are also exploring other electrochemical deposition techniques beyond CV such as potentiostatic and galvanostatic methods.

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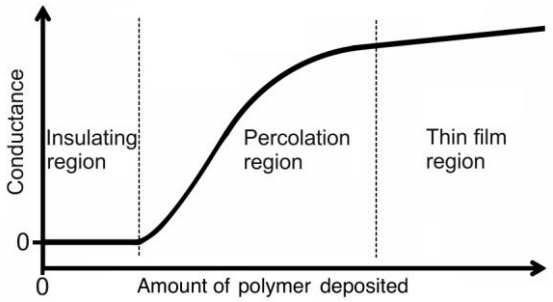

Graphical abstract

Bridging electrode gaps with conducting polymers around the electrical percolation threshold

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Highlights

- PEDOT is grown as a percolation network using cyclic voltammetry (CV).
- The conductivity of the network increases with the number of CV scans.
- SEM imaging of the networks corroborate the conductivity measurements.