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Electropolymerization of catalytically active PEDOT from an ionic liquid on a flexible carbon cloth using a sandwich cell configuration

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Abstract: We report the electropolymerization of poly(3,4-ethylenedioxythiopene) (PEDOT) from an ionic liquid, butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C$_4$mpyrTFSI) onto flexible carbon cloth electrodes. A continuous, homogeneous and well adhered coating of the individual cloth fibres is achieved by employing a sandwich cell arrangement where the carbon cloth which is soaked with electrolyte is placed between two indium tin oxide electrodes isolated from each other by a battery separator. The resultant PEDOT modified carbon cloth electrode demonstrates excellent activity for the oxygen reduction reaction which is due to the doping level, conductivity and morphology of the PEDOT layer and is also tolerant to the presence of methanol in the electrolyte. This simple approach therefore offers a route to fabricate flexible polymer electrodes that could be used in various electronic applications.
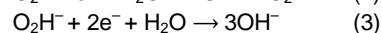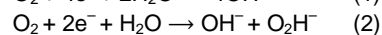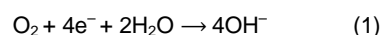
Introduction

The demand for energy is continually increasing due to rapid advances in technology and the significant emergence of electronic gadgets. The transformation from using fossil fuels to alternative renewable green energy sources is also of the upmost importance. Indeed, the motivation to develop new energy devices to keep up with such technological evolution and cover the increasing demand for energy has become overwhelming among the scientific community. Such devices should be light, durable and able to store (e.g. metal-air batteries) or generate a high amount of energy (e.g. fuel cells) with respect to their mass and volume.[1]

In general, fuel cells utilize noble metal nanoparticles such as platinum and platinum based composite materials immobilized on high surface area support materials as cathodes, for the oxygen reduction reaction (ORR) as they are highly active and exhibit high current density.[2] However, there are some drawbacks that limit the application of such nanomaterials in fuel cells and metal-air batteries such as cost, poor mechanical attachment in the case of composite electrodes and the propensity to dissolve.[3] On the other hand, conducting polymers and, especially, poly(3,4-ethylenedioxy-thiopene) (PEDOT) have been shown to be good non-metal based catalysts and an alternative to Pt for the ORR which has been demonstrated by many groups.[4] PEDOT is a versatile material and has been used in many other applications including organic solar cells, organic light emitting diodes and antistatic coatings.[5] The ability to use this processable material as a replacement for precious Pt as well as being able to fabricate flexible electrodes for organic electronic applications is highly attractive.

The ORR proceeds at PEDOT via two pathways under alkaline conditions; a 4-electron step where oxygen is completely reduced in one direct step to hydroxide (Equation 1) as reported for vapor phase polymerized films[4a] or two consecutive 2-electron steps where oxygen undergoes reduction through a hydrogen peroxide anion intermediate and then to hydroxide (Equation 2, 3) which generally occurs at electropolymerized films.[6] The discrepancy in activity between the two synthetic approaches is difficult to explain and indeed there still remains much debate as to the origin of the active site for the ORR at PEDOT and the role of morphology, counter ion, electrolyte and synthesis solvent. In fact it has even been reported by Katashinskii et al[7] that PEDOT is inactive for the ORR.

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad (1)$$
$$O_2 + 2e^- + H_2O \rightarrow OH^- + O_2H^- \quad (2)$$
$$O_2H^- + 2e^- + H_2O \rightarrow 3OH^- \quad (3)$$

Given the ease with which electrochemical deposition of conducting polymers can be achieved under ambient conditions using inexpensive equipment, significant research attention has focused on fabricating electropolymerized PEDOT films. This included studies on the effect of a number of factors such as, counter ion incorporation,[8] electropolymerization techniques[6a] and electropolymerization potentials[9] on the structure, electrochemical and catalytic properties of PEDOT. In all of these studies, PEDOT was electropolymerized from either an aqueous or organic solvent.[10] Although, PEDOT has been chemically polymerized and characterized in a variety of ionic liquids,[11] there is no reported work, to the best of our knowledge that has subsequently investigated these polymers specifically for their electrocatalytic activity for the ORR.

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In this work, a novel technique of PEDOT electropolymerization onto carbon cloths in a sandwich cell configuration from ILs is presented as well as the influence of such an approach on PEDOT's electrocatalytic behaviour for the ORR under alkaline and acidic conditions. Significantly, this approach and choice of substrate opens up the area of miniaturized and flexible conducting polymer based electrodes that may be utilized in energy generation and storage technology that could be incorporated in applications such as wearable electronic devices.

Results and Discussion

The electropolymerization of PEDOT was carried out from two separate solutions containing EDOT dissolved in either C_4mpyr-TFSI ionic liquid or acetonitrile using a concentration of 0.6 mol kg^{-1}. Initial experiments performed with a typical 3 electrode setup in a conventional glass electrochemical cell using a carbon cloth working electrode suspended in the IL solution resulted in significant dissolution of PEDOT during the electropolymerization process. This could be observed by eye as a dark coloration of the electrolyte diffusing away from the carbon cloth while the electrode was under potential control. Therefore to promote the adhesion of PEDOT to the carbon cloth a different experimental setup was required and is illustrated in Figure 1.
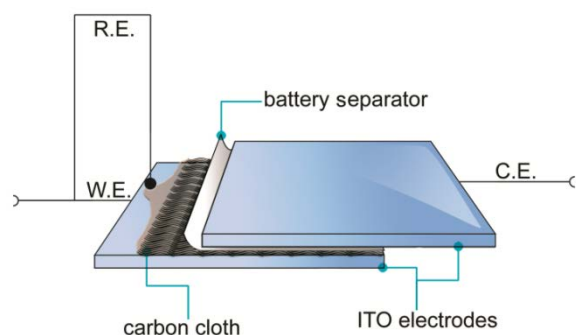

Figure 1. Illustration of the electropolymerization method used to polymerise PEDOT onto carbon cloths. The carbon cloth is wetted with EDOT in C_4mpyrTFSI IL or 1 M LiTFSI in acetonitrile and covered with a battery separator from one side and then sandwiched between two ITO-glass electrodes.

With this configuration the carbon cloth was wetted with electrolyte and confined between 2 ITO electrodes where the one directly connected to the carbon cloth acted as the working electrode and the other as the counter electrode. The ITO electrodes maintained their integrity as evidenced by their high conductivity after the electropolymerization experiment, however, they were discarded after the process and a new pair of electrodes was used for each experiment. A standard battery separator was employed to avoid short circuiting the two electrodes. The reference electrode was positioned within a drop of electrolyte that was placed on the carbon cloth as shown schematically in Figure 1. To initiate the electropolymerization reaction, a potential of 0.90 V was applied and then held for

different times. It was found that polymerisation times less than 15 minutes resulted in low polymer coverage while polymerisation times greater than 30 minutes resulted in over grown polymer structures that covered the carbon bundles and obscured the individual fibres. As a result, two polymerisation times were used in this study (i.e. 15 and 30 minutes) to study the effect of PEDOT loading which resulted in the uniform deposition of PEDOT over the carbon cloth surface without any visual detachment of the polymer from the cloth. In contrast, a polymer coating produced from acetonitrile using the same setup was non-uniform, brittle and detached easily from the substrate. Furthermore, the solvent dried out during the polymerization process due to the low volume required using this approach and the fabric needed to be wetted constantly. This was not a problem with the non-volatile ionic liquid that was used.

Figure 2 shows SEM images of PEDOT electrodeposited from the IL onto carbon cloth for periods of 15 min (Figure 2b, e) and 30 min (Figure 2c, f). For comparison SEM images of the unmodified cloth are also shown in (Figure 2a, d). It can be seen that after 15 min of polymerization that the individual fibres can be easily distinguished, even though there is clear evidence of a uniform coating over the individual fibres, which increases their diameter from 35 to ca. 38 µm. Upon increasing the deposition time to 30 min the thickness of the fibres increases to ca. 50 µm and a significant polymer coating can be seen. Importantly the coverage is still uniform, although some nodular growth is seen along each fibre and from the lower magnification image (Figure 2e) the cloth does not show any patchy or clumped growth anywhere on the sample. The loading of PEDOT onto the carbon cloth was 3.95 mg cm^{-2} and 7.11 mg cm^{-2} for electropolymerization times of 15 and 30 minutes respectively. Significantly, the carbon cloth maintained a great degree of flexibility after the electropolymerization of PEDOT from the IL (Figure 3) and did not show any evidence of the polymer flaking off the cloth.

This was in contrast to electropolymerization carried out in acetonitrile using the sandwich cell configuration as in Figure 1 which resulted in a powder-like nodular coverage (Figure 4). The PEDOT film exhibited poor adhesion to the carbon cloth's fibres and poor structural integrity. However, the film produced via this setup was still markedly more uniform than the patchy and dense film fabricated via the conventional 3 electrode setup using a suspended carbon cloth as the working electrode in a large volume of electrolyte (Figure S2). These results are in agreement with studies carried out in organic or aqueous solvents which usually result in a very rough morphology with separated islands of polymer in contrast to ionic liquid grown films.[12] This suggests that there are two contributing factors to such improved morphology and particularly adhesion when ILs are used, i.e. a highly uniform electric field is applied under this type of cell configuration and the ionic liquid facilitates slower growth of the polymer given its viscosity (59.9 cP) compared to more conventional solvents such as acetonitrile (0.35 cP). This approach to fabricating conducting polymers may be of significant advantage to other systems where adhesion is problematic. Recently a polymer of similar functionality poly(3,4-

ethylenedioxy-pyrrole) (PEDOP) required the use of an intermediate adhesion layer of polypyrrole for successful coverage of a stainless steel mesh substrate for use as a superoleophobic surface.[13]
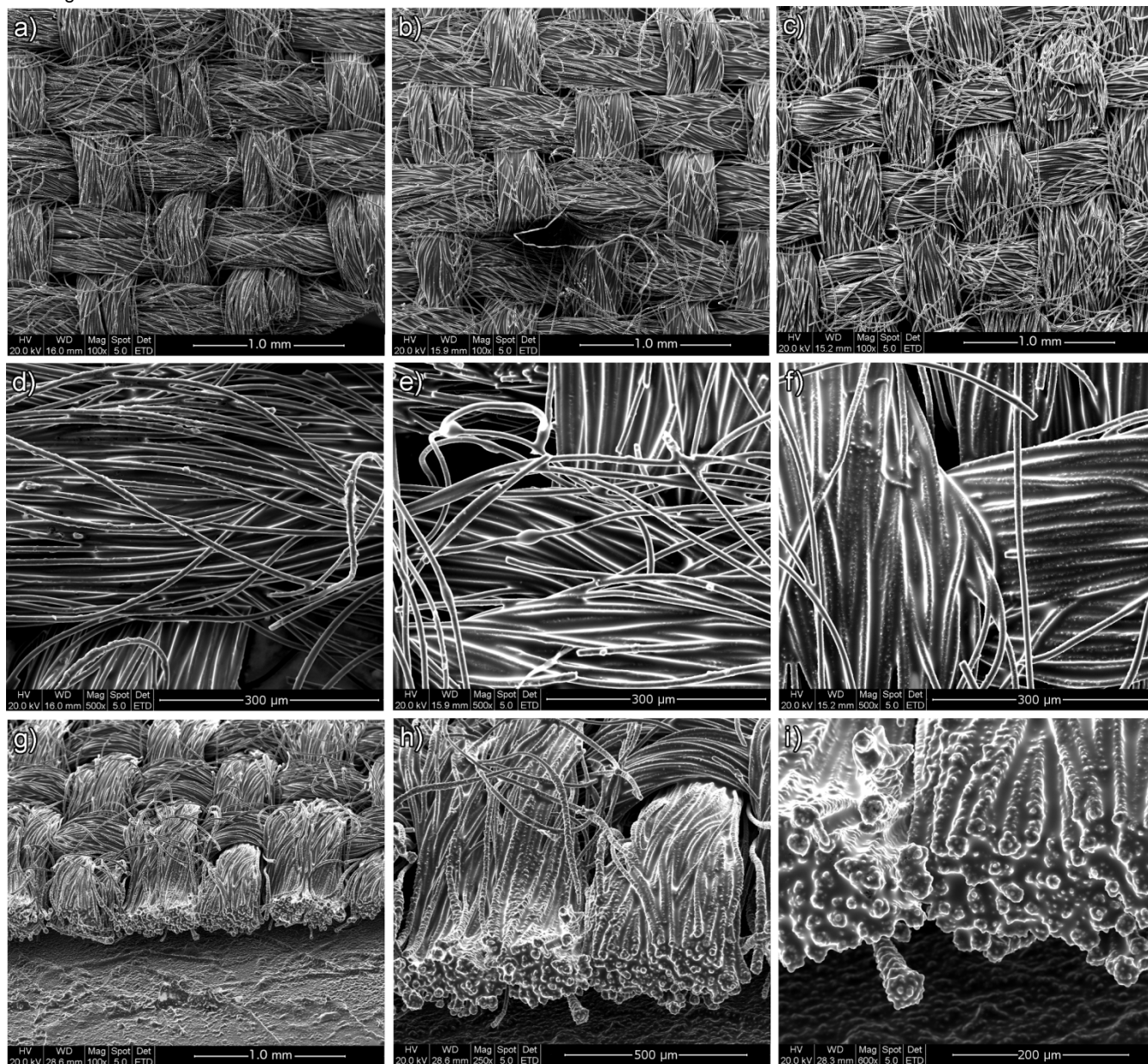

Figure 2. SEM micrographs of bare carbon cloth (a and d), PEDOT-coated carbon cloth after 15 minutes (b and e) and 30 minutes (c and f) of polymerization and the side views of the 30 minutes deposition sample(g, h and i)

Figure 3. A digital photograph showing the flexibility of the PEDOT(IL)-coated carbon cloth.

In all cases the purity of PEDOT was confirmed by Raman spectroscopy which is shown in Figure 5 and the relevant bands are assigned in Table 1. The spectra are compared with previous literature reports of neutral and doped PEDOT.[14] The data show a strong band at ~ 1451 cm^{-1} for both films that corresponds to C$_\alpha$=C$_\beta$ symmetric vibrations. This band can be attributed to the PEDOT film being in a doped state, where the position of the band shifts to more positive values when PEDOT is doped.[14a] Comparing our data to previous studies, the C$_\alpha$=C$_\beta$ symmetric vibration in neutral "de-doped" PEDOT shifts from

1414 cm^{-1} to 1445 cm^{-1} when doped for both films, which is consistent with a previous study which reported that this band shifted to 1451 cm^{-1}.[14a] This indicates that the electropolymerized PEDOT from the IL is in a doped state for both films. Also, the C$_\alpha$–C$_\alpha$ (inter-ring) stretching band at 1252 cm^{-1} shifts to 1267 cm^{-1}, which is consistent with the previous report. Therefore the Raman data for PEDOT obtained in our work shows that doped PEDOT was successfully electropolymerized on the carbon cloth. Raman spectra were also recorded for the carbon cloth (Figure 5) but no significant signal was detected.
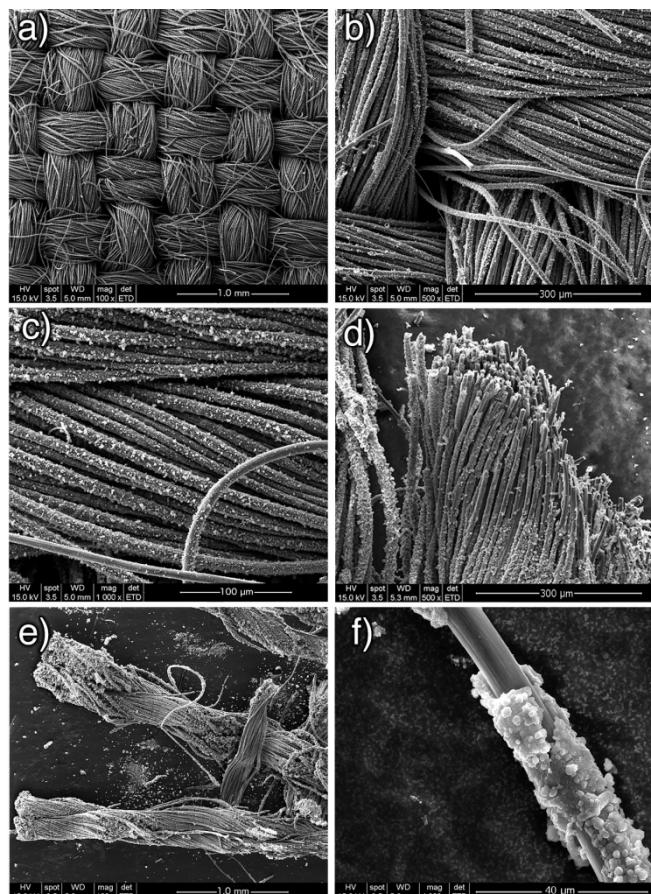

Figure 5. Raman spectra of carbon cloth and electropolymerised PEDOT-coated carbon cloths showing the characteristic peak at that cm^{-1} corresponds to C$_\alpha$=C$_\beta$ symmetric vibrations.

Although the morphology of the film may be influential for the applicability of this material, the role of conductivity should also be considered for any electrocatalytic or electronic application. The conductivity for the 15 minutes electropolymerized PEDOT (IL)-coated carbon cloth was measured to be 179 S cm^{-1} which increased to 476 S cm^{-1} for the thicker film electropolymerized for 30 minutes, while the PEDOT electropolymerized from MeCN gave a much lower value of 79 S cm^{-1}, nearly six times lower than the thickest PEDOT (IL) sample. This may be attributed to different morphology but more likely the number of counter ions incorporated within the polymer structure (i.e. doping level) as the latter is known to significantly impact on conductivity. In comparison, the vapor deposited PEDOT films reported previously exhibited conductivities of the order of ~ 1025 S cm^{-1} [4a, 15].

Figure 4. SEM micrographs of PEDOT-coated carbon cloth electropolymerized from acetonitrile after 30 minutes using the sandwich cell configuration as in Figure 1 (a) and higher magnifications showing the flaky powder-like polymer coating on the carbon cloth (b and c). d and e micrographs showing the poor structural integrity of the film where the polymer crumbled and fell off the fibres during sample preparation, and a single carbon fibre with partial coating showing the poor contact between the polymer film and the substrate (f).
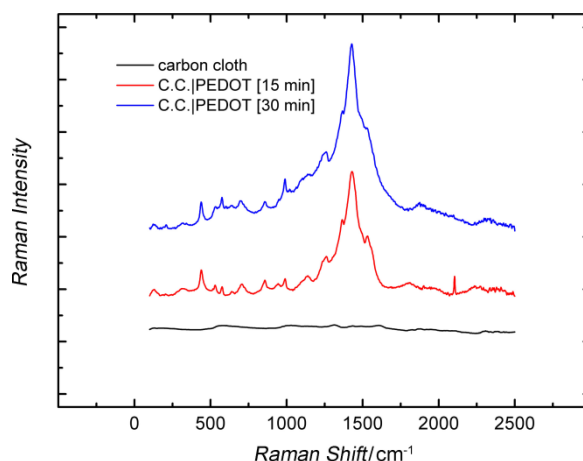
Table 1. Summary of Raman shifts (cm⁻¹) of PEDOT and their assignments according to the literature

Raman shift (cm⁻¹)			
Neutral[a] (literature)	Doped[a] (literature)	Doped (this work)	Band assignment
1516	1516	1528	Asymmetric $C_\alpha=C_\beta$ stretching
1414	1445	1451	Asymmetric $C_\alpha=C_\beta$ (–O) stretching
1370	1370	1373	$C_\beta–C_\beta$ stretching
1252	1263	1267	$C_\alpha–C_\alpha$ (inter-ring) stretching
1097	1097	1114	C–O–C deformation
990	990	995	Oxyethylene ring deformation
699	699	703	Symmetric C–S–C deformation
578	578	582	Oxyethylene ring deformation
1516	1516	1528	Asymmetric $C_\alpha=C_\beta$ stretching
1414	1445	1451	Asymmetric $C_\alpha=C_\beta$ (–O) stretching

[a] References 8 and 9

Previous studies have shown that the number of counter ions incorporated in chemically synthesised PEDOT films (and hence conductivity) are lower than that achieved using electropolymerization as the former is more rapid and inhibits counter ion incorporation.[16] Comparatively, the use of solvents with different viscosities influences the rate of polymerization and therefore the number of counter ions incorporated in to the film. In these studies the same counter ion (i.e. TFSI⁻) was used in both solvents and therefore it is expected that the rate of electropolymerization in the IL is significantly lower than MeCN, given its higher viscosity, allowing more TFSI⁻ ions to be incorporated in to the final PEDOT film. The doping levels for the 30 and 15 minutes samples were therefore calculated via XPS (Figure 6) to be 0.32 and 0.21, respectively, by comparing the intensity of the two sulfur peaks that are attributed to the thiophene ring (binding energies of 163.9 and 165.1 eV for the S $2p_{1/2}$ and S $2p_{3/2}$ core level respectively)[4c] and TFSI anion (binding energies of 168.8 and 169.8 eV for the S $2p_{1/2}$ and S $2p_{3/2}$ core level respectively) (Table 2).[17]
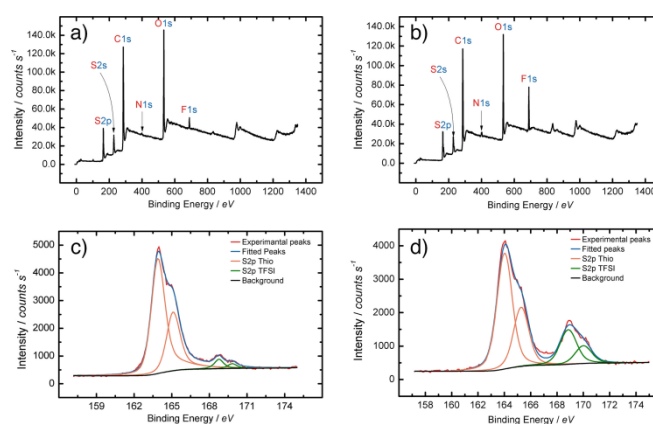.

Figure 6. XPS survey spectra for (a) 15 minutes PEDOT-modified carbon cloth, and (b) 30 minutes PEDOT-modified carbon cloth. And the de-convoluted XPS spectrum for S 2p peaks for (c) 15 minutes PEDOT-modified carbon cloth, and 30 minutes PEDOT-modified carbon cloth

Table 2: The de-convoluted S 2p peaks of PEDOT-Carbon cloth and the calculated doping level

Peak position (eV)	163.9	165.1	168.8	169.8	
Peak assignment	Thiophene S2p$_{1/2}$	Thiophene S2p$_{3/2}$	TFSI S2p$_{1/2}$	TFSI S2p$_{3/2}$	Doping level
15 min. PEDOT	11.9	16.2	2.5	3.7	0.22
30 min. PEDOT	12.3	14.9	4.0	4.6	0.32

It was found from previous studies that both vapour phase deposited and electropolymerized PEDOT films could be used as oxygen reduction electrocatalysts.[6a] Interestingly the films reported here (Figure 2) are quite dense and compact and are consistent with previously reported films that were electropolymerized on a platinum substrate from the same IL.[12b] They are also consistent with the compact films that are generated via vapour phase deposition. Cyclic voltammetric experiments were then carried out in oxygen saturated alkaline medium at carbon cloth and PEDOT covered carbon cloth electrodes (Figure 7). It can be seen that that there is a significant increase in current to 4.2 mA cm⁻² recorded at the PEDOT electrode compared to the bare carbon cloth and a shift in the onset potential to a less negative value of ca. -0.20 V where the latter value and current density are consistent with ORR at acid treated commercially available PEDOT:PSS films.[18] The response at the carbon cloth electrode is not unexpected as carbon does have some activity for the ORR.[19] It also confirms that the underlying electrode is not the major contributor to electrocatalytic activity as recently reported by Bard who demonstrated that the activity of PEDOT for the hydrogen evolution reaction was dictated by the underlying

metal electrode via permeation of electrolyte through pinholes in the polymer film.[20] It is also noteworthy that the capacitive nature of the response is greater at the PEDOT electrode indicating an increased surface area which is comparable to the behaviour observed at PEDOT:PSS films with incorporated reduced graphene oxide (rGO) that had been treated with concentrated H_2SO_4.[21]
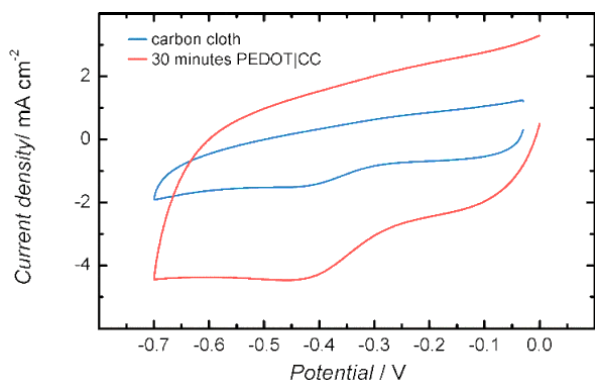

Figure 7. Cyclic voltammograms of bare carbon cloth (blue) and 30 min. PEDOT-modified carbon cloth (red) in oxygen saturated 0.1 M NaOH solution recorded at 20 mV s^{-1}.

Linear sweep voltammetric experiments at a rotating disk electrode (RDE) were also carried out in alkaline and acidic media to investigate the ORR reaction at PEDOT modified carbon cloth electrodes. These experiments were conducted by attaching the cloth electrode to a carbon paste RDE as shown in Figure S3. Typical linear sweep voltammograms recorded in an oxygen saturated aqueous solution containing 0.1 M NaOH are shown for the bare carbon cloth electrodes and where PEDOT had been electropolymerised in the IL for 15 min respectively (Figure 8a, b). To elucidate the number of electrons transferred during the ORR the equation developed by Koutecky and Levich, was used and a rotation rate study was conducted (Figure 8c,d). This equation relates the kinetically controlled current and the diffusion current to the total current (i_k, i_d, i respectively, Equation 4).[6a, 22]

$$i^{-1}=i_k^{-1}+i_d^{-1} \; ; \; i_d=0.62nFAD^{2/3}\omega^{1/2}\upsilon^{-1/6}c \qquad (4)$$

where n is the number of electrons, F is Faraday constant, A is the surface area of the electrode (calculated to be approximately 0.125 cm^2 as the effective diameter is 0.4 mm), D and c are the diffusion coefficient (1.9×10^{-5} cm^2 s^{-1}) and solubility (1.2×10^{-6} mol cm^{-3}) of oxygen in aqueous solutions, υ is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}) and ω is the rotation rate in rad s^{-1}.[23] Plotting i^{-1} vs $\omega^{-1/2}$ results in a line that intercepts the y axis to give i_k^{-1} and its slope allows the number of electrons to be determined. The average number of electrons was calculated from the slope for the 15 minutes PEDOT (IL)-coated carbon cloths at -0.6 V and found to be 1.8, (Figure 8d) thus indicating that the ORR is carried out via a 2-electron step while 1.1 electrons were calculated to be transferred at the bare carbon cloth (Figure 8c). For PEDOT electropolymerised in

acetonitrile (MeCN), the number of electrons was calculated to be 1.2 (Figure S4). This low number is attributed to both the poor coverage and contact between PEDOT and the carbon cloth electrode which results in a surface which severely inhibits the ORR.
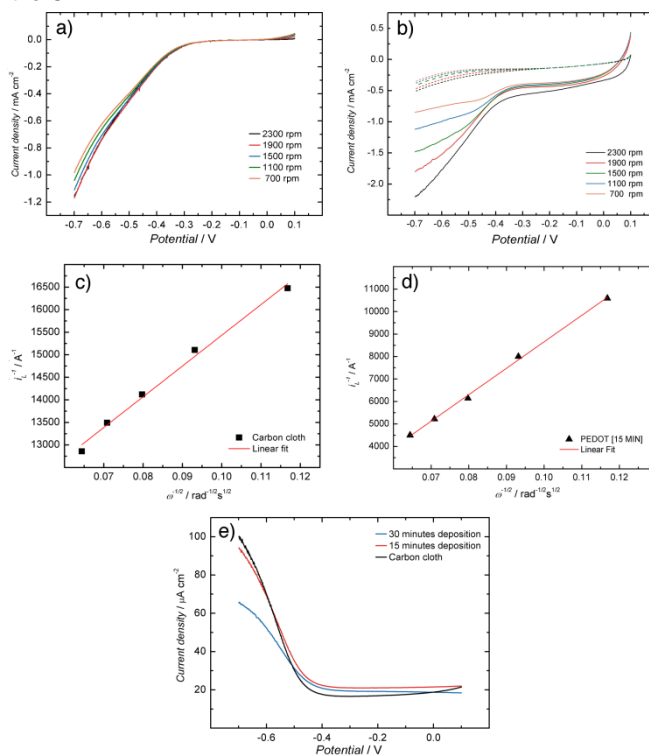

Figure 8. Linear sweep voltammograms recorded at 20 mV s^{-1} of (a) the ORR in 0.1 M NaOH saturated with $O_{2(g)}$ for (a) carbon cloth, (b) PEDOT (IL)-coated carbon cloth after 15 min of electropolymerization, the dashed lines in (b) are measurements conducted in de-gassed solutions, (c) Koutecky-Levich plots for current values recorded at -0.6 V for (c) carbon cloth and (d) PEDOT covered carbon cloth electrode (d) tip current recorded at a Pt UME (biased at 0.2 V) during a SECM tip generation-current collection experiment.

LSV curves recorded for the 30 min electropolymerized sample from the IL were very unusual and are shown in Figure S5. The origin of this type of response is unclear at present given that the cyclic voltammetric data recorded under quiescent conditions (Figure 7) does not show any unusual behaviour. The capacitive current for this high surface area material would not be expected to contribute to such an unusual behaviour and may be related to employing the RDE technique to a thick sample that must be immobilised onto a carbon paste electrode. However it must be noted that this behaviour was observed on numerous samples prepared in this manner. Therefore a Koutecky-Levich analysis was not performed to elucidate the number of electrons transferred during the ORR. An alternative approach to the RDE technique that avoids rotating the electrode is scanning electrochemical microscopy (SECM). In particular the substrate generation tip collection mode (detailed in supporting information and Figure S1) is excellent at determining intermediates generated during a reaction in an analogous manner to the rotating ring disk electrode. The

substrate, in this case the PEDOT-coated carbon cloth, is biased at negative potential that is sufficient for a reaction to take place at the surface (e.g. reduction of oxygen) to generate a product which can be detected at the ultramicroelectrode (UME)'s tip (i.e. unwanted intermediate species such as hydrogen peroxide). In this mode the tip is biased at a potential sufficient for the generated product to be either reduced or oxidised. Under these conditions there are two types of current which are measured, namely the generation current (at the substrate) and the collection current (at the tip) and the closer the tip is to the substrate, the higher the collection current. SECM SG-TC measurements showed a tip collection current that corresponds to the reduction of hydrogen peroxide generated from the ORR, at the bare carbon cloth and thinner PEDOT film (Figure 8e) which is consistent with the transfer of 2 electrons that were calculated from the RDE studies. However at the thicker PEDOT film the collection current is much smaller which indicates that the ORR proceeds via less formation of the hydrogen peroxide intermediate. Overall, the mechanism appears to be consistent with a redox cycling process where initially PEDOT is electrochemically reduced at ca. -0.20 V upon which O_2 is adsorbed on the surface. PEDOT then rapidly reoxidizes back to its preferred oxidized state which results in the reduction of the adsorbed O_2.[4a] This cyclic redox process is then maintained at the highly conducting polymer film. As the thicker film is rougher, more highly doped and more conducting there may be more active sites available for this reaction to occur which favours less peroxide formation. It is unlikely that the counter ion is directly playing a role as PEDOT electropolymerized in acetonitrile using LiTFSI as supporting electrolyte showed inferior performance to PEDOT electropolymerized in the IL.

The same sets of experiments were conducted with PEDOT (IL) under acidic conditions in 0.1 M H_2SO_4 and are illustrated in Figure S6 where again unusual behaviour was observed for the thicker film. From a Koutecky-Levich analysis it was found that for the samples electropolymerized at 15 min the ORR proceeded via the transfer of 2.7 electrons. This demonstrates the suitability of this material as an effective electrocatalyst material given its applicability over such a large pH range. In addition, the ORR at the PEDOT (IL)-coated carbon cloth was not perturbed by the addition of methanol to the solution (Figure 9) in contrast to the behaviour often observed at Pt electrodes which have poor methanol tolerance.[18] Therefore this material would also be advantageous for use in a direct methanol fuel cell where methanol crossover through the membrane of the cell can often be problematic.[18, 24]

Conclusions

A novel method for the electropolymerization of doped PEDOT from an IL in a sandwich configuration onto a carbon fibre cloth has been demonstrated. This approach does not lead to PEDOT diffusing into solution as observed for cloth electrodes simply immersed in the IL but rather gives a continuous coating over the individual fibres whose thickness is controlled by the electropolymerization time. The use of an ionic liquid was also

crucial for the formation of a uniform film that coated each of the individual fibres as analogous experiments carried out using acetonitrile resulted in non-uniform and patchy growth due to poor adhesion to the carbon cloth. The resultant flexible electrode was active for the ORR over a wide pH range with the thicker sample showing less formation of the hydrogen peroxide intermediate during the course of the reaction which is possibly due to its higher conductivity attributed to the incorporation of more TFSI- anions in the film. Also the electrode fabricated from the IL showed markedly improved performance over PEDOT electropolymerized in acetonitrile. Significantly, this method of synthesis opens up a way to electropolymerize a variety of other conducting polymers on to flexible electrodes that may have many other applications in flexible or wearable electronic or energy storage or conversion devices.
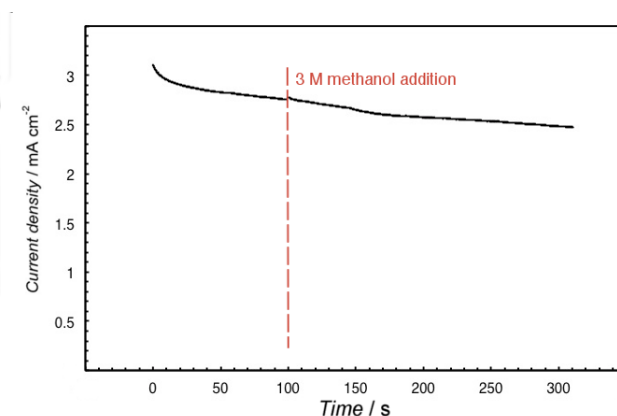

Figure 9. Chronoamperometry response at a PEDOT (IL)-coated carbon cloth (30 min electropolymerization time) fixed on an RDE rotating at 700 rpm and biased at -0.7 V in 0.1 M NaOH saturated with $O_{2(g)}$ after the addition of 3 M methanol to the electrolyte.

Experimental Section

Materials and equipment

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl-)imide (C_4mpyrTFSI, ≥ 98.5%) ionic liquid, 3,4-ethylenedioxythiopene (EDOT) (Sigma-Aldrich), NaOH and H_2SO_4 (BDH), battery separator (Solupor 7P, Lydall Solutech BV) and carbon cloth (AvCarb® Carbon Fabrics, Ballard Material Products, Inc.) were used as received without further purification. The electropolymerization and electrochemical measurements were carried out using a CH Instruments (CHI 920D SECM) scanning electrochemical microscopy potentiostat and CH Instruments (CHI 730E RDE) rotating disk electrode apparatus. ITO glass electrode, carbon paste RDE and 10 µm Pt ultramicroelectrode (UME) were used as working electrodes in electropolymerization, RDE measurements and SECM measurements respectively. Ag/AgCl (3 M KCl) electrode was used as a reference electrode in all experiments. ITO glass electrode was used as a counter electrode in PEDOT polymerization experiments and a Pt wire in RDE and SECM measurements respectively.

Electropolymerization procedure

The solution for PEDOT electropolymerization was prepared by dissolving EDOT in C_4mpyrTFSI ionic liquid or 1 M LiTFSI acetonitrile solution to a concentration of 0.6 mol kg^{-1}. Two thirds of the carbon cloth with dimensions of 1 × 3 cm was wetted by the prepared solution and covered by the battery separator on one side then sandwiched between

two staggered ITO glass electrodes. A drop of the solution was placed on top of the electrode and in contact to the carbon cloth to make a contact to the reference electrode (Figure 6). Electropolymerization was carried out by biasing the potential at 0.9 V vs. Ag/AgCl for 15 and 30 minutes.[21] After the electropolymerization was finished, the carbon cloth was rinsed with ethanol several times and dried under a stream of nitrogen gas. The resultant carbon cloth had a uniform dark and hard region where the PEDOT was deposited. The loading of PEDOT on carbon cloth was determined by weighing the cloth before and after the electropolymerization experiment.

RDE and SECM measurements
5 mm disks were cut out of the PEDOT-coated carbon cloths using a hole-puncher and attached to a carbon paste RDE for maximum surface contact. The measurements were carried out in oxygen saturated NaOH and H_2SO_4 (0.1 M) solutions by linear scanning of the potential from 0.1 V to - 0.7 V vs. 3 M Ag/AgCl and varying the rotation speeds from 700 rpm to 2300 rpm. This was followed by measurements in nitrogen purged H_2SO_4 solutions.

Analogous to the rotating ring disc electrode, SECM measurements were carried out using a four-electrode arrangement with PEDOT-coated carbon cloth as the substrate working electrode and the 10 µm Pt UME as the tip working electrode in the same solutions used in RDE measurements. Using 1 mM potassium ferrocyanide solution as a redox mediator, the UME was positioned to 10 µm above the PEDOT-coated carbon cloth. Then the mediator solution was replaced with oxygen saturated NaOH and H_2SO_4 (0.1 M) solutions and the UME was biased at 0.2 V (i.e. in order detect peroxide if produced during the ORR) while linear scanning of the potential of the substrate from 0.1 V to -0.7 V was carried out.

Surface characterization
The morphology of the PEDOT-coated carbon cloth was examined by scanning electron microscopy using FEI Nova Nano-SEM microscope. The samples were examined under the microscope without being coated with gold or carbon films. In addition, Raman spectrometer (Perkin Elmer, Raman Station 400F, 785 nm laser) was used for spectroscopic analysis of the composites.

Conductivity measurements
The conductivity was calculated from equation 5:

$$\sigma = \frac{1}{R(A/\ell)} \qquad (5)$$

where σ is conductivity in S m^{-1}, R is resistance in Ω, A is the area of contact and ℓ is the length of the sample between the probes. The resistance was measured with two cylindrical probes. The probes were clamped to fix the distance between them and then made to contact the modified carbon cloth from the sides without piercing through the polymer surface. This way allows the contact between the probes and the polymer without the carbon cloth. Also, the conductivity of the carbon cloth was measured, separately, to be higher than the PEDOT-coated cloth.
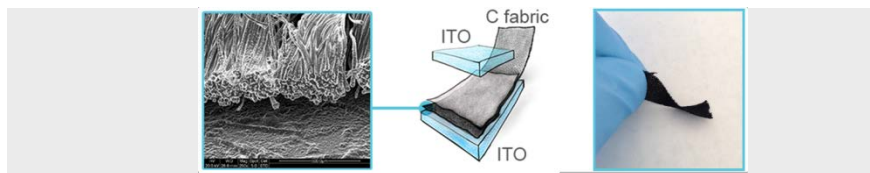
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Keywords: PEDOT • ionic liquid • electropolymerisation • electrocatalysis • flexible electrode

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Layout 2:

FULL PAPER

The electropolymerisation of PEDOT from the ionic liquid butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C$_4$mpyrTFSI) on flexible carbon cloth electrodes using a sandwich cell configuration is reported. Compact films with high doping levels and conductivity are fabricated which demonstrate catalytic activity over a wide pH range for the oxygen reduction reaction which is also tolerant to the presence of methanol. This approach may open the way to electropolymerise other conducting polymers for uses in flexible and wearable devices.

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Electropolymerization of catalytically active PEDOT from an ionic liquid on a flexible carbon cloth using a sandwich cell configuration