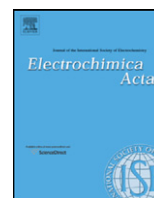




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Electrochemical reduction of graphene oxide in electrically conducting poly(3,4-ethylenedioxythiophene) composite films

Tom Lindfors^{a,*}, Anna Österholm^{a,2}, Jussi Kauppila^b, Markus Pesonen^c

^a Department of Chemical Engineering, Process Chemistry Centre, Laboratory of Analytical Chemistry, Åbo Akademi University, FI-20500 Turku, Finland

^b Turku University Centre for Materials and Surfaces (MATSURF), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, FI-20014 Turku, Finland

^c Physics, Department of Natural Sciences and Center for Functional Materials, Åbo Akademi University, FI-20500 Turku, Finland

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ABSTRACT

Here we show that the graphene oxide (GO) can be electrochemically reduced in composite films of poly(3,4-ethylenedioxythiophene) (PEDOT) and GO. EDOT was electropolymerized in an aqueous GO dispersion at a constant potential resulting in the incorporation of GO in the PEDOT matrix. Scanning electron microscopy (SEM) images revealed that the formed PEDOT–GO films had a layered structure. X-ray photoelectron spectra measured after 10, 20 and 30 min of electrochemical reduction at -0.85 V, verified that the reduction efficiently removed the epoxy and hydroxyl groups from the GO surface. The number of oxygen-containing functional groups decreased considerably already after 10 min of electrochemical reduction and the C:O ratio of the composite films increased with increasing reduction time confirming that GO was successfully reduced in the polymer matrix. In contrast to chemical reduction in 0.15 M NaBH₄, we show that the PEDOT matrix withstands the electrochemical reduction without any degradation in electroactivity. We also studied the effect of pH of the GO dispersion on the subsequent redox behavior of the PEDOT–GO films. Increasing the pH from 2.5 to 4.5 improved the electroactivity of the films and also facilitated film formation probably due to the presence of a higher amount of ionized carboxylic groups on the GO surface. Electrochemical impedance measurements showed that increasing the pH of the GO dispersion resulted in films with a higher redox capacitance. Atomic force microscopy measurements revealed that the electrochemical reduction slightly increased the surface roughness of the composite films. The simple and fully electrochemical synthesis and reduction procedure of the PEDOT–GO films are expected to be useful in the fabrication of interfacial materials for electrochemical all-solid-state devices where it is desirable to have reversible ion-to-electron transduction in combination with high redox capacitance.

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1. Introduction

Electrically conducting polymers (ECPs) can be used as ion-to-electron transducers in potentiometric all-solid-state ion-selective electrodes (ISEs) [1]. In these ISEs, the ECPs serve as intermediate solid-contact (SC) layers between the electrically conducting substrate and the ion-selective membrane (ISM). The ECPs are usually deposited onto the conducting substrate either electrochemically or by solution processing. For obtaining solid-contact

ISEs (SCISEs) with good potential stability, it is essential that the SC material is hydrophobic [2] and that it has a sufficiently high capacitance [3]. It was recently shown that SCISEs made of hydrophobic SC and ISM materials had a very good potential stability [2]. Composites of ECPs and carbon materials often have higher specific capacitances than ECPs and carbon materials alone [4], and therefore, these types of composites could be suitable candidates as intermediate SC materials in SCISEs. In this study, we have first optimized the electropolymerization of composite films of poly(3,4-ethylenedioxythiophene) (PEDOT) and graphene oxide (GO) [5], and then studied the electrochemical reduction of GO incorporated in the PEDOT matrix to determine its influence on the redox capacitance of the PEDOT films.

ECPs are so-called pseudocapacitors, i.e. they store charge, not only in the electrical double layer, but also faradaically in the polymer matrix. Among the ECPs, poly(aniline) (PANI) usually shows the highest specific capacitance as a result of its high doping level [6]. Normally the redox capacitance is higher for nanostructured

* Corresponding author. Tel.: +358 2 215 4419.

E-mail addresses: Tom.Lindfors@abo.fi (T. Lindfors),

Anna.Osterholm@chemistry.gatech.edu (A. Österholm), Jussi.Kauppila@utu.fi (J. Kauppila), Markus.Pesonen@abo.fi (M. Pesonen).

¹ ISE member.

² Current address: Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA, USA.

ECPs because the entire ECP matrix is more accessible for oxidation and reduction due to the more porous film structure. It has been reported that a nanostructured PANI film, with reasonably good cycling stability, exhibited a rather high specific capacitance of 724 F/g [7]. This is only slightly lower than for amorphous hydrated RuO₂ (840 F/g) which is often used in supercapacitors [8]. Because of the nanostructure formation, it is expected that electrochemically polymerized ECP films could exhibit a higher redox capacitance than solution processed films.

Carbon nanotubes (CNTs), graphene and its derivatives typically have lower specific capacitances than ECPs as their capacitance is mainly due to the formation of an electrochemical double layer at the electrode/electrolyte interface. For example, graphene based supercapacitors were reported to have a specific capacitance of 135 F/g active material/chemically modified graphene [9]. Despite their lower capacitances, porous carbon materials usually have good cycling stability and mechanical properties in addition to their high surface areas. Thus, they can improve the mechanical stability and additionally the specific capacitance of the ECP by increasing the electrical conductivity of the carbon-ECP composite materials. For example, the composite of mesoporous carbon and ordered whisker-like PANI had a specific capacitance of 900 F/g [10], whereas it was 1126 F/g for a composite of PANI and reduced GO (RGO) [4].

The pseudocapacitance of PEDOT is lower than for PANI varying between 30 and 170 F/g [6,11–14] depending on the polymerization procedure [6]. Even though PEDOT has usually a lower specific capacitance, it is widely used due to its electrochemical stability in a relatively wide potential window in aqueous solutions and its good environmental stability. In contrast to PANI, the pH insensitivity of PEDOT is an advantage for its use as an ion-to-electron transducer in SCISEs [3]. Composites of PEDOT and CNTs were reported to have a specific capacitance of 160 F/g, good cycling stability over several thousand cycles and high chemical stability in H₂SO₄, KOH and acetonitrile [6]. By substituting CNTs with graphene, the capacitance improved considerably to 374 F/g [15]. Recently, GO was incorporated by electrochemical polymerization in PEDOT films without using any additional dopants or surfactants [5]. The reason for the successful incorporation is that GO flakes carry a negative surface charge when dispersed in water which allows them to serve as counter ions during electropolymerization. The possibility of electropolymerizing PEDOT–GO without using additional dopants is a clear advantage over PANI which has to be electropolymerized in acidified GO solutions resulting in the simultaneous incorporation of acid anions in the PANI matrix. Composite films of PEDOT–RGO have also been electrochemically polymerized in ethanol from a colloidal dispersion of RGO and 3,4-ethylenedioxythiophene (EDOT) [16]. Lightly sulfonated RGO [17], PEDOT–GO hydrogels [18] and PEDOT–graphene composites have been synthesized by chemical oxidative polymerization from an aqueous media containing polystyrene sulfonate as stabilizing agent [15]. Furthermore, stable aqueous dispersions of PEDOT nanorods have been prepared with GO as stabilizing agent [19].

Chemical reduction with hydrazine [20,21] is often used to reduce GO in ECP–GO composites [21–23]. Reduction of GO in PANI–GO composites has also been carried out in strongly alkaline NaOH [4,22]. As the reduction with hydrazine is accompanied by nitrogen incorporation into the RGO structure [21] and hydrogen gas accumulation on the ECP–GO film surfaces, the electrochemical reduction of GO seems to be, not only, a more practical reduction method but also cleaner, safer [23], and faster than the reduction using milder reductants such as L-ascorbic acid [24]. Graphene oxide in electrochemically prepared PPy–GO films has been electrochemically reduced using cyclic voltammetry or constant potential in KCl [25], Na₂SO₄ [26] and in phosphate buffer solution (PBS) at pH = 7.4 [27].

Here we present a simple and fully electrochemical route for the polymerization and reduction of PEDOT–GO films. The electropolymerization was carried out in aqueous GO dispersions and the electrochemical reduction of PEDOT–GO was carried out in 0.1 M KCl at a constant potential of –0.85 V. The removal of oxygen-containing functional groups from the GO surface as a function of reduction time was followed by X-ray photoelectron spectroscopy (XPS). The electrochemically reduced PEDOT–GO composites were also characterized by cyclic voltammetry (CV), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The electrical conductivities were determined with the four-probe technique. Electrochemical impedance spectroscopy (EIS) was used to evaluate the influence of the reduction time on the areal capacitance of the PEDOT–GO films.

2. Experimental

2.1. Graphite oxide

Graphite oxide was synthesized from graphite with a modified Hummers' method [28] and has been described in detail elsewhere [5]. The final pH of the dispersion was 2.5 and the concentration of graphite oxide was approximately 4.4 mg/ml. The C:O ratio of solution cast films of GO was determined to be 2.28.

2.2. Electrochemical polymerization of PEDOT–GO

The electrochemical polymerizations were performed using an Autolab PGSTAT20 equipped with GPES software and an impedance module (FRA). GC and tin-oxide (TO) glass were used as working electrodes and a GC rod as the counter electrode. The GC working electrodes were polished with 0.3 and 0.05 μm Al₂O₃ and the TO glasses were rinsed with deionized water and ethanol, and then cleaned in a Harrick plasma cleaner. All potentials are given vs. the Ag/AgCl/3 M KCl reference electrode. The EDOT monomer was used as received and 0.01 M EDOT was added to an aqueous graphite oxide dispersion which was then ultrasonicated for 45 min to exfoliate the graphite oxide to GO. All measurements were performed in oxygen-free solutions which were blanketed with N₂ gas during the measurements. The PEDOT films were electrodeposited at the constant potentials of 0.94, 0.97 and 1.05 V either on GC ($A = 7.1 \text{ mm}^2$) or TO ($A = 120 \text{ mm}^2$). GO has a negative surface charge even at low pH [20], and therefore it is able to serve as the counter ion in the electropolymerization of PEDOT in GO dispersions [5]. The influence of the pH of the GO dispersion was studied by electropolymerizing PEDOT–GO in GO dispersions with pH = 2.5 and 4.5. The pH of the latter dispersion was adjusted with NaOH.

For the cyclic voltammetric, XPS and SEM measurements, the PEDOT–GO films were deposited on GC ($Q = 0.0352 \text{ C}; 0.5 \text{ C cm}^{-2}$). For SEM, AFM, and the conductivity measurements, the composite films were deposited on TO ($Q = 0.750 \text{ C}; 0.625 \text{ C cm}^{-2}$). Potentiostatic polymerization to a constant charge ensures that similar amounts of polymer are deposited each time. AFM measurements showed that the PEDOT–GO films on TO had a film thickness of 0.93–0.95 μm. Potentiostatic polymerization also allows for a better control of the polymerization reaction since the safe potential range is very limited in the aqueous electrolytes. For the reduction studies in sodium borohydride (NaBH₄), PEDOT was electropolymerized at 0.92 V ($Q = 0.0352 \text{ C}; 0.5 \text{ C cm}^{-2}$) in the presence 0.1 M sodium polystyrene sulfonate (NaPSS).

2.3. Electrochemical reduction of GO in PEDOT–GO films

The electrochemical reduction was carried out in oxygen-free 0.1 M KCl by keeping the potential at –0.85 V (vs. Ag/AgCl/3 M KCl) for 10, 20 or 30 min. In some experiments, the electrochemical

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