

Article

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# Synthesis and Characterization of Diazonium Salts with PEG Appendages and Resulting Films Afforded by Electrodeposition for use as a Battery Separator Material

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ABSTRACT: The coating of three dimensional nanostructured electrodes is a significant challenge for the future of many energy storage devices and, if successful, could profoundly increase battery power. The synthesis of a new class of monomers that can be electrochemically polymerized is a key first step to affording a conformally coated, nanoscale lithium-ion battery separator and is presented herein. Characterization of the monomers was accomplished through NMR and IR spectroscopy. Planar films electrodeposited from the monomers were characterized using redox probe experiments and impedance spectroscopy. The films are chemically grafted to the underlying substrate, conformal, pinhole free, less than 10 nm thick and exhibit electrical resistivity values as high as 28,000 M $\Omega$ /cm.

#### **INTRODUCTION**

Energy demands are steadily increasing worldwide. Although fossil fuels have been used to supply the demand via combustion, the effects on our environment cannot be overlooked. This has led to a demand for greener energy sources, although many of these sources (such as wind and solar) are intermittent. Because of this, there is a parallel need for better energy storage devices that can charge and discharge rapidly. Lithium-ion batteries are energy storage systems that are currently used to power mobile electronic devices such as cell phones and laptops. High power density lithium-ion batteries are even used to power electric vehicles and power tools, but higher power densities are still desired in order to reduce charge time and increase possible use in high power applications. Furthermore, with enough electric vehicles with high power density batteries, the idea of a wide spread smart grid would become economically feasible.

Lithium-ion batteries store 2-3 times more energy per weight than nickel-metal-hydride rechargeable batteries.<sup>1</sup> Although lithium-ion batteries are revolutionizing technology, improvements are needed to keep up with the world's ever increasing energy storage demands. Current battery technology uses layered thin films, which have low surface areas due to their two dimensional geometry. The films are microns thick, enabling modest power densities at best.<sup>2,3</sup> To maximize the power density, nanoscale three-dimensional (3D) battery structures need to be fabricated. A nanoscale 3D structure would greatly increase the interfacial surface area of the battery, and therefore increase charge/discharge rates (current) and thus, pow-ACS Paragon Plus Environment

er. In fact, 3D nanostructured cathodes and anodes have already been fabricated.<sup>4</sup>

The major challenge in this field is the development of a conformally coated, nanoscale material that can perform as a separator and an electrolyte between high surface area electrodes in an energy storage device. This problem has been a major challenge for several reasons. First, nanoscale materials are fragile and hard to work with. The separator cannot be made independently of the anode or cathode since assembly would be essentially impossible with such a thin material; therefore, the separator needs to be fabricated in situ. Second, the separator needs to conformally coat the 3D nanostructure. Promising work has been done using atomic layer deposition to coat electrodes with a thin ceramic layer (Al<sub>2</sub>O<sub>3</sub>) to minimize solvent decomposition and solid electrolyte interface (SEI) formation, but the method is time-intensive and not yet cost effective for commercial use.<sup>5,6</sup> Third, controlling the thickness of the separator can be difficult, especially for films only 10s of nanometers thick. For polymerizations, this usually requires a self-limiting polymerization mechanism to avoid incomplete or non-uniform film coverage. Fourth, regardless of thickness, the separator must be able to handle the physical stresses that occur during charging/discharging wherein significant expansion/contraction processes in the electrodes can occur. If the separator cannot withstand these stresses, electrical shorts between the electrodes in the device will develop. Fifth, the separator has to be electronically insulating when less than 100 nm thick, but also must be ionically conducting. These challenges are great and progress in the field of nanoscale separators has been slow.

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59 60 Electrodeposition of a self-limiting polymer-based separator can, in principle, address all of these issues, assuming the monomer is chosen such that it affords an ionically conducting and electronically insulating film. Electrodeposition as a synthetic technique is ideal because it allows for conformal coating onto 3D structures employing simple equipment. Using either the cathode or anode as the active electrode, the separator can be deposited directly onto the electrode surface, minimizing handling and the possibility of physical damage. Choosing a self-limiting electrodeposition polymerization process affords a conformal coating with a very thin and uniform film.<sup>7</sup> As the polymerization occurs, the electrode becomes electronically insulating, leading to self-limiting behavior. In other words, polymerization occurs more rapidly over regions of highest electrical conductivity (i.e. bare surfaces), which results in a complete, uniform modification of the conducting surface.

The use of a polymer-based separator has appeal because viscoelastic polymers can accommodate the stresses associated with expansion and contraction of the electrodes, as previously mentioned.<sup>8</sup> Polymers with appropriate viscoelastic properties can be viewed simultaneously as viscous liquids and elastic solids, allowing for movement of the polymer when a stress is applied. This behavior is in stark contrast to ceramic based separators which are hard and brittle.<sup>9</sup> In theory, employing a viscoelastic polymer should allow the separator to maintain a physical separation between cathode and anode, while maintaining good separator interfacial contact to each, even during the expansion/contraction processes.

In terms of designing polymer films with the desired properties, the monomer choice is a critical factor to consider. Films must conduct ions, specifically Li<sup>+</sup>, and must also be electronically insulating. Ideally, the monomer should graft to the electrode surface, increasing the intimate contact between the polymer and the electrode, as well as the mechanical robustness of the film, thus decreasing the likelihood of shorts. Herein we describe an approach focused on achieving nanoscale polymer films that can be grafted to the electrode surface. Diazonium salts were chosen because they have been shown to graft to electrode surfaces and exhibit great self-limiting deposition characteristics.<sup>10-12</sup> In addition, diazonium salts can be deposited out of acidic aqueous conditions ( $pH \le 3$ ) if the monomers are soluble.12 The grafting of diazonium salts involves a 1e- reduction of the diazonium functional group followed by loss of N<sub>2(g)</sub> and phenyl radical formation.<sup>12</sup> The phenyl radical then reacts with the electrode surface to form a chemical bond. Diazonium salts have been electrografted onto many electrode materials such as carbon, metals, oxides, semiconductors, and polymers.12

To test the hypothesis that a diazonium-based film could be grafted, be nanoscale in thickness, and function as a lithium-ion battery separator material, four monomers were synthesized that all had diazanium functionalities. The secondary hypothesis of this research is that monomer structure, specifically, PEG tail length and position on the benzene ring will influence ionic conductivity and electrical resistivity of the resulting polymer film.

To evaluate the deposited films, thickness measurements were attempted using profilometry and scanning electron microscopy imaging. The extent of grafting was evaluated by impedance spectroscopy on sonicated samples. Impedance spectroscopy was further used to determine ionic and electronic conductivities across thin film (2D) samples. Table 1 summarizes criteria that were used to judge the diazonium-based films along with the best reported values found in the literature for comparison.<sup>13-15</sup>

Three of the four monomers have never been reported in the literature and none have been used in lithium-ion battery separator applications. The monomers are: 4-(2-(2-(2-methoxy)ethoxy)ethyl)benzene diazonium tetrafluoroborate (p-triethoxy, synthesized by Bahr et al.<sup>16</sup>), 2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzene (o-triethoxy), diazonium tetrafluoroborate 4-(polyethylene glycol)benzene diazonium tetrafluoroborate (p-PEG), and 2-(polyethylene glycol)benzene diazonium tetrafluoroborate (o-PEG).<sup>16</sup> The p-PEG, o-PEG, ptriethoxy, and o-triethoxy short hand notation will be used for the remainder of this paper. The structures are provided in Figure 1. We demonstrate that the monomer structure influences the electrical resistivity of the resulting films through PEG tail length and position on the benzene ring. The films described herein are extremely thin (3-10 nm), conformally coat the electrodes, and exhibit resistivity values as high as  $28000 \text{ M}\Omega/\text{cm}$ .

#### EXPERIMENTAL

#### CHEMICALS

Dichloromethane was purged with nitrogen and dried over 4 Å molecular sieves before storing in a glove box. All other reagents were obtained commercially and used as received.

#### APPARATUS

Cyclic voltammetry (CV) and chronoamperometry experiments were carried out using a CH Instruments Electrochemical Workstation Model 750 D. Impedance measurements were carried out using a GAMRY Instruments Reference 3000 potentiostat/galvanostat. Acetonitrile (99.9 %) was purchased from Macron Chemicals and used as received. Nuclear magnetic resonance spectroscopy was carried out using a Varian Mercury-Inova 300 NMR Spectrometer Systems. Infrared spectroscopy (IR) measurements were performed using Nicolet 380 FT-IR spectrophotometer and the samples were prepared in KBr pellets.

### SYNTHESIS

All syntheses were modified from a publication by Bahr *et al.* who reported the synthesis of p-PEG.<sup>16</sup> For the diazotization reaction, the method published by Tang *et al.* was found to be more repeatable, yielded more product, and the products were of a higher purity according to NMR than the method published by Bahr *et al.*<sup>16,17</sup> For increased purity, a silica column was employed on the o-PEG salt (14, *vide infra*) with 5 % MeOH in CH<sub>2</sub>Cl<sub>2</sub> (by volume) as the eluent. Each diazonium salt synthesis involves 4 steps starting from an alcohol, see Scheme 1. This reaction scheme is therefore useful for many starting materials as long as an alcohol group is present.

2-(2-(2-Methoxyethoxy)ethoxy)ethylp-toluenesulfonate (1) was synthesized using the methodpublished by Bahr *et al.*<sup>16</sup> A clear and colorless oil wasafforded at 93 % yield. 'H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.80 (d, 2H),7.35 (d, 2H), 4.14 (t, 2H), 3.68 (t, 2H), 3.64 to 3.54 (m, 6H),3.52 (t, 2H), 3.37 (s, 3H), 2.49 (s, 3H).

**Poly(ethylene glycol) p-toluenesulfonate (2)** was synthesized following the method published by Bahr *et al.*<sup>16</sup> Polyethylene glycol (Mn = 400 g/mol) was used instead of tri(ethylene glycol)monomethyl ether. A clear and colorless oil was afforded at 82 % yield. 'H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.61 (d, 2H), 7.15 (d, 2H), 3.95 (t, 2H), 3.33 to 3.53 (m, 16H), 2.24 (s, 3H).

**4-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)nitrobenzene** (3) was synthesized using the method published by Bahr *et al.*<sup>16</sup> One modification was made, that being 5 % methanol in dichloromethane (by volume) was used as the eluent for the column chromatography. A clear and light yellow oil was afforded at 82 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.18 (d, 2H), 6.99 (d, 2H), 4.23 (t, 2H), 3.90 (t, 2H), 3.80 to 3.60 (m, 6H), 3.55 (t, 2H), 3.38 (s, 3H).

**2-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)nitrobenzene** (4) was synthesized following the method published by Bahr *et al.*; except o-nitrophenol was used instead of pnitrophenol and 5 % methanol in dichloromethane (by volume) was used as the eluent for the column chromatography.<sup>16</sup> A yellow oil was afforded at 82 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.81 (d, 1H), 7.51 (t, 1H), 7.12 (d, 1H), 7.03 (t, 1H), 4.27 (t, 2H), 3.91 (t, 2H), 3.76 (t, 2H), 3.65 (m, 4H), 3.55 (t, 2H), 3.38 (s, 3H).

**4-(Polyethylene glycol)nitrobenzene** (5) was synthesized following the method published by Bahr *et al.*; except polyethylene glycol was used instead of tri(ethylene glycol)monomethyl ether and 5 % methanol in dichloromethane (by volume) was used as the eluent for the column chromatography.<sup>16</sup> A yellow oil was afforded at 56 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.25 (d, 2H), 7.02 (d, 2H), 4.26 (t, 2H), 3.93 (t, 2H), 3.75 (m, 4H), 3.75 to 3.62 (m, 14H). **2-(Polyethylene glycol)nitrobenzene (6)** was synthesized following the method published by Bahr *et al.*; except polyethylene glycol was used instead of tri(ethylene glycol)monomethyl ether, o-nitrophenol was used instead of p-nitrophenol, and 5 % methanol in dichloromethane (by volume) was used as the eluent for the column chromatography.<sup>16</sup> A yellow oil was afforded at 63 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.84 (d, 1H), 7.52 (t, 1H), 7.12 (d, 1H), 7.03 (t, 1H), 4.27 (t, 2H), 3.91 (t, 2H), 3.74 (m, 4H), 3.74 to 3.60 (m, 20H).

**4-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)aniline** (7) was synthesized using the method published by Bahr *et al.*<sup>16</sup> "Acidic ethanol" used in the synthesis was afforded by adding 2 mL conc. HCl to 50 mL EtOH which was the same for all the aniline syntheses. A reddish-brown oil was afforded at 92 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.78 (d, 2H), 6.73 (d, 2H), 4.08 (t, 2H), 3.85 (t, 2H), 3.79-3.63 (m, 6H), 3.59 (t, 2H), 3.41 (s, 3H). IR (neat) 3432, 3356, 3233, 2876, 1630, 1513, 1456, 1351, 1238, 1107, 943, 826 cm<sup>-1</sup>.

**2-(2-(2-(2-Methoxy)ethoxy)ethyl)aniline** (8) was synthesized following the method published by Bahr *et al.;* except compound **4** was used as the starting material instead of compound **3**.<sup>16</sup> A reddish-brown oil was afforded at 94 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.85 (m, 4H), 4.17 (t, 2H), 3.84 (t, 2H), 3.73 (t, 2H), 3.68 (m, 4H), 3.58 (t, 2H), 3.40 (s, 3H). IR (neat) 3470, 3360, 3202, 2877, 1619, 1511, 1461, 1352, 1281, 1223, 1118, 947, 851, and 747 cm<sup>-1</sup>.

**4-(Polyethylene glycol)aniline** (9) was synthesized following the method published by Bahr *et al.;* except compound **5** was used as the starting material instead of compound **3**.<sup>16</sup> A reddish-brown oil was afforded at 88 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.80 (m, 4H), 4.04 (t, 2H), 3.82 (m, 4H), 3.75 to 3.55 (m, 30H). IR (neat) 3440, 3356, 2872, 1636, 1511, 1465, 1356, 1294, 1244, 1118, 943, 834, and 730 cm<sup>-1</sup>.

**2-(Polyethylene glycol)aniline (10)** was synthesized following the method published by Bahr *et al.;* except compound **6** was used as the starting material instead of compound **3**.<sup>16</sup> A light brown oil was afforded at 98 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.83 (m, 4H), 4.16 (t, 2H), 3.85 (t, 2H), 3.73 (m, 4H), 3.72 to 3.60 (m, 28H). IR (neat) 3465, 3361, 2872, 1619, 1507, 1461, 1352, 1281, 1223, 1123, 947, 843, and 742 cm<sup>-1</sup>.

4-(2-(2-(2-(2-Methoxy)ethoxy)ethyl)benzene diazonium tetrafluoroborate (11; p-triethoxy) was synthesized using the method published by Tang *et al.*<sup>17</sup> A reddish-brown tar was afforded at 95 % yield. <sup>1</sup>H NMR (dacetone)  $\delta$ : 8.75 (d, 2H), 7.55 (d, 2H), 4.55 (t, 2H), 3.92 (t, 2H), 3.67 (t, 2H), 3.58 (m, 4H), 3.46 (t, 2H), 3.27 (s, 3H). IR (neat) 3115, 3060, 2893, 2250, 1582, 1490, 1455, 1340, 1286, 1072, 938, 847, and 742 cm<sup>-1</sup>.

**2-(2-(2-(2-Methoxy)ethoxy)ethyl)benzene diazonium tetrafluoroborate (12; o-triethoxy)** was synthesized following the method published by Tang *et al.*<sup>17</sup> A reddish-brown tar was afforded at 84 % yield. <sup>1</sup>H NMR (d-acetone)  $\delta$ : 8.59 (d, 1H), 8.31 (t, 1H), 7.82 (d, 1H), 7.54 (t, 1H), 4.75 (t, 2H), 4.02 (t, 2H), 3.72 (t, 2H), 3.62 (m, 4H), 3.51 (t, 2H), 3.32 (s, 3H). IR (neat) 3110, 2885, 2267, 1594, 1569, 1490, 1452, 1352, 1310, 1085, 939, 851, and 768 cm<sup>-1</sup>.

4-(Polyethylene glycol)benzene diazonium tetrafluoroborate (13; p-PEG) was synthesized following the method published by Tang *et al.*<sup>17</sup> A reddish-brown tar was afforded at 78 % yield. <sup>1</sup>H NMR (d-acetone) δ: 8.80 (d, 2H), 7.60 (d, 2H), 4.58 (t, 2H), 3.93 (t, 2H), 3.67 to 3.47 (m, 30H). IR (neat) 3110, 2885, 2258, 1586, 1511, 1452, 1344, 1290, 1089, 955, 847, and 734 cm<sup>-1</sup>.

**2-(Polyethylene glycol)benzene diazonium tetrafluoroborate (14; o-PEG)** was synthesized following the method published by Tang *et al.*<sup>17</sup> A reddish-brown tar was afforded at 27 %, the low final yield was due to column purification. <sup>1</sup>H NMR (d-acetone)  $\delta$ : 8.61 (d, 1H), 8.30 (t, 1H), 7.82 (d, 1H), 7.54 (t, 1H), 4.76 (t, 2H), 3.98 (t, 2H), 3.72 to 3.52 (m, 32H). IR (neat) 3110, 2885, 2267, 1590, 1569, 1494, 1356, 1297, 1089, 951, 838, 767, and 734 cm<sup>-1</sup>

#### ELECTROCHEMICAL TECHNIQUES

Cyclic voltammetry and film depositions (chronoamperometry) were performed using a glass cyclic voltammetry cell composed of a working and reference compartment connected by a Luggin capillary. The working compartment was degassed with nitrogen for 5 minutes to remove oxygen from the compartment prior to taking a CV or performing a deposition. The electrolyte solution was composed of 0.1 M TBAPF<sub>6</sub> in acetonitrile. The monomer concentration was chosen to be 10 mM, which was determined to be an appropriate concentration for the complete modification of the electrode surface. At low concentrations, ca. 1 mM, it has been reported (for other monomers) that surface modification does not occur.<sup>18</sup> After each deposition, the modified glassy carbon (GC) electrode was sonicated for 15 minutes in neat acetonitrile to remove any non-grafted components in the film. Impedance spectroscopy was performed using a soft contact method published by Rhodes et al.7 The diazonium modified GC electrode was lowered into a pool of In/Ga. Gold evaporated onto glass was used as a plate to hold the In/Ga and provide good electrical contact to the eutectic. The frequency range used was 1 Hz to 1 MHz with a voltage amplitude of 10 mV.

#### **RESULTS AND DISCUSSION**

Monomer structure is an important consideration for the physical properties of the resulting polymer film. All of the monomers chosen for this study have a diazonium "head" that can undergo grafting to multiple types of surfaces.<sup>12,19</sup> Also, the diazonium functionality allows for direct reduction of the monomer onto the electrode surface without the use of a radical initiator, and should result in self-limiting characteristics which produce very thin films.<sup>10-12</sup>

The "tail" of connecting ethylene glycol repeating units was chosen to incorporate ion mobility into the resulting polymer film. Two different tail lengths (triethoxy and PEG) were synthesized to evaluate if tail length affected ionic conductivity or electrical resistivity. The position of the tail on the benzene ring was also investigated for the same reasons. One hypothesis was that if the tail and diazonium functional groups are in the para-position relative to each other, the benzene rings might pack more tightly onto the electrode surface leading to a film with higher density. Steric hindrance has been shown to influence packing density in a predictable matter for self-assembled monolayers.<sup>20,21</sup> A denser film should afford a lower ionic conductivity and a greater electrical resistivity. Furthermore, with a PEG-type tail in the para-position to the grafting site, lithium ion transport into the PEG region might be difficult. In contrast, with a tail in the orthoposition, the PEG moiety would be directly adjacent to the electrode surface and not blocked by the benzene rings, potentially allowing for better ion mobility very near the electrode surface. Having the PEG tail in the ortho-position should also lead to a less dense film because the benzene rings should not be able to pack as tightly onto the electrode surface for steric reasons. To summarize, the secondary hypothesis of this research is that monomer structure, specifically, PEG tail length and position on the benzene ring will influence ionic conductivity and electrical resistivity of the resulting polymer film.

Infrared spectroscopy was used to identify key functional groups during the synthesis of the diazonium monomers. The nitro stretching peak (ca. 1500 cm<sup>-1</sup>) was difficult to identify prior to the hydrogenation step due to multiple peaks near 1500 cm<sup>-1</sup> (the peak nearest to 1500 cm<sup>-1</sup> was present for each intermediate product).<sup>22</sup> IR was successfully used to identify the amine stretching frequency (3250-3500 cm<sup>-1</sup>) after hydrogenation of the nitrobenzene confirming successful reduction to the aromatic amine.<sup>23</sup> After the diazotizing reaction, the amine peaks were greatly suppressed and a sharp peak at 2260 cm<sup>-1</sup> was present, consistent with the presence of the diazonium functional group.<sup>24</sup>

Cyclic voltammetry was used to determine the reduction potentials of the diazonium salts (Figure 2). All diazonium salts exhibit a broad irreversible reduction peak, common for diazonium salts.<sup>11,25</sup> All peaks occur in the range of -0.5 to -0.9 V vs SSCE, therefore the depositions were performed at -1.0 V vs SSCE. As seen in Figure 2, the o-PEG does show an additional wave at ca. -1.6 V vs SSCE, most likely due to an impurity present that we were not able to identify. This was surprising since o-PEG was the only diazonium salt purified by column chromatography; however, by depositing at -1.0 V electrochemical reactions with the impurity were likely avoided. Ortho substituted diazonium salts have more negative reduction potentials likely due to the proximity of the electron-donating ether group to the diazonium. In general, electron-donating groups are expected to shift the reduction potential to more negative values. The concentration of diazonium

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59 60 salt was the same for all the cyclic voltammograms, but the peak current in the CV varied significantly for the monomers. Differences in the self-limiting nature of the reduction for each of the monomers is likely the reason for the different peak heights. Comparing the four diazonium salts, there is a strong correlation between lower initial current in the voltammogram and lower final current at the end of the deposition.

Chronoamperometry was used to deposit the diazonium based films onto a GC electrode. Deposition curves can be seen in Figures 3-6. Insets show the current decrease on a log scale for better comparison. After 15 minutes the current dropped at least 2 orders of magnitude in all cases and as much as 5 orders of magnitude for p-PEG. This demonstrates the remarkable self-limiting nature of diazonium-based films. As expected, para substituted diazonium salts showed better shutoff current (vide infra) as well as the best self-limiting reduction. Again, this is likely due to the ability of the benzene rings of the diazonium to pack more tightly onto the electrode surface for steric reasons. The PEG based monomers also exhibited better self-limiting behavior (relative to the shorter, methoxyterminated monomers), likely due to steric exclusion of fresh monomer to the electrode surface by the longer chain tails.

After each deposition, the coated GC electrode was sonicated in neat acetonitrile for 15 minutes to remove any non-grafted components from the film before any characterization. Similar treatment of non-grafted films typically removes the film or at least introduces "bare patches" which were not evident in the impedance tests or redox shut-off experiments (*vide infra*).

Impedance spectroscopy was used to determine the electronic resistance and ionic conductivity of the films. Open circuit potential (OCP) was measured for 30 seconds prior to impedance measurements and impedance measurements were taken about OCP. Over 30 seconds, sample OCP varied less than 50 µV and was considered stable. None of the films exhibit a diffusional (Warburg) tail at low frequency in the Nyquist plot (Figure 7); hence, none of the films exhibited ionic conductivity.<sup>26,27</sup> This is not surprising since the as-deposited films should be void of any ions. Attempts to measure impedance with plasticized films (1.0 M LiClO<sub>4</sub> in ethyl carbonate/dimethyl carbonate (70/30 by volume) were unsuccessful because an oxide layer formed instantly on the In/Ga eutectic upon contact with the plasticizer. However, ion permeation through the film is suggested by redox probe experiments (vide infra, Figures 8-11). A depressed semicircle at medium to high frequency can be modeled with a resistor in parallel with a capacitor, a simple Randles circuit. The model can be attributed to the film resistance that is in parallel with the film capacitance. The semicircle is depressed which is likely due to leaky or imperfect interfacial capacitance.<sup>27</sup> Resistance values for the films can be found in Table 2. The values are all in the  $k\Omega$  range, which is comparable to nanoscale poly(phenylene oxide)

type films reported by Rhodes *et al.*<sup>7</sup> Para-substituted films exhibit higher resistances than their ortho counterpart consistent with the hypothesis that the benzene rings should pack more tightly. Polymers formed from the shorter tail monomers in each pair also had the higher resistance, consistent with less steric hindrance and tighter packing onto the electrode surface.

The thickness of the films was calculated using the capacitance values obtained from the impedance spectroscopy. Using the equation below for capacitance, the thickness was calculated.

$$C = \kappa \varepsilon_0 A/D$$

In the equation above, C = capacitance (F),  $\kappa = dielectric$ constant,  $\varepsilon_0$  = permittivity of free space (F/cm), A = area of electrode ( $cm^2$ ), and D = film/dielectric thickness (cm). The dielectric constant of the films was estimated to be  $2.7 \pm 0.2$ , which is an average of 4 dielectric constants of polymer films with similar molecular architectures to the ones prepared here: poly(phenylene oxide), 2.59; polycarbonate, 2.92; an azopolymer with aliphatic and aromatic fragments, 2.5; poly(phenylene oxide), 2.77.7,28,29 The area of the electrode was constant throughout all experiments and was equal to 0.71 cm<sup>2</sup>. The capacitance values were determined using the same fit as the resistance values, given in Table 1. All films were extremely thin, as expected based on their self-limiting property. Based on the above calculation, three films (o-triethoxy, p-triethoxy, and p-PEG) were estimated to be 3 nm thick while o-PEG was estimated to be 10 nm thick. Attempts to measure the thickness of the films using profilometry or SEM imaging were unsuccessful because the film thicknesses were below the accurate detection limits of the instruments.

Using the calculated thicknesses and the measured resistances, the resistivities were calculated for all four films (Table 2). All films exhibit high resistivity values (1200-28000 M $\Omega$ /cm), consistent with being insulators.<sup>30</sup> It is difficult to compare these values with those of commercially available separators because those resistivity values are typically reported as a Gurley number, which is the permeability of the separator to air.<sup>31</sup> Air permeability is proportional to the resistivity of a separator, but for a given morphology (which must be known).<sup>31</sup> Since the morphology of the diazonium based films reported here is not known, a Gurley number could not be calculated. However, for this application the more relevant number is the breakdown voltage of the films, Attempts to perform solid-state linear sweep voltammetry on the films (not shown) resulted in a breakdown of all of the films near 1.5 V (using the same experimental procedures as impedance measurements described previously, however with the reference electrode shorted to the auxiliary electrode). This implies that although the films described here have high electrical resistivities, they are not thick enough to hold up to the voltages of typical lithium cells (ca. 3.2 V). Future work will involve modifying the electrochemical polymerization conditions to afford significantly thicker films, while maintaining good grafting and high electrical resistivities.

In order to determine if the deposited films contained pinhole defects or exhibited incomplete coverage, ferrocene and 1, 1', 3, 3'-tetra-t-butyl ferrocene were used as probe molecules in a redox shut-off experiment. The ferrocene probes showed a small irreversible anodic peak for all four films (Figures 8-11). This data alone was inconclusive with regards to the presence or absence of pinholes, because the small current measured could also be attributed to the diffusion of ferrocene through the polymer film. Consequently, 1, 1', 3, 3'-tetra-t-butyl ferrocene was also examined. In contrast to the unsubstituted ferrocene, the bulkier 1, 1', 3, 3'-tetra-t-butyl ferrocene yielded essentially no current on the modified GC with the exception of the o-triethoxy film (Figure 11). If the two ferrocenes were accessing the electrode surface through pinholes significantly larger than molecular dimensions, the ferrocene and 1, 1', 3, 3'-tetra-t-butyl ferrocene probe molecules would give similar electrochemical responses. The differences in the voltammetry of the two differently sized ferrocene molecules is clear evidence that they are permeating the films via pathways that are of molecular dimensions, such as diffusion through the films, as opposed to directly accessing the electrode surface through pinholes. Interestingly, although o-triethoxy films were more electrically resistive than o-PEG, the probe experiment suggests o-triethoxy is better at allowing molecules, and possibly ionic species, to transport to the electrode surface. Further evidence for this is seen in the deposition curves, which show worse shut-off/blocking effects for otriethoxy. The data suggests that o-triethoxy-like polymers may well be more suitable as a separator material for ionic transport reasons, but would also require the thickest film due to its lower electrical resistivity. The fact that ferrocene was able to reach the electrode surface and oxidize, for all films, is noteworthy. This suggests that transport of molecules (and possibly ions) through the film is possible and that there is a size dependency to the transport that could be of some importance in applications that require ionic permeability of these films, such as a separator in a lithium-ion battery.

Comparing ortho vs. para substitution in Figures 8-11, the data suggests that para substituted films are better at blocking the electrode from probe molecules than the ortho substituted films are. As anticipated, with the tail in the ortho position transport of molecules through the film to the electrode is facile, which is consistent with our hypothesis about the relative ability of the benzene heads to pack. Furthermore, assuming the site of attachment is at the original position of the diazonium group, the ortho position forces the PEG tail to be directly adjacent to the electrode surface, possibly facilitating molecule and ion movement very near the electrode surface.

Finally, glass transition temperature  $(T_g)$  is also an important consideration for a separator material because the

ionic conductivity will be very low as the polymer loses chain mobility. Due to the extremely thin nature of the diazonium-based films, as well as the fact that they are robustly grafted to the electrode surface, it was not possible to isolate a large enough sample size for differential scanning calorimetry.

#### CONCLUSION

A new class of monomers with a diazonium functional group was successfully synthesized and characterized. The monomers have a diazonium head group that can undergo reductive grafting to electrode surfaces and also leads to self-limiting polymerization.

The original hypothesis of this research was that diazonium-based monomers could be electrochemically deposited onto an electrode surface and would be chemically grafted to the surface. Due to the self-limiting behavior of such processes, the expectation was that the films would be nanoscale in thickness and could serve as a platform coating to function as a lithium-ion battery separator and electrolyte material. Each monomer proposed was successfully electrochemically polymerized to give very uniform, conformal and pin-hole-free films. The fact that these films were not removed by post-polymerization sonication suggests that the films are indeed grafted to the electrode. Impedance spectroscopy has provided electronic conductivities of dry films in air. The monomer structure influences electrical resistivity through PEG tail length and position on the benzene ring. The films were extremely thin (3-10 nm) and exhibited resistivity values as high as 28000 M $\Omega$ /cm. Films afforded from parasubstituted diazonium salts exhibit higher resistivity values than ortho substituted salts, and blocked the electrode better during redox shut-off experiments. Therefore para substitution decreases transport (probe molecules or monomer) to the electrode surface but increases electrical resistivity. In other words, ortho substitution appears to facilitate mobility through the film while para substitution increases electrical resistivity of the film. While it was not possible to obtain ionic conductivities of plasticized, ion-doped films, redox-shutoff experiments confirm the lack of pinholes larger than molecular dimensions and the ability of small molecules (i.e., ferrocene) to permeate through the films. Table 3 summarizes the criteria used to evaluate these diazonium-based films in the context of how they might perform as lithium-ion battery separators.

Finally, increasing the thickness of the films is still desired as this would increase the voltage window for operation. The films described here constitute a first step toward developing a nanoscale lithium-ion battery separator material that undergoes grafting to the electrode surface. These are critical components in the conformal coating of a three-dimensional electrode surface.



Figure 1. Monomer structures. From top to bottom: p-triethoxy, o-triethoxy, p-PEG, o-PEG.



Figure 2. Cyclic voltammograms for all four diazonium salts; CVs were taken in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, scan rate = 100 mV/sec, the glassy-carbon electrode was polished using 0.3  $\mu$ m  $\beta$ -alumina on a polishing pad before each scan.



Figure 3. Deposition curve for 2-(polyethylene glycol)benzene diazonium tetrafluoroborate (o-PEG). Inset shows current on a log scale.



Figure 4. Deposition curve for 4-(polyethylene glycol)benzene diazonium tetrafluoroborate (p-PEG). Inset shows current on a log scale. The noise is due to very low current, which was near the limitations of the potentiostat.





Figure 6. Deposition curve for 4-(2-(2-(2-methoxy)ethoxy)ethoxy)benzene diazonium tetra-fluoroborate (p-triethoxy). Inset shows current on a log scale.



Figure 7. Nyquist plotted impedance data with fits for all four diazonium-based films deposited.



Figure 8. Cyclic voltammograms from ferrocene and 1,1',3,3'-tetra-t-butyl ferrocene probe experiments for p-PEG film.





Figure 9. Cyclic voltammograms from ferrocene and 1,1',3,3'-tetra-t-butyl ferrocene probe experiments for o-PEG film.



Figure 10. Cyclic voltammograms for ferrocene and 1,1',3,3'-tetra-t-butyl ferrocene probe experiments for p-triethoxy film.

#### **Chemistry of Materials**



SCHEMES



Scheme 1. Reaction scheme used to synthesize diazonium salts starting from an alcohol. The reaction is applicable to many alcohols.<sup>16, 17</sup>

Figure 11. Cyclic voltammograms for ferrocene and 1,1',3,3'-tetra-t-butyl ferrocene probe experiments for o-triethoxy film.

#### TABLES

Table 1. A summary of the physical properties that were used as criteria to judge diazonium-based films. Included are ideal values along with some of the best reported values in literature.

Physical Property	Ideal	Reported in Literature
Reductively Polymerized	yes	yes (polymers in general) (Ref 15)
Electronic Conductivity	zero	7 x 10 <sup>-12</sup> S/cm (Ref 14)
Ionic Conductivity	$\geq 10^{-2}$ S/cm	1.6 x 10 <sup>-4</sup> S/cm (Ref 13)
Conformal/Uniform Coating	yes	21 ± 2 nm (Ref 14)
Thickness	10-50 nm	21-43 nm (Ref 14)
Grafted	yes	yes (Ref 15)
Tg	-100 °C	-80 °C (Ref 13)

Film	Resistance (kΩ)	Capacitance (nF)	Thickness (nm)	Resistivity (kΩ*cm)
p-triethoxy	11.5 ± 0.1	59.0 ± 0.3	$2.9 \pm 0.2$	2.8 ± 0.2 E+06
o-triethoxy	$4.34 \pm 0.02$	54.0 ± 0.3	3.1 ± 0.2	9.9 ± 0.6 E+05
p-PEG	9.40 ± 0.05	53.0 ± 0.2	$3.2 \pm 0.2$	2.1 ± 0.1 E+06
o-PEG	1.66 ± 0.01	$17.0 \pm 0.1$	$10 \pm 1$	1.2 ± 0.1 E+05

Table 2. Values obtained by impedance spectroscopy

Table 3. A summary of the physical properties that were used as criteria to judge diazoniumbased films. Included are ideal values along with some of the best reported values in literature.

Physical Property	Diazo-film	Ideal	Reported in Lit.
Reductively Polymerized	yes	yes	yes (polymers in general) (Ref 15)
Electronic Conductivity	3.6 x 10 <sup>-10</sup> S/cm	zero	7 x 10 <sup>-12</sup> S/cm (Ref 14)
Ionic Conductivity	none	$\geq 10^{-2}$ S/cm	1.6 x 10 <sup>-4</sup> S/cm (Ref 13)
Conformal/Uniform Coating	Conformal	yes	21 ± 2 nm (Ref 14)
Thickness	3-10 nm	10-50 nm	21-43 nm (Ref 14)
Grafted	yes	yes	yes (Ref 15)
Тд	unknown	-100 °C	-80 °C (Ref 13)

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### Author Contributions

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### ABBREVIATIONS

EC/DMC = ethyl carbonate/dimethyl carbonate, GC = glassy carbon, PEG = poly(ethylene glycol), TBAPF<sub>6</sub> = tetrabutylammonium hexafluorophosphate, CV = cyclic voltammetry.

### REFERENCES

- (1) Bruce, P. G.; Scrosati, B.; Tarascon, J.-M. Angew. Chem. Int. Ed. **2008**, 47, 2930–2946.
- (2) Lee, S. W.; Yabuuchi, N.; Gallant, B. M.; Chen, S.; Kim, B.; Hammond, P. T.; Shao-Horn, Y. *Nat. Nano.* 2010, *116*, 531-537.
- (3) Long, J. W.; Dunn, B.; Rolison, D. R.; White, H. S. *Chem.l Rev.* **2004**, *104*, 4463–4492.
- (4) Arthur, T. S.; Bates, D. J.; Cirigliano, N.; Johnson, D.
  C.; Malati, P.; Mosby, J. M.; Perre, E.; Rawls, M. T.; Prieto, A. L.; Dunn, B. *MRS Bull.* 2011, *36*, 523–531.
- Leung, K.; Qi, Y.; Zavadil, K. R.; Jung, Y. S.; Dillon,
  A. C.; Cavanagh, A. S.; Lee, S.-H.; George, S. M. J.
  Am. Chem. Soc. 2011, 133, 14741–14754.
- Woo, J. H.; Trevey, J. E.; Cavanagh, A. S.; Choi, Y. S.;
  Kim, S. C.; George, S. M.; Oh, K. H.; Lee, S.-H. J. Electrochem. Soc. 2012, 159, A1120 –A1124.
- (7) Rhodes, C. P.; Long, J. W.; Rolison, D. R. *Electrochem.l Solid-State Lett.* **2005**, *8*, A579–A584.
- (8) Painter, P. C.; Coleman, M. M. Fundamentals of Polymer Science an Introductory Text, Second Edition; CRC Press: Boca Raton, 1997; pg 416.
- (9) Tilley, R. Understanding Solids The Science of Materials; John Wiley & Sons, Inc.: West Sussex PO19 8SQ, England, 2004; pg 159.
- (10) Adenier, A.; Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. *Chem. Mater.* **2006**, *18*, 2021–2029.
- (11) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* 1997, *11*9, 201–207.

- (12) Belanger, D.; Pinson, J. Chem. Soc. Rev. 2011, 40, 3995-4048.
- (13) Meyer, W. H. *Adv. Mat.* **1998**, *10*, 439–448.
- (14) Rhodes, C. P.; Long, J. W.; Doescher, M. S.; Fontanella, J. J.; Rolison, D. R. J. Phys. Chem. B 2004, 108, 13079–13087.
- (15) Danda, C. K.; Cai, R.; Wang, W.; Baba, A.; Advincula, R. C. Polym. Mat.: Sci. and Eng. 2008, 98, 444–445.
- (16) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. J. Am. Chem. Soc. 2001, 123, 6536–6542.
- (17) Tang, Z.; Zhang, Y.; Wang, T.; Wang, W. Synlett **2010**, 2010, 804–808.
- (18) Andrieux, C. P.; Pinson, J. J. Am. Chem. Soc. 2003, 125, 14801–14806.
- (19) Pinson, J.; Podvorica, F. Chem. Soc. Rev. 2005, 34, 429-439.
- (20) Weidner, T.; Bretthauer, F.; Ballav, N.; Motschmann, H.; Orendi, H.; Bruhn, C.; Siemeling, U.; Zharnikov, M. *Langmuir* 2008, 24, 11691–11700.
- (21) Elbing, M.; Błaszczyk, A.; von Hänisch, C.; Mayor, M.; Ferri, V.; Grave, C.; Rampi, M. A.; Pace, G.; Samorì, P.; Shaporenko, A.; Zharnikov, M. Adv. Funct. Mater. 2008, 18, 2972–2983.
- (22) Kuhn, A.; von Eschwege, K. G.; Conradie, J. J. Phys. Org. Chem. 2012, 25, 58–68.

- (23) Brown, W. H.; Foote, C. S. Organic Chemistry, Second Edition; Saunders College Publishing: Orlando, Florida, 1998; pg 510.
- (24) Nuttall, R. .; Roberts, E. .; Sharp, D. W. . Spectrochim. Acta 1961, 17, 947–952.
- (25) Creager, S. E.; Liu, B.; Mei, H.; DesMarteau, D. *Langmuir* 2006, 22, 10747-10753.
- (26) Atebamba, J.-M.; Moskon, J.; Pejovnik, S.; Gaberscek, M. J. Electrochem. Soc. 2010, 157, A1218– A1228.
- (27) Taylor, R.; Spotnitz, R.; Kendig, M.; Buchheit, R.; Loveday, D.; Contu, F. A Short Course on Electrochemical Impedance Spectroscopy: Theory, Applications, and Laboratory Instruction 2012.
- (28) Tokarzewski, L.; Dziewiecka, B. J. Polym. Sci. Polym. Chem. Ed. **1981**, 19, 1577–1580.
- (29) CRC Handbook of Chemistry and Physics; 92nd ed.; CRC Press, 2011.
- (30) Resistivity-Cost; http://www-materials.eng.cam.ac.uk/mpsite/interactive\_charts/resisti vity-cost/NS6Chart.html (accessed Aug 27, 2012).
- (31) Arora, P.; Zhang, Z. M. Chem. Rev. 2004, 104, 4419-4462.

## TOC graphic



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