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ARTICLE

Increasing Applications of Graphite Thermoplastic Electrodes (TPEs) with Aryl Diazonium Grafting

Berg, Kathleen E., [a] Leroux, Yann R.,[b] Hapiot, Philippe,[b] and Henry, Charles S.*[a]

Abstract: Carbon composite thermoplastic electrodes (TPEs) consist of graphite and thermoplastic made using an easy, solvent-assisted fabrication. TPEs have the advantages of high conductivity, good electron transfer kinetics, low cost, reusability, and easy patterning, but have only been used with aqueous solvents due to solvent compatibility with the poly(methyl methacrylate) (PMMA) template. The limited solvent compatibility hinders the application range and surface modifications. Here, cyclic olefin copolymer (COC) TPEs in glass templates are presented that are compatible with additional solvents. TPEs are grafted with aryl diazonium salts in acetonitrile, showing covalent surface TPE modification for the first time. Further investigation is carried out with scanning electrochemical microscopy (SECM). The TPEs are post-functionalized with a ferrocene moiety via click chemistry. The diazonium electrografting and click chemistry modifications open up future studies and broader applications of TPEs.

Introduction

Carbon electrodes have advantageous features, such as low cost, chemical inertness, biocompatibility, and wide potential windows but can suffer from low conductivity and are challenging to pattern.[1] Carbon composite electrodes (carbon mixed with a binder material) are the easiest to pattern but typically have low electrochemical performance.[1c, 2] The binder material affects the physical and electrochemical properties of the electrode; binders that have been used in carbon composite electrodes include pasting liquids for screen printed electrodes,[3] paraffin wax,[4] epoxy,[5] and various plastics.[6] Recently, a new form of carbon composite electrodes called thermoplastic electrodes (TPEs) were reported that use a simple fabrication method to generate complex electrode geometries while maintaining high conductivity, good electron transfer kinetics, reusability, and low cost.[7] The first report used poly(methyl methacrylate) (PMMA) as the binder, but cyclic olefin copolymer (COC) and polycaprolactone (PCL)[8] have also been used as binders; the TPE performance changes with polymer type, carbon type, and the polymer to plastic ratio, and the graphite types used here were based upon these previous studies. While TPEs exhibit promising results, they have not yet been used in sensing applications nor have they been used in non-aqueous solutions, limiting the available surface modification possibilities that often require processes in organic solvents.

Electrode modification is of great interest to many applications and is often required to achieve the desired sensitivity and/or selectivity.[9] Electrode modification with aryl diazonium salts has been studied since the seminal reports from Pinson and coworkers in 1992[10] because of the easy preparation, fast electroreduction, and strong covalent bond formed with carbon surfaces.[11] Although the initial report was electrografting onto glassy carbon (GC) in acetonitrile,[10] variations to achieve grafted aryl layers on various materials[12] include using ionic liquids,[13] spontaneous reduction,[11a, 14] UV-assisted,[15] grinding a paste,[16] scratching,[17] and *in situ* generation of diazonium cations.[18] Because most screen printed carbon electrodes have limited solvent compatibility, they have primarily been modified via an *in situ* diazonium generation,[19] although there is one report of a screen printed electrode being modified in acetonitrile.[20] Once modified, post-functionalization and/or activation can be used to detect the target analytes.

Click chemistry is a fast, easy, and selective surface post-functionalization method.[9d, 21] Azide-Alkyne cycloaddition is one of the most popular click chemistry reaction and is a Cu(I)-catalyzed, 1,2,3-triazole forming reaction using a variation of the Huisgen 1,3-dipolar cycloaddition.[22] Click chemistry has become commonly used across many fields of chemistry, including reproducible functionalization of electrodes for sensing applications.[23] The covalent bond enables a robust attachment with generally fast electron transfer kinetics, relative to adsorption, of bio-compounds (enzymes, antibodies, etc.) and is especially useful for fabricating biosensors due to the reaction's selectivity in mild conditions.[23-24]

Here, TPEs were fabricated in a glass template to achieve a wider range of solvent compatibility, including non-aqueous solvents. The TPEs were successfully modified using aryl diazonium salt electroreduction in acetonitrile, showing efficient covalent TPE surface modification. The surface modification was further investigated with scanning electrochemical microscopy (SECM).[25] Finally, the aryl diazonium modified TPEs were functionalized in ethanol/water with a ferrocene moiety via click chemistry. The present study greatly expands upon the possible future use of TPEs by the ability to use non-aqueous solvents and to perform surface modifications and post functionalization.

Results and Discussion

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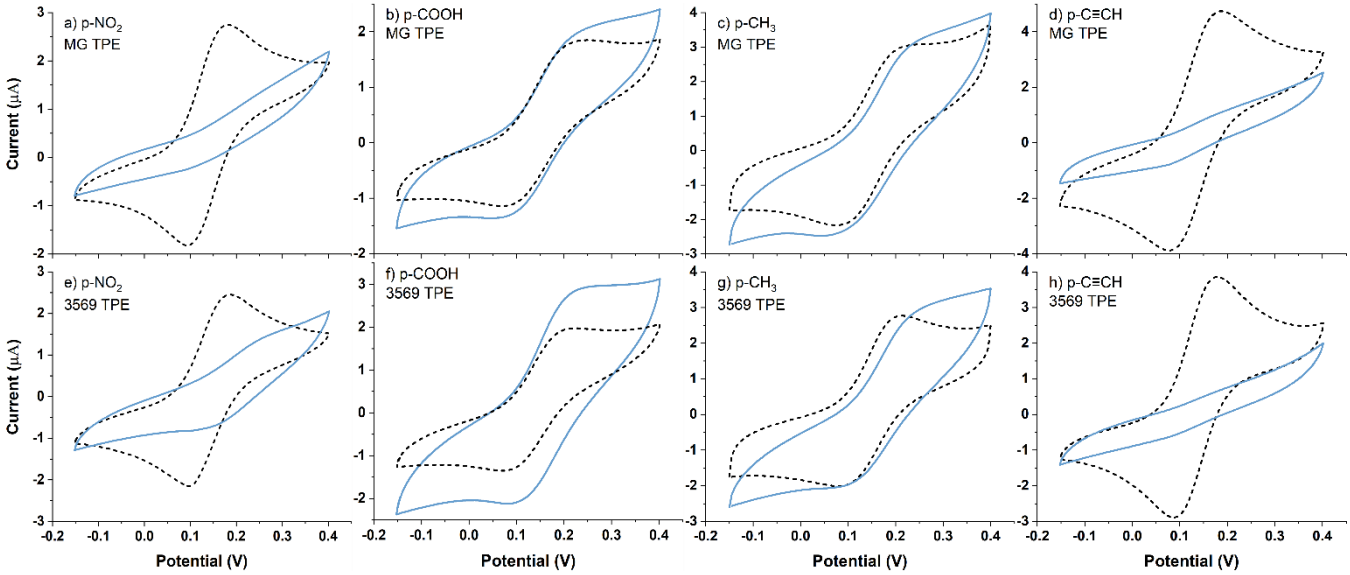

The organic films deposited onto TPEs by electrografting are insulating and thus increase the blocking properties of the electrodes. Variations in the electrochemical response of redox probes in solution before and after the modification are used to follow the quality of the grafting. Two different redox probes were chosen: ferrocyanide ($Fe(CN)_6^{3-/4-}$) and ferrocene (Fc). Ferrocene is an outer sphere redox compound for which the electron transfer is unaffected for layers thinner than a few nm. $Fe(CN)_6^{3-/4-}$ exhibits inner sphere properties and requires a direct interaction with the substrate for an efficient electron transfer.[31] TPEs have been fabricated from PMMA, COC, and PCL thermoplastics, but they have always been used in a PMMA template[7-8]. Because the PMMA template restricts solvent compatibility to aqueous solutions, we began with *in situ* diazonium generation and modification in aqueous solution using the method introduced by Baranton and Bélanger for GC surfaces.[18a] However, $Fe(CN)_6^{3-/4-}$ detection after modification indicated the modification was unsuccessful (Figure S1). To circumvent the PMMA template solvent compatibility issues, a COC TPE in a glass template was fabricated. The combination of COC and glass enables a wider range of solvents to be used with TPEs because COC is compatible with polar organic solvents due to its hydrocarbon structure and glass is relatively inert in organic solvents.[32] We were then able to modify the TPE surface with aryl diazonium reduction via electrochemistry in organic solvents. We modified TPE surfaces made from two carbon types, MG and 3569, using nitro-, carboxylic acid-, methyl-, and ethynyl-para substituted aryl diazonium compounds in acetonitrile to show the general nature of the approach.

As expected, for the p-nitro aryl diazonium grafting by successive cyclic voltammetry (Figure S2), there is a broad reduction peak at 0.1 V that disappears simultaneously with the lowering of the background current with subsequent cycles, suggesting successful modification of the TPE electrodes. For both carbon types, the $Fe(CN)_6^{3-/4-}$ peaks are considerably distorted after modification (Figure 1a,e). However, the before and after modification ferrocene CVs have the same peak height with just a 10 mV increase in peak potential difference for both carbon types (Figure 2a,e). The observed changes of $Fe(CN)_6^{3-/4-}$ oxidation associated with the lack of changes of ferrocene oxidation suggests that the modification layer is thin (≤5 nm).[31] Such inhibition, and the lack of sigmoidal shape that results from microelectrode-type behavoir, also suggests the formation of an aryllayer on the active sites and the absence of pinholes. The absence of pinholes was not confirmed. However, the GC electrode modified with the same method is blocked both for ferrocene oxidation or $Fe(CN)_6^{3-/4-}$ detection after modification indicating a thicker layer (Figure S3). The grafting difference between the GC and TPE indicates a difference of activity and is likely a result of the difference in surfaces, where the TPEs are heterogeneous mixtures of plastic and carbon while the GC is uniform carbon. Post-modification CVs were then run with the nitrophenyl-modified electrodes. The nitro group was reduced to the phenylhydroxylamine in acidic media, which can easily be detected by the appearance of a new reversible system (Figure 3). The CVs begin with a negative sweep to reduce the nitro group group to phenylhydroxylamine that could be oxidized to nitrosobenzene. The reversible couple at around 130 mV is only present in the second CV after reduction of the nitrophenyl layer has occurred. By integrating the electrochemical current of the reduction peak at 130 mV and accounting for the two electron process, the phenylhydroxylamine surface concentration value was calculated to be $14(\pm1)\cdot10^{-10}$ mol·cm^{-2} for the MG carbon and $10.6(\pm0.8)\cdot10^{-10}$ mol·cm^{-2} for the 3569 carbon TPEs. The oxidation peak at 250 mV with the introduction of the reduction peak at 130 mV matches with successful reduction of the nitro substituent to phenylhydroxylamine, further supporting the successful nitro-aryl grafting on the surface.

Figure 1. $Fe(CN)_6^{3-/4-}$ before (black dashed) and after (solid red) TPE modification in acetonitrile via aryl diazonium salt reduction with nitro- (a and e), carboxylic acid- (b and f), methyl- (c and g), and ethynyl (d and h) para substituents with two different carbon types, MG (a, b, c, and d) and 3569 (e, f, g, and h). 100 mV/s scan rate in 100 mM KCl with SCE reference.

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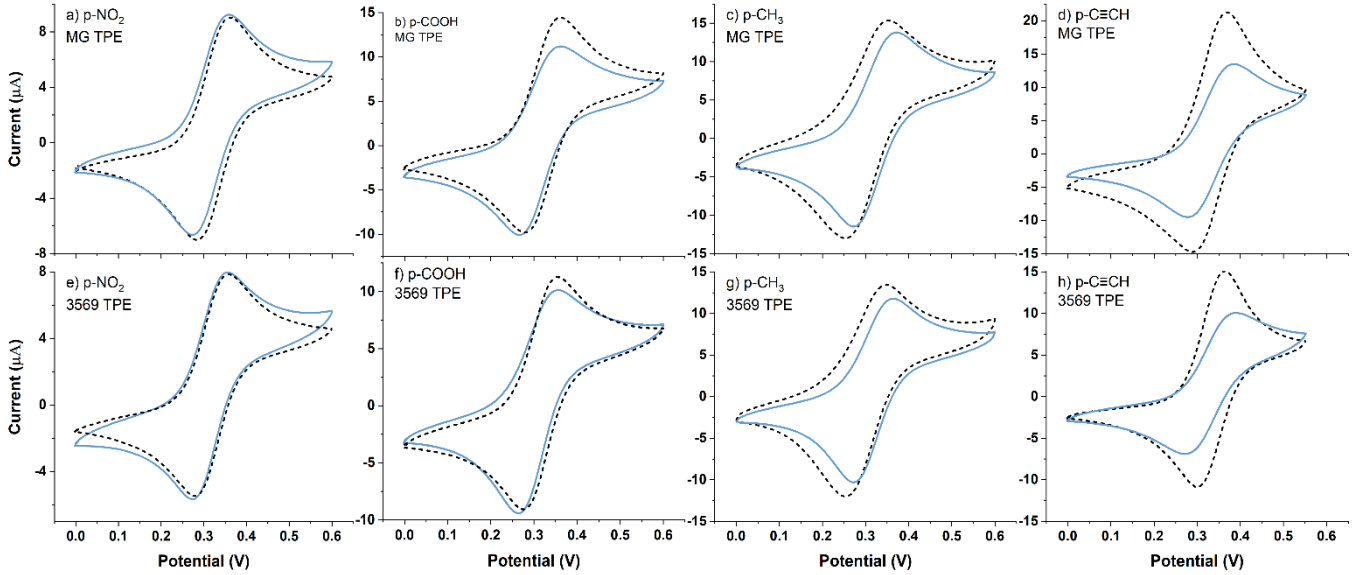

Different modification results are seen with the p-carboxylic acid aryl diazonium salt. The diazonium electroreduction CVs for both carbon types show two peaks at 70 and -250 mV in the first cycle, and then on subsequent cycles, the peaks disappear and the background current is lower (Figure S2). Observation of two reduction peaks during aryl diazonium reduction could be ascribed to catalytic and non-catalytic reductions on clean GC surfaces.[33] For both TPEs, the $Fe(CN)_6^{3-/4-}$ redox peaks lose definition and the background appears to become more resistive (Figure 1b,f), which could be a result of the $Fe(CN)_6^{3-/4-}$ interaction with the carboxylic acid groups, which are deprotonated at neutral pH. Unlike with the nitro-aryl modification, the ferrocene peak currents were reduced by approximately two-thirds for the MG and one-third for the 3569 carbon for both oxidation and reduction but its shape is not considerably affected, only by a 20 mV peak potential increase (Figure 2b,f). It is also noticeable that the ferrocene oxidation signal persists but not the $Fe(CN)_6^{3-/4-}$ signal. From both observations, it is likely that the modification layer is thin (≤5 nm) in some areas and thicker in other areas because ferrocene, unlike $Fe(CN)_6^{3-/4-}$, is not surface sensitive. The peak shape does not become sigmoidal, as seen with CVs from microelectrodes, which suggests that the areas with thin coverage are large (tens of μm-scale).

Figure 2. Ferrocene before and after TPE modification in acetonitrile via aryl diazonium salt reduction with nitro- (a and e), carboxylic acid- (b and f), methyl- (c and g), and ethynyl (d and h) para substituents with two different carbon types, MG (a, b, c, and d) and 3569 (e, f, g, and h). 100 mV/s scan rate in 100 mM KCl with SCE reference.

Modification results similar to the p-carboxylic acid aryl diazonium are seen with the p-methyl- and p-ethynyl aryl diazonium. The p-methyl aryl diazonium electroreduction CV shows a peak at -200 mV that is still present during the subsequent reduction cycle (Figure S2). The peak and background current are both lower with each CV cycle. The effects of reducing the diazonium salt can be seen in the ferrocene and $Fe(CN)_6^{3-/4-}$ CVs. For both MG and 3569 carbon types, a clear $Fe(CN)_6^{3-/4-}$ peak is not present after TPE modification (Figure 1c,g), but the ferrocene peak is still present with a one-fourth lower reduction peak current (Figure 2c,g). The ferrocene peak potential difference is the same before and after modification with each carbon type. For the p-ethynyl aryl modification, $Fe(CN)_6^{3-/4-}$ detection for both carbon types is non-existent after modification (Figure 1d,h). Ferrocene peak height is also mitigated by about one-third for both carbon types (Figure 2d,h), accompanied by a 30 mV peak potential difference increase for the MG TPE and a 50 mV increase for the 3569 TPE. Based on the similar $Fe(CN)_6^{3-/4-}$ and ferrocene data, it is likely that the p-methyl and p-ethynyl aryl modification layers are similar in structure to the p-carboxylic acid aryl layer, where the resulting grafted layer has varying thicknesses. The surface coverage variation is not surprising given TPEs heterogeneous surface of plastic and carbon. The layer thicknesses and variation within the layer is consistent with literature values using similar electroreduction conditions.[11g, 34]

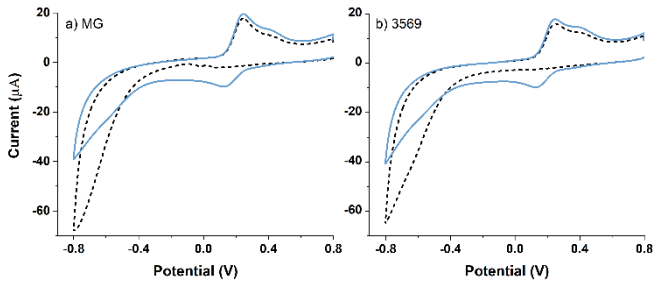

Figure 3. CVs (first cycle is dashed black, second cycle is blue) of p-nitro(benzene) modified electrodes with two carbon types: MG (a) and 3569 (b). 100 mV/s scan rate in 100 mM H_2SO_4 with SCE reference.

To better understand the grafted layer,[35] before and after SECM images (Figure S4) of the p-carboxylic acid aryl modified

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TPEs were taken with ferrocene, $Fe(CN)_6^{3-/4-}$ in a pH neutral solution, and $Fe(CN)_6^{3-/4-}$ in an acidic solution. The images were used to generate the values for relative current shown in Figure 4. The $Fe(CN)_6^{3-/4-}$ redox couple is sensitive to surface oxides and has slower electron transfer kinetics with increasing pH indicative of electrostatic repulsion between the surface bound carboxylate and the negatively charged redox couple.[31, 36] Ferrocene is not sensitive to surface oxides and is good for comparison with the bulk solution measurements. For both MG and 3569 carbon types, ferrocene normalized current from the image decreased after modification, 1.21 to 0.87 for MG carbon and 1.47 to 1.07 for 3569 carbon, which is comparable to the bulk solution CVs. The 3569 carbon TPE surface had more electroactive variability than the MG before modification, as seen by the 0.146 and 0.002 RMS values, respectively. Both carbon types have similar RMS values (0.001 for MG and 0.003 for 3569) after modification though. $Fe(CN)_6^{3-/4-}$ normalized current in the neutral solution also decreased after modification for both carbon types, 0.88 to 0.63 for MG and 0.69 to 0.54 for 3569. In the acidic solution, $Fe(CN)_6^{3-/4-}$ normalized current values remained about the same or increased after modification with the p-carboxylic acid aryl layer. The MG TPE was 1.10 (0.002 RMS) before modification and 1.05 (0.002 RMS) after modification. The 3569 TPE was 0.79 (0.217 RMS) before and 1.14 (0.042 RMS) after modification. The decrease in RMS values, along with the images, support the hypothesis that the grafted areas of a thin layer are large (µm scale).

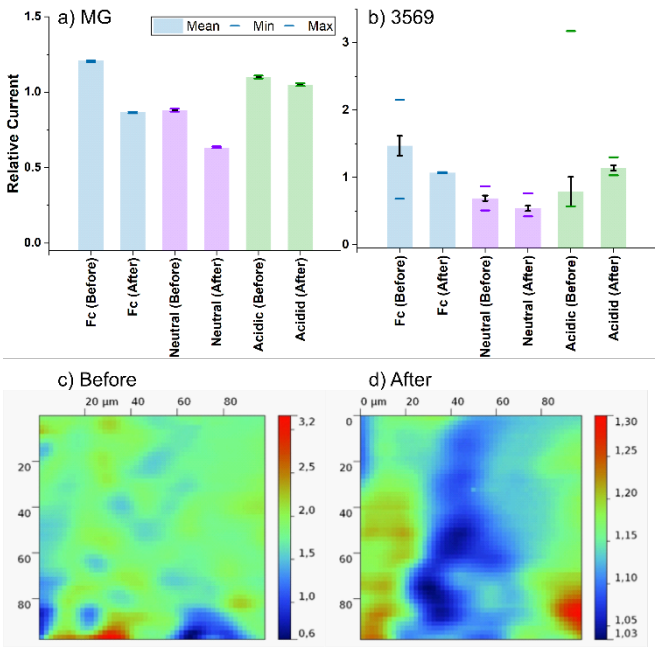

Figure 4. SECM image results from before and after p-carboxylic acid aryl modification using ferrocene in 100 mM KCl (Fc), $Fe(CN)_6^{3-/4-}$ in 100 mM KCl (neutral), and $Fe(CN)_6^{3-/4-}$ in 100 mM H_2SO_4 (acidic) with a) MG and b) 3569 carbon type electrodes. Relative current is the current normalized by the infinite current(i/i_{inf}). Example SECM Images of before (c) and after (d) 3569 modification using $Fe(CN)_6^{3-/4-}$ in 100 mM H_2SO_4 (acidic).

Finally, as a proof of concept, we used click chemistry to couple azidomethylferrocene with the p-ethynylphenyl modified TPE in ethanol/water.[30] The post-functionalization CVs of each carbon TPE type are shown in Figure 5. By integrating the electrochemical current, the surface concentration value of ferrocene moieties, Γ_{Fc}, was calculated to be $4.3(\pm0.3)\cdot10^{-10}$ mol·cm^{-2} for the MG carbon and $3.8(\pm0.3)\cdot10^{-10}$ mol·cm^{-2} for the 3569 carbon TPEs. The peak potential differences were 140 mV and 130 mV for MG and 3569 carbons, respectively. The two surface concentration values are close to the maximum possible surface concentration of ferrocene ($4.5\cdot10^{-10}$ mol·cm^{-2}).[37] Both surface concentration values are larger than those achieved with a GC electrode ($2.2\cdot10^{-10}$ mol·cm^{-2}) via the same functionalization method.[30] The cause of the higher ferrocene surface concentration relative to a GC electrode is currently unclear and warrants further investigation. One possible cause is the difference in surface roughness between the TPEs and GC; however, previous atomic force microscopy (AFM) results suggest that the TPEs have similar surface roughness to GC electrodes. Two AFM images, one taken from each electrode type, are in Figure S5. It is also interesting to note that the ferrocene surface concentration is about half of the phenylhydroxylamine surface concentration, which is likely the result of the initial grafting or post-functionalization success. Different grafted layer properties were deduced between the nitro- and ethynyl-aryl modifications via before and after ferrocene CVs (Figure 2). Regardless, the successful demonstration of click chemistry on TPEs opens new avenues for surface modification of these materials.

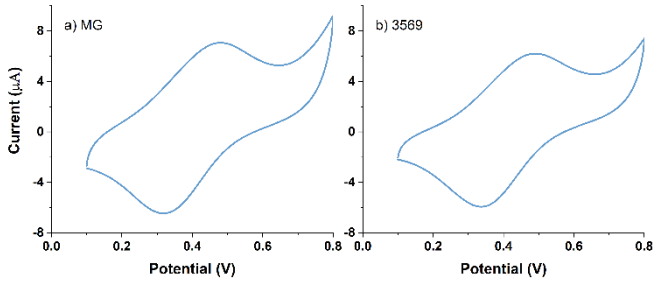

Figure 5. CVs of Fc-modified TPEs via click chemistry of two carbon types: MG (a) and 3569 (b). 100 mV/s scan rate in 50 mM KCl with SCE reference.

Conclusions

The presented work fabricates a carbon composite TPEs with a broader range of solvent compatibility than previous TPEs, thus combining TPEs high electrochemical performance, low cost, and easy fabrication with a broader range of viable electrochemistry. The TPE surfaces were successfully modified with various aryl diazonium salts using electroreduction in acetonitrile. Post-functionalization click chemistry of the TPEs was then successful using a ferrocene moiety, showing that other click chemistry and immobilization of many functional groups is possible in future studies and applications.

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Experimental Section

Chemicals were reagent grade from Sigma-Aldrich (MO, USA) and prepared with 18.2 MΩ·cm water (Milli-Q system, Billerica, MA, USA). All aryl diazonium salts were synthesized according to previously published procedures.[26] Two graphite types were used: 3569 graphite ("3569", 99.9% purity carbon, 96.9% is ≤75 µm diameter, Asbury Graphite Mills Inc, NJ, USA) and MG-1599 graphite ("MG", 99.5-99.9% purity carbon, 16 µm diameter, Great Lakes Graphite Inc., MA, USA). TPEs were fabricated as described previously.[7-8] Briefly, COC (8007, TOPAS, MI, USA) was dissolved in toluene. Graphite was added in 1:3 plastic:carbon by mass (75% carbon by mass) and thoroughly mixed. The solvent was evaporated, and the carbon composite material was heat pressed into 2.5-mm diameter Pyrex glass electrode templates. The excess carbon material was sanded off. TPEs were freshly polished with P4000 (5 µm grit) sand paper before testing.

Bulk electrochemical experiments were performed with an Autolab PGSTAT 12 (Methohm, Utrecht, Netherlands) using a saturated calomel electrode (SCE) reference and Pt wire counter electrode. SECM measurements were performed using a homemade setup similar to that previously described[27] with an Autolab PGSTAT 12 (Methohm, Utrecht, Netherlands) potentiostat. The SECM setup is equipped with an adjustable stage for the tilt angle correction and is controlled by SECMx software written by Wittstock, G., *et al.*[28] SECM measurements were performed using a typical 3-electrode configuration in feedback mode, with a 10 µm diameter Pt electrode (CH Instruments Inc, TX, USA) as working electrode, Ag/AgCl (saturated KCl) reference electrode, and a Pt wire as a counter electrode. 100 x 100 μm^2 images were taken at L (d/a) of 1, and values are reported as current relative to the infinite current with the following solutions: 1 mM $Fc(MeOH)_2$ in 100 mM KCl, 1 mM $K_4Fe(CN)_6$ in 100 mM KCl (neutral), and 1 mM $K_4Fe(CN)_6$ in 100 mM H_2SO_4 (acidic). SECM image data analysis was performed with Gwyddion software.[29]

For aqueous derivatization of PMMA TPEs, the procedure described by Baranton and Bélanger was followed with 4-aminobenzoic acid.[18a] CVs of 1 mM $K_4Fe(CN)_6$ in 100 mM KCl were run before and after modification. For reductive aryl diazonium grafting in acetonitrile, TPEs (and a 2.5 mm diameter GC electrode) were modified in a 10 mM diazonium salt and 100 mM tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in an ice bath. CV modification parameters were as follows: +0.6 V to −0.5 V at 100 mV/s scan rate for four cycles. CVs of 1-5 mM aqueous solutions of $Fc(MeOH)_2$ and $K_4Fe(CN)_6$ in 100 mM KCl were run before and after modification (same solution for each before and after modification CV). Post p-nitro aryl diazonium modification CVs were run in 100 mM H_2SO_4 with the following electrochemical parameters: +0.8 V to −0.8 V and back with 100 mV/s scan rate, twice. For the azidomethylferrocene click chemistry coupling, 1:1 water:ethanol solution of 100 mM $CuSO_4$ and 200 mM L(+)-ascorbic acid were stirred in the presence of 10 µM azidomethylferrocene and the modified TPE.[30]

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Keywords: carbon • diazonium reduction • electrochemistry • surface-modified electrode • thermoplastic electrode

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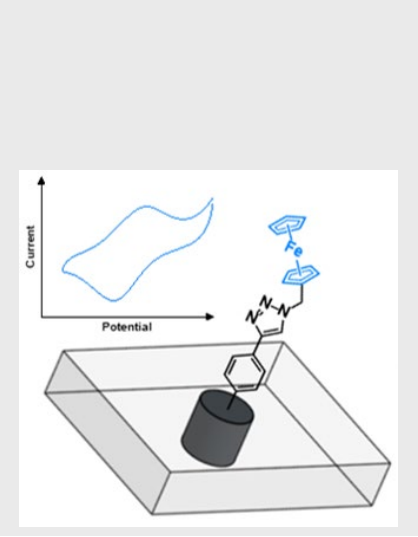

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Increasing Applications of Graphite Thermoplastic Electrodes (TPEs) with Aryl Diazonium Grafting

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