Effect of Carbon Support on the Properties of Electrochemically Deposited Platinum and Polyaniline

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Carbon has unique and desirable properties for use in applications such as fuel cells and batteries. The properties can vary widely depending on its structure and surface characteristics. Two types of carbon, a synthetic graphite produced from petroleum coke and an extruded graphite rod, were characterized using Raman spectroscopy and X-ray Photoelectron spectroscopy and the features were correlated with electrochemical properties of the material. The graphite rod was found to have a more disordered structure, greater sp3 character, and a greater surface oxygen content as compared to the synthetic graphite from coke. Our results show that the characteristics of electrodeposited platinum and polyaniline depend on the type of substrate; the preferable carbon for producing composite materials for catalyst applications is the graphite from petroleum coke.

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Carbon used as a support material in fuel cells and batteries can vary in properties depending on the structure and impurities present. Reviews on carbon supports have indicated that graphite is commonly chosen to support catalytic metals due to its inert character and conductivity, and the support itself can affect performance of the fuel cell.1–4 Composite electrodes can be produced from potentiostatic depositions of platinum and/or polyaniline (PANI) directly onto the carbon surface. Carbon supported platinum (C/Pt) is widely used for its known activity toward alcohol oxidation.5–7 and carbon supported PANI (C/PANI), or even carbon-platinum supported PANI (C/Pt-PANI) electrodes are also attractive for the fabrication of composite catalyst materials.8,9 Previous studies have shown that PANI can be used as a viable matrix for the insertion of catalytically active atomic-sized metal clusters, using platinum as a support due to its benefits of being conductive, lightweight and inexpensive.10 However, in order to choose the appropriate carbon for a support electrode, understanding the effects that the substrate has on the PANI film is necessary. Dinhi and Birss have compared the effects of differing types of support materials, such as noble metals and glassy carbon, on PANI properties. Impedance and CV studies on PANI grown by cycling were correlated with electrochemical properties of the material. The graphite rod was found to have a more disordered structure, and an extruded graphite rod, were characterized using Raman spectroscopy and X-ray Photoelectron spectroscopy and the features were more capacitive on the Pt and Au supports. However, with a larger cycling window for film deposition, the presence of surface oxygen groups was seen on the metal substrates leading to slower film growth.12 This study focuses specifically on graphitic substrates and how their structure and surface properties effect platinum deposition, as well as the growth of PANI film at constant potential. PANI growth was investigated on the surface of the carbon and on the C/Pt surface. For this study, we are using a novel synthetic graphite produced from petroleum coke in a proprietary process that results in an ordered structure (vide infra). As a comparison, a widely available extruded graphite rod was also included. From here on, the substrates will be referred to as ‘coke’ and ‘graphite’ respectively. Initial characterization of both substrates was completed using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Characterization of the two carbon samples reveal differences in the surfaces as well as in the overall crystalline structure that could account for differences in electrochemical behaviors of the samples.

Experimental

The petroleum coke was purchased from Advanced Carbon Engineered Solutions (North Bay, Ontario) with dimensions of 13 mm OD and 1 mm thick, with a resistivity of 5.5 μΩcm·m, and bulk density of 1.88 g/cm³. The extruded rod was purchased from Graphite, LLC (Buffalo Grove, IL) with dimensions of 12.7 mm OD and 5 mm thick with a resistivity of 7.6 μΩcm·m and a bulk density of 1.70 g/cm³. Each was mechanically polished with 30 μm paper (Aluminum Oxide, Allied), rinsed with iso-propanol (70%, EMD), and dried in oven at 65 °C before use. Electrodepositions of platinum and polyaniline (PANI), and electrochemical characterizations were done with an electrochemical workstation (660, CH Instruments) in a three-electrode cell, using a platinum wire mesh counter electrode, and Ag/AgCl in 1 M KCl/1 M NaNO₃ as a reference. Platinum depositions were carried out at E₁/₂ = 0.02 V using a solution of 1 × 10⁻² M H₂PtCl₆·6H₂O (99.9%, Strem) in 0.1 M HClO₄ (70%, Macron). PANI depositions were done at E₁/₂ = 0.85 V from 0.1 M aniline (99+%, Alfa Aesar) in 2 M HBF₄ (48%, Strem) and subsequently cycled in 0.1 M HClO₄. RuHex solution used for carbon characterization was made with equal molar hexammineruthenium (III) chloride (Aldrich, 98%) and hexammineruthenium (II) chloride (Aldrich, 99.9+%) in 1 M KNO₃. Characterization of the carbon was carried out using X-ray photoelectron spectroscopy (XPS, Kratos), Raman spectroscopy (confocal, WITec GmbH), and scanning electron microscopy (SU-8230, Hitachi). The thickness of the PANI fibers and Pt features were estimated using ImageJ software from NIH.

Results and Discussion

The XPS survey scans of both substrates reveal that the only significant bands present were from carbon and oxygen with possible trace metals present in the graphite substrate. The core-level C1s spectrum (Figure 1A) shows a narrower and more intense peak for coke at binding energy (BE) of 283.8 eV; this indicates a majority of sp² carbon in the sample. The graphite surface has a broader, less intense peak at BE of 284.7 eV, which indicates both sp² and sp³ carbons are present, with the majority being sp².15–17 For the core-level O1s spectrum the broader peak of graphite indicates more surface oxygen-containing groups (Figure 1B). For the coke samples, the broad O1s peak centered at BE of 532 eV indicates both C=O and C–O groups are present on the surface. For graphite, C=O is seen from the peak at BE of 531.3 eV; however, the peak at BE of 529.8 eV may indicate the presence of trace metal oxides that are also on the surface.15–18 The atom ratios (%) of O/C differ greatly between the two samples. For the graphite sample, the O/C ratio is 0.56 and for the coke sample it is 0.05, confirming that the oxygen content of the graphite sample is 11 times greater. With the increase in intensity of the O1s scan for graphite, the greater oxides on the surface as well as the presence of
possible metal oxides shows a less pure starting surface for the deposition of PANI. This could inhibit the PANI ever reaching a state of continued growth through uneven adsorption of the monomers on the graphite surface.

The atoms in graphitic carbon are arranged in sheets as a system of bonded hexagons, ideally with sp² hybridization. With three valence electrons used in the sp² hybridization, the fourth forms a π bond, giving the carbon its conductivity. Disruptions and disorder in the hexagonal structure can change the hybridization and the overall properties of the substrate. These differences in the structure of carbon samples can be seen in the Raman spectra (Figure 2). The D band near 1350 cm⁻¹ is attributed to the breathing mode of rings, while the G band near 1575 cm⁻¹ is attributed to bond stretching of the sp² of both rings and chains. The D band can be considered a measure of the disorder in a system, therefore the greater the number of defects of the sp² structure in the carbon, the more intense the D band. Also, the D' band around 1620 cm⁻¹ is seen for graphite in Figure 2B but is not seen for coke in Figure 2A. This D' band is caused by sufficient defects in the carbon causing a phonon confinement where normally the phonons would be Raman inactive. The D/G intensity ratio can give an indication of the sp² or sp³ character as referenced to pure graphene, though the D band can be due to other defects in the sample. The coke sample (Figure 2A) shows a less intense D band compared to G but the graphite (Figure 2B) has a smaller D/G intensity ratio, this suggests a possible higher sp³ content in the graphite sample. This is consistent with the XPS results in Figure 1, which also suggest a higher sp³ character for graphite.

These XPS and Raman experiments suggest that the graphite substrate has an increased resistance. This increase in resistance is likely due to three characteristics of the graphite: more oxygen groups on the surface (seen in XPS, Fig. 1B), the greater structural defects in the sp² character, as well as the greater overall sp³ content (seen in the Raman spectra, Fig. 2B). This resistance will affect Pt deposition efficiency and could inhibit PANI polymerization by keeping the film from reaching a state of continued growth. The greater surface oxygen groups can also affect Pt deposition by causing the nucleation seeds from the H₂PtCl₆ precursor to be unevenly dispersed on the surface. The surface groups also increase hydrophilicity of the carbon and therefore keep aniline monomers from adsorbing on the surface, resulting in a thinner polymerized PANI film. Conversely, the coke substrate was not found to have many surface oxygen groups

**Figure 1.** XPS spectra for coke (1) and graphite (2) substrates showing the core-level C1s (A) and O1s (B) scans.

**Figure 2.** Raman spectra of G band for coke (A) and graphite (B). Four different positions were sampled on the carbon surface in (A), while two were sampled on the surface in (B). Spectra were collected using Nd:YAG laser at 532 nm and a 600 g/mm diffraction grating with an acquisition time of 0.01s.
Figure 3. Cyclic voltammogram of coke (1) and graphite (2) substrates in 2.5 mM RuHex in 1 MKNO$_3$ at 50 mV/s. Shown is last scan after reaching steady state.

(Fig. 1B) and maintains a greater sp$^2$ character with less defects (Fig. 2A). This suggests that the coke surface will have a greater efficiency in Pt deposition due to less resistance, and the greater presence of $\pi$ electrons in the sp$^2$ structure will enhance the radical polymerization of the PANI on the surface.

Each carbon sample was also characterized by CV in 2.5 mM RuHex in 1 MKNO$_3$. The redox peak potentials appear at $-0.19$ V and $-0.27$ V respectively, Figure 3. The 80 mV peak separation for both substrates confirms that the rate of electron transfer is not affected by the difference in structure or molecular differences of the electrode surfaces.

To compare the electrochemically active surface, a platinum layer was deposited on each of the carbon surfaces using a constant potential ($E_{\text{const}} = 0.02$ V), Figure 4A. The chronamperogram for graphite shows evidence of hydrogen evolution and a slight decrease in current over time, most likely due to the increased resistance discussed previously. This hydrogen evolution leads to faster nucleation, and uneven growth of the Pt layer, seen in the SEM image (Figure 4B). The platinum deposition on the coke sample results in the opposite. The chronanperogram in Figure 4D has an exponential increase of current over time, signaling a 2D or 3D growth process. The SEM of deposited platinum has a more bulbous structure indicating greater surface area coming from slower and steady growth and larger nucleation sites (Figure 4E). The CV of each C/Pt, shown in Figures 4C and 4F, is similar in the anodic region, showing the hydroxide adsorption, and the cathodic region showing the reduction potential of the oxide formed during the anodic sweep to +0.75 V. In the cathodic region, the coke sample shows slightly greater resolution in the hydrogen adsorption and desorption peaks between $-0.4$ V to 0.0 V, most likely due to the more structured facets seen in the SEM image after conditioning in 1 M H$_2$SO$_4$ by fast cycling at 1 V/s, in Figures 5B and 5D.

For the coke sample, the structure of the Pt surface did not undergo large physical changes after conditioning, but the bulbous areas reduced in size from approximately 850 nm to 700 nm (Figure 5C). However, the Pt on the graphite showed greater rearrangement to a flat and continuous sheet (Figure 5A). Furthermore, the conditioning process rearranged the structure of both samples to allow better hydrogen adsorption on the surface as seen by the peaks at $E = -0.5$ V, Pt(100) facet, and $E = -0.25$ V, Pt(110) facet, Figure 5B. For graphite, there is greater hydrogen adsorption on the Pt(100) facet than for coke sample with values of 2.41 mC/cm$^2$ and 2.15 mC/cm$^2$ respectively. Conversely, there is greater adsorption on the Pt(110) facet for coke at 2.0 mC/cm$^2$, over graphite, 1.66 mC/cm$^2$. The coke sample shows approximately the same adsorption for both facets after conditioning.

Figure 6 shows the polymerization of aniline from 2 M HBF$_4$ at $E_{\text{const}} = +0.85$ V onto the surface of each carbon. The PANI films were cycled in 0.1 M HClO$_4$ to exchange the BF$_4^-$ anion inserted during polymerization, and as characterization of the film. The downward slope of the PANI on the graphite sample (Figure 6A) indicates that the polymerization never reaches a state with continued growth and...
branching. In contrast, the upward slope of the deposition on the coke sample (Figure 6D) indicates steady growth of the polymer film likely resulting from the $sp^2$ character enhancing aniline radical formation. In this sense, polymerization on the graphite surface may take longer to reach the state of continued growth due to the presence of surface oxygen-containing groups as previously discussed. Because each PANI film deposition was carried out to the same charge, the difference in rate of deposition also confirms the difference in growth on each carbon substrate. The SEM images of the PANI film on each carbon sample show differences in the openness of the structure between the graphite support (Figure 6B) and the coke support (Figure 6E), with B even showing the carbon support through the matrix. The PANI structure is also slightly more two-dimensional in the coke sample (6E) as compared to graphite (6B). The PANI fiber thickness on the coke electrode is also slightly smaller at approximately 150 nm compared to the graphite electrode at 200 nm. In the CVs for the PANI on carbon surfaces (Figures 6C and 6F), the characteristic peaks corresponding to the insertion and expulsion of protons ($E \approx 0.25$ V and $-0.2$ V) and the insertion and expulsion of anions ($E \approx 0.8$ V and 0.4 V) are different. The PANI-on-graphite sample shows smaller peak areas, which indicates a thinner film and less protonation of the polymer. The upward slope of the PANI-on-graphite CV indicates a larger resistance, which is estimated from the CV to be twice that of the PANI-on-coke sample. The separation in the peak potentials of the PANI-on-graphite electrode are also 100 mV greater than in the PANI-on-coke electrode showing a different conformation of the polymer.

Similar results are seen with the deposition of PANI on the C/Pt surfaces (Figure 7), to those previously discussed involving PANI deposition directly on carbon (Figure 6). For the polymerization curves, the graphite/Pt electrode (Fig. 7A) shows only a slight increase, again indicating the slower PANI growth, while the coke/Pt electrode (Fig. 7B) has a greater increase in slope indicating continued growth and branching. Similar results are also seen in the CVs of PANI on the C/Pt surfaces regarding decreased peak areas, larger separation of peak potentials, and larger resistance of the graphite/Pt support (Figures 7C and 7F). The SEM images reveal that the PANI film on graphite/Pt support is very thin with much of the underlying platinum layer showing through (Figure 7B). The PANI on the coke/Pt support shows a much thicker and more compact layer that is almost twice as thick (Figure 7E). Calculation of the PANI layer using method described in Genies and Tsintavis show that the PANI on graphite-platinum support is 3.2 μm thick while the PANI on coke-platinum is 7.5 μm.

Conclusions

This study shows differences on two carbon samples: a synthetic graphite plate from a novel petroleum coke process, and an extruded graphite rod. These show differences in graphitic structure and surface characteristics that contribute to differences in the electrodeposition of Pt and PANI on the surfaces. The surface oxygen content, the defects in the $sp^2$ character, as well as the $sp^3$ content were key in determining which carbon sample is sufficient for use in further studies using PANI.
Figure 6. Comparison of PANI deposited directly onto graphite (top) and coke (bottom) surfaces. The i-t curves shown are for constant potential deposition ($E = 0.85 \ V$, $Q = 0.42 \ C/cm^2$) from aniline solution described in Experimental. Characterization of the films was done by CVs in 0.1 M HClO$_4$ at 50 mV/s for graphite support (C) and coke support (F).

Figure 7. Comparison of PANI deposition onto carbon surfaces (A) and onto C/Pt surfaces (C). The curves shown are for constant potential deposition ($E = 0.85 \ V$, $Q = 0.42 \ C/cm^2$) from aniline solution described in Experimental. Characterization is done by CVs in 0.1 M HClO$_4$ at 50 mV/s.

as a support matrix for atomic metal clusters. The graphite substrate shows increased resistance from more defects in the sp$^2$ structure and the greater sp$^3$ content. This causes less efficient and uneven Pt deposition on the surface. The greater surface oxygen content on the graphite also results in thinner and less dense PANI films due to lack of continued growth. The less-defected sp$^2$ structure and less oxygen groups on the surface of the coke sample results in even Pt layer with more facets and a thicker and even PANI film. The effects in the Pt and PANI depositions can be clearly seen in the CVs of the deposited PANI films in 0.1 MHCIO$_4$. The PANI deposited on the coke substrate gives resolved characteristic peaks of the H$^+$ and anion exchanges, showing that the sp$^2$ structure is more ideal for PANI film growth. The graphite substrate is less desirable, most likely due to the increase in sp$^3$ content and the concomitant loss of $\pi$ bonding which results in a
less conducting material. Of the two carbon substrates used in these experiments, the synthetic graphite from the novel petroleum coke process proved to be optimal because of its higher sp² carbon content and less surface oxygen content.

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References

1. A. L. Dicks, J. Power Sources, 156, 128 (2006).
2. R. L. McCreery, Chem. Rev., 108, 2646 (2008).
3. K. Kinoshita and K. Zaghib, in Journal of Power Sources, 110, 416 (2002).
4. E. Antolini, L. Giorgi, F. Cardellini, and E. Passalacqua, J. Solid State Electrochem., 5, 131 (2001).
5. F. Gloaguen, J. M. Leger, and C. Lamy, J. Appl. Electrochem., 27, 1052 (1997).
6. L. Ma, D. Chu, and R. Chen, Int. J. Hydrogen Energy, 37, 11185 (2012).
7. S. W. Xie, S. Chen, Z. Q. Liu, and C. W. Xu, Int. J. Electrochem. Sci., 6, 882 (2011).
8. D. W. Hatchett, R. Wijeratne, and J. M. Kinyanjui, J. Electroanal. Chem., 593, 203 (2006).
9. L. Niu, Q. Li, F. Wei, X. Chen, and H. Wang, J. Electroanal. Chem., 544, 121 (2003).
10. A. P. Jonke, M. Josowicz, and J. Janata, J. Electrochem. Soc., 158, E147 (2011).
11. A. P. Jonke, M. Josowicz, J. Janata, and M. H. Engelhard, J. Electrochem. Soc., 157, P83 (2010).
12. A. P. Jonke, J. L. Steeb, M. Josowicz, and J. Janata, Catal. Letters, 143, 531 (2013).
13. E. L. Gawron, T. Krizek, M. A. Kowalik, M. Josowicz, and J. Janata, J. Electrochem. Soc., 162, H423 (2015).
14. H. N. Dinh and V. I. Birss, J. Electrochem. Soc., 147, 3775 (2000).
15. R. Giorgi, Appl. Surf. Sci., 47, 17 (1993).
16. P. K. Chu and L. Li, Mater. Chem. Phys., 96, 253 (2006).
17. NIST X-ray Photoelectron Spectroscopy Database Version 4.1, (2012) http://srdata.nist.gov/xps/.
18. S. Biniak, G. Szymański, J. Siedlewski, and A. Światkoski, Carbon N. Y., 35, 1799 (1997).
19. A. C. Ferrari and J. Robertson, Phys. Rev. B, 64, 75414 (2001).
20. K. N. Kudin et al., Nano Lett., 8, 36 (2008).
21. A. G. Pandolfo and A. F. Hollenkamp, J. Power Sources, 157, 11 (2006).
22. K. Bade, V. Tsakova, and J. W. Schultz, Electrochim. Acta, 37, 2255 (1992).
23. S. Domínguez-Domínguez, J. Arias-Pardilla, Á. Berenguer-Murcia, E. Morallón, and D. Cazorla-Amorós, J. Appl. Electrochem., 38, 259 (2008).
24. T. Frelink et al., Electrochim. Acta, 40, 545 (1995).
25. D. A. Stevens and J. R. Dahn, J. Electrochem. Soc., 150, A770 (2003).
26. I. Sapurnina, A. Riede, and J. Stejskal, Synth. Met., 123, 503 (2001).
27. E. M. Genies and C. Tsintavis, J. Electroanal. Chem., 200, 127 (1986).