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Case Western Reserve University
Cleveland, OH 44106
October 20–22, 1997

K. Kinoshita and D. Scherson, Eds.

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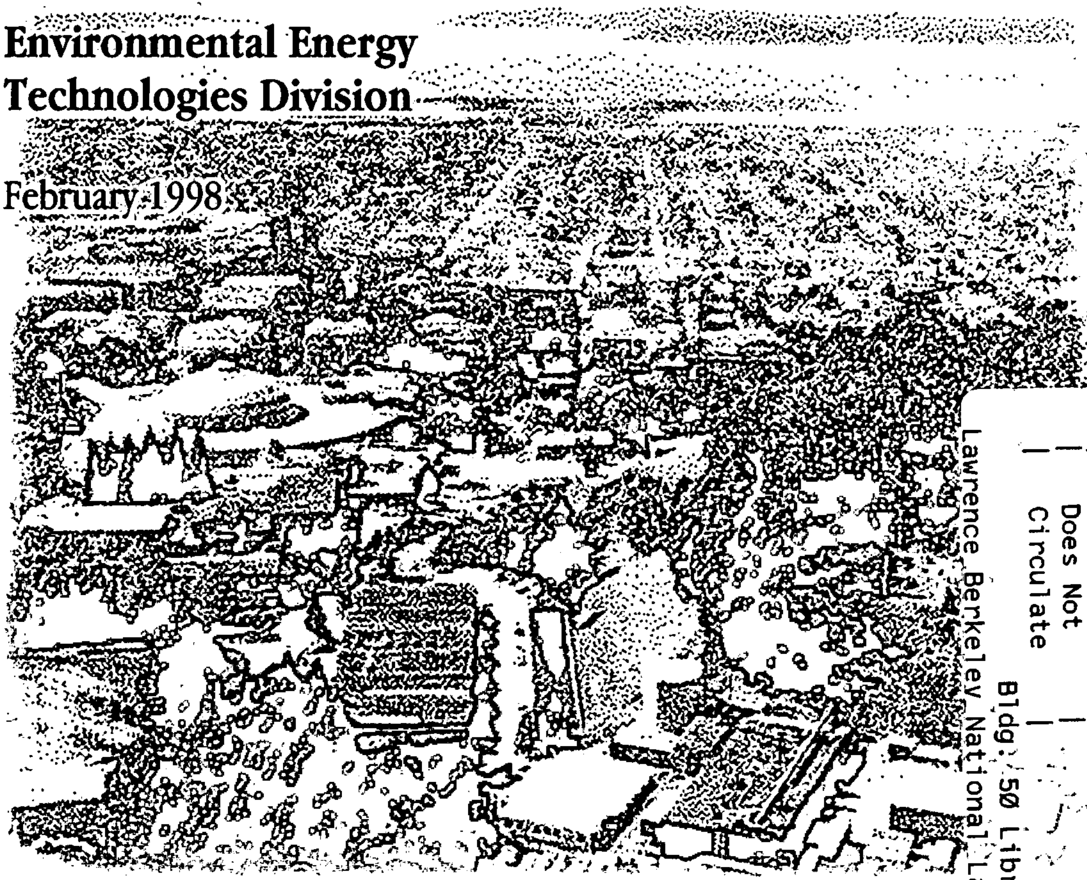

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George S. Dively Executive Education Building
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Executive Summary

A conference on Electrochemistry of Carbon Allotropes: Graphite, Fullerenes and Diamond was held at Case Western Reserve University, Cleveland, OH, on October 20-22, 1997. This Conference provided an opportunity for electrochemists, physicists, materials scientists and engineers to meet and exchange information on different carbon allotropes. The presentations and discussion among the participants provided a forum to develop recommendations on research and development which are relevant to the electrochemistry of carbon allotropes.

Disordered and graphitic carbons are widely used in electrochemical energy conversion and storage technologies, e.g., Li-ion cells negative electrode and conductive matrix in positive electrode), electrochemical capacitors (positive and negative electrodes), low-temperature fuel cells (electrocatalyst support), to name a few. The surface chemistry of these carbons, which is often influenced by the presence of surface functional groups such as hydroxyl [>-OH], carbonyl [>=O], carboxyl [>-COOH], and lactone [>-C(=O)-O-<)], is not completely understood. In particular, the role of these surface groups on the irreversible capacity loss and Li insertion of carbons for Li-ion cells is not fully resolved, and this is a fertile area for research.

The surface properties of carbons vary widely because carbons are available in different crystallographic structures, ranging from highly graphitized to highly disordered. Improved performance and better utilization of carbons in electrochemical applications requires R&D that is directed at the characterization and modification of carbon surfaces. In particular, modifying the carbon surface to optimize its properties for a particular electrochemical application is needed. This approach would be beneficial for improving the performance of advanced rechargeable lithium batteries and fuel cells.

Fullerenes and carbon nanotubes, because of their unique structure and the availability of chemical binding sites on their surface, may play a role in electrochemical applications. However, R&D of these carbon materials is still in the early stages, with the focus on understanding their electrochemical properties. Attention has already been directed at the extremely high hydrogen storage capacity of carbon nanotubes at one university, but these observations have not been duplicated by other laboratories. Electrochemical experiments with carbon nanotubes and investigations of their practical applications in electrochemical devices are still in their infancy.

Electrochemical research on doped diamond films is still in the early stages. These films appear to be highly resistant to corrosion in aqueous media, and this property should be explored further in electrochemical applications. Demonstrations of this form of carbon in electrochemical-based detectors to monitor low concentration levels of chemical species have been described. Because of the high electrochemical stability of doped diamond films, high signal/noise ratios are possible, leading to the detection of low levels of chemical species. This application of doped diamond films is expected to receive more attention.

Introduction

Carbon continues to play a prominent role in a variety of electrochemical applications, including energy conversion and energy storage devices and analytical chemistry. Further evidence of the extraordinary versatility of this ubiquitous element is provided by the rather recent discovery of fullerenes and exotic fullerene-type derivatives, and the development of novel pathways for the synthesis of highly conducting boron-doped diamond films. Progress toward the design and optimization of new carbon-based materials relies on achieving a better understanding of the factors that control their chemical and interfacial reactivity, and Li^+-intercalation properties.

A conference was held at Case Western Reserve University, Cleveland, OH, on October 20-22, 1997 to address the following topics which are relevant to the electrochemistry of carbon allotropes:

- Graphitized and disordered carbons, as Li-ion intercalation anodes for high-energy-density, high-power-density Li-based secondary batteries
- Carbons as substrate materials for catalysis and electrocatalysis
- Boron-doped diamond film electrodes
- Electrochemical characterization and electrosynthesis of fullerenes and fullerene-type materials.

Over 80 attendees participated in the conference which involved 22 invited speakers who presented overviews of their R&D activities on amorphous carbon, graphitized carbon, fullerenes and boron-doped diamond films. The agenda for the Conference is presented in Appendix A. Abstracts of the presentations are presented in Appendix B, therefore only a broad summary of these presentations is provided here.

Conference Summary

<u>Surface Chemistry</u>. Because carbons are available in a wide range of physical structures (i.e., particles, fibers, solid blocks), they also possess differing physicochemical properties. One approach to understanding the complex surface properties of carbons is to focus on studies involving a well-defined carbon structure; and highly oriented pyrolytic graphite (HOPG) is well-established as the standard. The history and manufacture of HOPG were described at the Conference by Dr. Arthur Moore, who was involved in its development. The availability of HOPG to the research community has led to a much improved understanding of the surface structure and chemical reactivity of carbons.

An important discovery reported at the Conference involved the observation by the research groups of Scherson and Penner that point defects, which are invisible by both the scanning tunneling microscope (STM) and the atomic force microscope (AFM), are present on terraces of the graphite basal plane. The reactivity of the graphite basal plane is significantly affected by the presence of these defects which are present at areal densities from 10^9-$10^{10}/cm^2$. For example, these "invisible" defects are responsible for nucleating the growth of metal nanocrystals both from the gas phase (as shown by Scherson et al.), and electrochemically from electrolyte solutions (as shown by Penner et al.). One important consequence of these defects is that a mechanism of metal nucleation and growth is obtained which permits metal (Ag, Pt, Cu, Zn, and Cd) particles to grow electrochemically with size selectivity with particle diameters from 20 to 100 Å. Moreover, the particles prepared by this method have a narrow particle size distribution.

The most common surface groups that are found on the carbon have oxygen functionalities such as hydroxyl (>-OH), carbonyl (>=O), carboxyl (>-COOH), and lactone (>-C(=O)-O-<). The presence of surface groups plays a major role in the electrochemical behavior of carbon. For example, the oxygen functional groups on carbon are not desirable in double layer capacitors because they promote gassing during charge/discharge cycling. The presence of oxygen on carbon in Li-ion cells may also have some undesirable consequences, such as increasing the irreversible capacity loss and gas evolution.

Graphitized and Disordered Carbons. In this last decade of the 20th century, a new electrochemical application for graphitized and disordered carbons was commercialized. That is, in Li-ion cells where the carbonaceous material serves as the host structure for storing Li^+ ions in the negative electrode. The rate of growth of this battery technology is about 20% per year, and it is becoming a very important energy source for portable electronic devices. It is also being seriously considered as a power source for electric vehicles and demonstration projects have already begun in Japan (Sony/Nissan). One of the major difficulties with these carbonaceous materials is the irreversible capacity loss that occurs during the first charge cycle, compared to subsequent charges and discharge cycles. The electrochemical/chemical processes giving rise to irreversibility are still poorly understood. This is especially evident in the so-called hard carbons (non-graphitizable) and other partially carbonized materials which generally give very high Li storage capacity, but a very high irreversible capacity as well. This fact has hindered the application of such carbons.

Fullerenes and Carbon Nanotubes. The carbon allotrope called fullerenes consists of carbon atoms arranged in hexagonal and pentagonal arrays that form a spherical structure. Fullerenes and carbon nanotubes have attracted considerable interest by electrochemists because of their unusual structures and their electrochemical properties. Excellent overviews on chemistry/electrochemistry of fullerenes were presented at the Conference by Kadish, Ruoff and Echegoyen. A fullerene with the composition C_{60} is capable of undergoing six sequential redox steps: C_{60}^-, C_{60}^{2-}, C_{60}^{3-}, C_{60}^{4-}, C_{60}^{5-}, and C_{60}^{6-}. Carbon nanotubes are available in a range of diameters and lengths, with the ends capped by hemispherical carbon structures resembling half of the fullerene structure of the same diameter. The nanotube with the smallest diameter is about 7 Å, equivalent to the diameter of the fullerene C_{60}.

Doped Diamond Films. Diamond has a tetrahedral structure with carbon having sp^3 bonding. Pure diamond is an electronic insulator, but it can be made semiconducting or conducting by doping with increasing concentrations of boron atoms. Diamond films that are highly doped with boron ($>10^{19}/cm^3$) exhibit (i) metal-like electrochemical characteristics, (ii) excellent corrosion resistance, and (iii) an inert surface with poor adhesion and sizable nucleation overpotentials for electrodeposited metal adlayers (e.g., Ag). Furthermore, high quality films exhibit a low and stable background current and large overpotentials for oxygen and hydrogen evolution compared to polycrystalline Pt, glassy carbon and low-quality diamond films. Application of boron-doped diamond in flow-injection analysis has been demonstrated for detection of dissolved inorganic azide anion in aqueous media and aliphatic diamines in aqueous media. Detector performance characteristics for azide anion included a linear dynamic range of over four orders of magnitude, a limit of detection of 0.5 ppb, and excellent long-term stability.

Opportunities for Research and Development on Carbon Allotropes

Table 1 summarizes the recommendations for R&D on carbonaceous materials that are relevant to electrochemical technologies such as advanced batteries and fuel cells for transportation. A discussion on these recommendation follows.

The success in preparing Pt nanocrystals with well-controlled particle size on HOPG opens an opportunity for research using these materials. Pt nanocrystals deposited on HOPG can be employed to investigate particle size effects in electrocatalysis reactions such as the electrochemical oxidation of methanol and the reduction of oxygen. Although interesting and important particle size effects have been postulated to exist for these "structure sensitive" reactions, good model systems for investigating these effects have not previously existed. The results of these studies could be expected to positively impact the efficiency of fuel cells which employ Pt and Pt alloy nanocrystals. The metal particles that can be deposited on the defect sites of HOPG can be employed to prepare semiconducting metal salt particles. For example, Penner and co-workers have demonstrated that Cu(I) iodide nanocrystallites can be prepared from Cu metal precursor particles via an intermediate of Cu(I) oxide. The CuI nanocrystallites are narrowly dispersed in size, strongly luminescent at room temperature, and stable in air. Analogous procedures have been used to convert nanocrystals of Cd and Zn into nanocrystals of CdS and ZnO, respectively. Thus, the application of graphite as a support with unique properties for the nanometer-scale synthesis of electronic materials is one which is clearly worthy of further investigation.

Electrochemical applications where high-surface-area carbons and/or carbon particulates are used are strongly influenced by the surface properties of these materials. Consequently there is a need to investigate techniques to characterize and modify the surface properties of carbon materials for use in electrochemical technologies. In many current applications, the surface structure is poorly understood and the carbon is unstable with respect to chemical/ electrochemical reactions. Given the widespread use of carbons in both electrochemical and structural applications, surface chemistry and electrode kinetics studies on carbon are central issues that require more attention. Engineering the carbon and its surface properties to meet the needs of Li-ion cells is one example. Oxygen reactions with organic components in Li-ion cells is a technical issue that has not been fully resolved. In this regard, the type of carbon and the surface groups that are present have a major impact on the reversible and irreversible capacity of Li-ion cells. In addition, the surface properties of carbon influence the formation of the protective surface layer, its change in time, and may be partially responsible for the fade of capacity of Li-ion cells.

Boron-doped diamond films have significant potential in electrochemical applications because of their stability and resistance to adsorption of ionic species in solution. Current questions about diamond electrode behavior are centered on its surface structure and the influence of the surface on electrochemical reactivity. The lower background voltammetric currents and double layer capacitance of diamond films result in enhanced signal/ background ratios which are attractive in electroanalytical detectors. More research to exploit these attractive features of diamond films would benefit their entry into electrochemical applications such as electrosynthesis and waste remediation.

Both single and multi-walled carbon nanotube materials have the potential to dramatically impact numerous electrochemical technologies. The unique structural and electronic properties of carbon nanotubes could be quite useful in applications such as batteries, ultracapacitors and fuel cells. Key advantages of these new materials that need to be exploited are to organize, align and bundle individual carbon nanotubes to produce crystalline solids with ideally monodisperse pore sizes. These solids would be electronically conducting, in contrast to other materials possessing uniform pore sizes such as zeolites, and would therefore be conceptually better as electrodes in battery applications. Moreover, since the majority of the nanotubes are comprised of relatively unreactive van der Waals surfaces, these materials are expected to be relatively stable in corrosive and reactive environments. Studies of carbon nanotubes in thin-film form with the nanotube axis either in or perpendicular to the plane of the film would be quite interesting for exploring gas diffusion and electrochemistry, or for probing and optimizing the structure of the electrical double layer. These types of films could be quite useful for application in fuel cells or electrochemical capacitors. Individual carbon nanotubes could be used as very small microelectrodes, and microelectrode arrays could also be formed by organizing individual nanotubes properly. Electrochemical measurements on these types of electrodes might allow measurement of very fast heterogeneous rate constant and could be quite useful in electrochemical sensor applications. Thus, carbon nanotubes promise to improve the performance of key components in many electrochemical devices as well as enable new fundamental studies. Very little work has been done on the electrochemistry of carbon nanotubes materials, and much work needs to be done before films, electrodes, or crystals can be readily fabricated and their electrochemical properties can be assessed. Highly porous materials are useful for storage of gases that are consumed in fuel cells and other propulsion systems for transportation. However, the high capacity of carbon nanotubes for hydrogen gas storage that was claimed by Rodrigues and Baker at Northeastern University has not been independently verified. Further effort is needed to determine the hydrogen storage capacity of carbon nanotubes.

Table 1. Opportunities for Research and Development on Carbon Allotropes

Carbon material	Technology	Technical Issues	Research Opportunities
Graphitized and disordered carbons	Li-ion cell	• processes giving rise to irreversible capacity loss are still poorly understood • oxygen reacts with organic solvent and other components in Li- ion cells	• conduct a quantitative study of the polarization of lithiated carbon electrodes • investigate the formation and stability of the protective film on carbon electrode • investigate the role of chemisorbed oxygen on carbon and its reaction kinetics with organic-based components
Graphitized and disordered carbons	Electrode material Electrocatalyst support	• surface structure is poorly understood and probably unstable • surface composition of supported alloys is difficult to control	• develop techniques to characterize and modify carbon surfaces for electrochemical applications • develop improved methods to prepare supported electrocatalysts, particularly highly dispersed alloys
Highly Oriented Pyrolytic Graphite(HOPG)	Direct methanol fuel cell	• improved electrocatalysts for direct methanol oxidation are needed	• investigate the use of Pt and Pt alloy nanocrystals on HOPG as a model system to understand particle size effects in electrocatalysis
Boron-doped diamond	Corrosion-resistant coatings	• corrosion is major problem at anodic potentials in batteries and fuel cells	• determine if boron-doped diamond has significant advantages in electrochemical applications
Boron-doped diamond	Electrosynthesis and environmental remediation	• oxidation of metal electrodes at high anodic potentials limits their use in electrochemical applications	• evaluate potential for electroorganic synthesis and toxic waste remediation
Boron-doped diamond	Electrochemical sensor	• detection sensitivity using carbon is limited by background current	• determine detection limit and specificity of boron-doped diamond for electrochemical sensors

Table 1. Continued

Carbon material	Technology	Technical Issues	Research Opportunities
Carbon nanotubes	Porous electrodes Sensors	• unique structure has not been exploited for electrochemical applications	• demonstrate that nanotubes can be aligned in a preferred orientation and that improved electrochemical performance is obtained
Carbon nanotubes	Li-ion cell	• unique structure and electronic properties may limit electrode performance	• investigate performance as negative electrode
Carbon nanotubes	Hydrogen storage	• present options for hydrogen storage give low capacity	• confirm high hydrogen storage capacity
Fullerenes	Electrochemical	• electrochemical research is still in the early stages	• identify practical electrochemical applications

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- Cleveland Local Section of the Electrochemical Society
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- Eltech Systems Corp.
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- Solartron Instruments

The contributions of G. Blomgren, M. Heben, R. McCreery, R. Penner, S. Sarangapani and G. Swain to this report are gratefully acknowledged.

APPENDICES

Appendix A. Agenda

Time	Speaker	Title
	MONDAY MORNING	**October 20, 1997**
9:00 AM	R. Penner	Electrocrystallization of Metals at Graphite Basal Plane Surfaces
9:40	A. Vannice	Characterization of Allotropic Forms of Carbon and Cu/Carbon Catalysts with DRIFTS
10:40	D. Scherson	Model Systems for Metal Support Interactions in Electrocatalysis: Platinum Dispersed on the Basal Plane of Highly Oriented Pyrolytic Graphite
11:20	R. McCreery	Electrochemical Reactivity of sp^2 Carbon Surfaces: Dependence on Surface Structure and Reactive Sites
	MONDAY AFTERNOON	**October 20, 1997**
2:00 PM	K. Kadish	Electrosynthesis and Electrocharacterization of C60 Derivatives
2:40	M. Heben	Hydrogen and Lithium Storage in Carbon Nanotubes
3:40	L. Echegoyen	Fullerene Recipes: Add Six Electrons and Spread Them Really Thin
4:20	R. Ruoff	Studies on Carbon Nanotubes
	TUESDAY MORNING	**October 21, 1997**
8:40 AM	B. Miller	Electron Transfer and Phase Formation at Boron-doped Diamond Electrodes
9:20	J. Angus	Single-Crystal, Polycrystalline, and Chemically Modified Diamond Electrodes: A Voltammetric Comparison
10:15	G. Swain	The Electrochemical Properties of Boron-Doped Diamond Thin Film Electrodes: New Uses in Electroanalysis

10:55	J. Butler	Characterization Diamond Films Grown by Chemical Vapor Deposition
11:35	Y. Pleskov	A Comparative Study of Electrochemical Behavior of Single Crystal and Polycrystalline Boron-Doped Diamond
	TUESDAY AFTERNOON	**October 21, 1997**
2:00	M. Dresselhaus	Remarkable Properties of Newline Carbon Nanotubes
2:40	M. Wightman	Fast-Scan Cyclic Voltammetry at Carbon Fiber Electrodes
3:40	A. Moore	Highly Oriented Pyrolytic Graphite
4:20	W. Kuhr	Modification of Carbon Surfaces with Biopolymers: Effects of Electrochemical or Laser Activation
	WEDNESDAY MORNING	**October 22, 1997**
8:40 AM	G. Blomgren	Lithiated Carbon-Electrolyte Interfaces
9:20	R. Yazami	The Graphite-Lithium Electrode: Passivation Phenomena and Chemical Stability in Liquid Electrolytes
10:15	S. Sarangapani	Carbon in Fuel Cells - A Review
10:55	S. Lipka	Carbon Nanofiber Structures for Electrochemical Capacitors
11:35	J. Miller	High-Rate Carbon Double Layer Capacitors
12:15 PM		Closing Remarks

Appendix B. Abstracts for Presentations

Electrocrystallization of Metals at Graphite Basal Plane Surfaces

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On noble metal electrode surfaces, metal deposition usually occurs via a Stranski-Krastanov mechanism (layer-by-layer growth transitioning to 3-D growth) starting with the deposition of one or more underpotentially deposited metal monolayers. A much different mechanism is seen at basal plane-oriented graphite surfaces: At large overpotentials (>500 mV), metal deposition proceeds via a Volmer-Weber mode (i.e., immediate 3-D nucleation and growth) for zinc, cadmium, copper, silver, and platinum. Nucleation in these experiments is instantaneous and the size-selective growth of dispersions of metal nanocrystals on the graphite basal plane is therefore possible.

Characterization of Allotropic Forms of Carbon and Cu/Carbon Catalysts with DRIFTS

M. Albert Vannice, A. Dandekar and R. Rao
Pennsylvania State University, University Park, PA 16802-4400

Three allotropic forms of carbon-activated carbon, graphitized carbon fibers and synthetic diamond powder-have been characterized by BET, XRD, TPD and DRIFTS (Diffuse Reflectance FTIR Spectroscopy) measurements. The latter employed a specially modified DRIFTS cell. The influence of pretreatment on the surface groups present was examined. Treatment of the activated carbon with HNO_3 increased the surface acidic groups, and a high temperature treatment in H_2 removed them. The latter treatment increased C-H groups on the graphitized fibers and diamond powder. A wide range of Cu dispersion (Cu_{surf}/Cu_{total}) was obtained when copper was supported on these carbons, adsorption was utilized to identify CuO, Cu^{+1}, and Cu^{+2} surface sites based on the position of the CO band observed in the DRIFT spectrum. A significant variation in the kinetic behavior of these Cu/C catalysts was observed during the hydrogenation of crotonaldehyde and furfural.

Model Systems for Metal Support Interactions in Electrocatalysis: Platinum Dispersed on the Basal Plane of Highly Oriented Pyrolytic Graphite

A. Howells, G. S. Chottiner, I. T. Bae and D. A. Scherson
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Platinum vapor deposited at submonolayer coverages on the basal plane (bp) of highly oriented pyrolytic graphite (HOPG) in ultrahigh vacuum (UHV) was characterized *in situ* by X-ray photoelectron spectroscopy (XPS) and in air by scanning tunneling microscopy (STM). The effect of defect sites on the electronic and morphological nature of these deposits was investigated by first sputtering the HOPG(bp) with Ar^+, while blocking a section of the specimen with a mask and then exposing the entire surface to Pt vapor. An analysis of the XPS spectra indicated that in the Ar^+-sputtered region, the coverage, normalized by the Pt atom flux, was about 50% larger and the Pt binding energy ca. 0.2 eV higher, i.e., slightly more oxidized, than in the pristine region. STM images revealed discrete cluster-type features a few nm in average diameter and one to two atoms high, distributed fairly evenly within each region. However, the total amount of Pt contained within these clusters, as estimated from these images, could not account for more than 1-10% of that detected by XPS. The density of clusters was larger and their average size somewhat smaller in the sputtered, compared to the pristine regions, indicating that the presence of defect sites promotes the growth of a larger number of clusters, albeit of smaller size. The formation of large dendritic structures could be observed for HOPG(bp) surfaces which had been resistively heated, as opposed to being heated by electron bombardment from the rear. The latter technique may have resulted in electron beam damage to the HOPG surface, creating defect sites similar in their effect to those on sputtered samples. This provides evidence for Pt atoms having high atomic mobilities on rather pristine surface regions. Intentional sputtering of such pristine, resistively heated surfaces restored formation of small regularly shaped clusters. Direct correlations were found between the length of the Pt dosing and the amount of Pt on the surface as assayed by XPS yielding values between 0.5-7% of a monolayer. These experiments were performed on a single HOPG(bp) surface which had been uniformly sputtered using a movable mask. A small reduction in the Pt 4f binding energy (ca. 0.1 eV) was also observed as the Pt coverage varied over this range. Electrochemical experiments on such ensembles of Pt clusters are being carried out employing an externally actuated magnetically coupled manipulator that enables specimens to be transferred from UHV to high pressure environments without exposure to the ambient atmosphere.

Electrochemical Reactivity of sp^2 Carbon Surfaces: Dependence on Surface Structure and Reactive Sites

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Although sp^2 carbon in the form of graphite and glassy carbon (GC) is one of the most widely used electrode materials, its surface chemistry is among the least understood. Carbon's propensity toward oxidation and physisorption conspire to result in poor stability and reproducibility of surface structure, making it difficult to relate structure to electrochemical reactivity. Our approach has been to carefully characterize GC and graphite surfaces with Raman spectroscopy and XPS, for both native and modified surfaces. Of particular interest are surfaces with low O/C ratio, and those with compact, chemisorbed monolayers. Once these surfaces are in hand, the kinetics observed for various redox systems are related to the surface structure. Eleven redox systems studied to date fall into two general classes, first, outer sphere systems (e.g., $Ru(NH_3)_6^{+3/+2}$, $Ir\,Cl_6^{-2/-3}$) are relatively insensitive to surface condition, with an intentional monolayer having little effect on the electron transfer rate. Second, electrocatalytic systems (e.g., $Fe^{+3/+2}$, dopamine) require surface interactions, and in several cases specific reactive sites. The electron transfer rates of such systems are strongly dependent on carbon surface chemistry. Combined with the known electronic properties of graphite and glassy carbon, the structure/reactivity relationships revealed by our approach begin to provide a comprehensive picture of the factors controlling sp^2 carbon reactivity.

Electrosynthesis and Electrocharacterization of C_{60} Derivatives

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The reaction of chemically or electrochemically generated C_{60}^{2-} with alkyl halides (RX) can lead to the generation of organofullerenes of the type $(R)_2C_{60}$, $(R)(R')C_{60}$ or $(R)_4C_{60}$ depending upon the specific reaction conditions (1-4). This paper will discuss a probable mechanism for this reaction and will report electrochemical and spectroelectrochemical properties of selected synthesized compounds The most detailed characterization has been obtained for 1,4-$(PhCH_2)_2C_{60}$ where the initial C_{60} dianion was synthesized in the homogeneous phase by reacting C_{60} with quinone dianion prior to reaction of the resulting C_{60}^{2-} with $PhCH_2Br$ (2).

Also to be discussed will be the reactions of C_{60}^{2-} with different substituted benzyl derivatives of the type $Br\text{-}C_6H_4CH_2Br$ where Br is substituted at the *ortho*, *meta* or *para* position of the phenyl ring as well as the reaction of (1,4-$(PhCH_2)_2C_{60}$ $CH_2)_2C_{60}^{2-}$ with $C_6H_4CH_2Br$. On the basis of NMR and mass spectral data, the resulting compounds are formulated as 1,4-$(Br\text{-}PhCH_2)_2C_{60}$ for the first type of the reactions and $(PhCH_2)_4C_{60}$ for the second (5).

Each neutral C_{60} adduct was characterized as to its electrochemistry in benzonitrile containing TBAP as a supporting electrolyte and representative cyclic voltammograms of both 1,4-$(Br\text{-}PhCH_2)_2C_{60}$ and $(PhCH_2)_4C_{60}$ will be presented. The electrochemistry is not significantly altered by the type of substituents along the series of investigated disubstituted adducts of C_{60}. Both compounds undergo three one-electron reversible reductions between 0.00 and -1.90 V vs SCE and both exhibits half wave potentials which are shifted negatively with respect to the same electrode reactions of C_{60}. The difficult to reduce of the three compounds is $(PhCH_2)_4C_{60}$ is with the magnitude of the potential shift from the other two compounds depending on the specific electrode process.

Each anionic form of the compound was characterized by spectroelectrochemistry in order to determine whether the position of any near infrared bands might be diagnostic of the anion oxidation state in $[(R)_xC_{60}]^{n-}$ where $x = 2$ or 4, $n = 1$ or 2. The near-IR spectrum of $[(PhCH_2)_2C_{60}]^-$ consists of major bands at 989 and 1498 nm and minor bands appear at 874 and 1237 nm. Four absorption bands are also observed for $[(PhCH_2)_2C_{60}]^{2-}$. The major bands are located at 903 and 1294 nm and the minor bands appear at 806 and 1090 nm. As is the case of C_{60}, near-IR bands of the dianionic species, $(PhCH_2)_2C_{60}]^{2-}$ are blue-shifted with respect to those of the monoanionic species, $[(PhCH_2)_2C_{60}]^-$.

Similar well-defined bands are seen for the tetra-adducts. For example, the spectrum of $[(PhCH_2)_2C_{60}]^-$ has major bands at 1374 and 801 nm while the doubly reduced species exhibits major bands at 1185 and 749 nm. Other absorption bands are seen and will presented.

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Hydrogen and Lithium Storage in Carbon Nanotubes

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Both single-wall and multi-wall carbon nanotubes may be thought of as elongated containers once the tube caps are removed and the interiors are accessed. Our recent experiments indicate that hydrogen can be stabilized within the interiors of small-diameter single-wall nanotubes (SWNTs) by physical adsorption at 223 K while in contact with vacuum. The soots containing the SWNTs must first be gently oxidized for the strongly binding adsorption sites to become available. Although difficult to observe, the oxidation apparently removes the tube caps and allows the SWNT interiors to be accessed by molecular hydrogen. Hydrogen was found to be physically adsorbed by varying both the initial hydrogen coverage and the temperature programming rate in temperature programmed desorption spectroscopy experiments. Hydrogen adsorption on the cobalt nanoparticles present in the heterogeneous soot was also considered as a possible source for the strongly-bound hydrogen and found to not be significant. A desorption activation energy of 19.6 kJ/mol was measured. This value can be equated to the heat of adsorption in the case of physically bound species and is nearly 5x that expected for adsorption of H_2 on planar graphite. The enhanced heat of adsorption indicates that overlapping Van der Waals potentials within the internal tube cavities stabilize the adsorbed H_2. Extensive transmission electron microscopy data measured SWNT densities in the soots ranging from 0.1 to 0.2 wt%, establishing hydrogen storage densities per SWNT in the range of ~5 to 10 wt%. Our lab has also been investigating the use of larger-diameter multi-wall carbon nanotube as Li storage electrodes. Possible advantages include the potential for much higher Li capacities than can be achieved with conventional carbon materials. Preliminary results may also be discussed during this presentation if time permits.

Fullerene Recipes: Add Six Electrons and Spread Them Really Thin

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A brief historical account leading to the electrochemical detection of the hexaanions of C_{60} and C_{70} will serve as a starting point for this lecture. Then the anodic electrochemistry of several pristine fullerenes will be discussed. The power of electrochemical methods to analyze isomeric interconversions of methanofullerenes will be introduced, as well as the use of electrosynthetic methods to prepare these interesting derivatives. Particular emphasis will be given to fullerene derivatives containing crown ether adducts. The final section of this talk will emphasize the use of electrochemistry and other methods to probe the properties of self-assembled fullerene derivative monolayers.

Studies on Carbon Nanotubes

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Carbon nanofibers, and nanotubes, can be grown by vapor deposition from hydrocarbon precursors onto pre-formed catalytic metal particles. A standard method of growing nanofibers of carbon is to spray magnetite particles in a ferrofluid solution onto a substrate, reduce to iron particles, and expose to acetylene, ethylene, methane, or other hydrocarbons. Another type of pre-formed metal particle is produced in the channels of highly porous materials (silicas, zeolites) by incipient wetting followed by calcination and reduction. Our group is developing the idea of creating periodic nanoparticle arrays (NPA) for catalytic growth of carbon nanotubes. Such NPA can be made in several different ways, which will be discussed in this talk; of particular current focus is by nanoimprint lithography. Imprinters with up to 16 million identical nano-sized embossing elements are produced in a multi-step procedure using e-beam lithography and reactive-ion etching. The imprinter is then used to imprint an array of holes in a thin polymer film which has been spun-coated onto Si wafer. Metal deposition can then lead to the NPA in ways which will be described in some detail. In a separate experiment, we are in the process of designing and building a nano-stressing stage for stress-strain studies on nano-sized objects, particularly carbon nanotubes. This concept can be extended to a new form of mechanosynthesis, where individual nanotubes are stressed under compressive load so that they buckle. There exists a very steep gradient in the strain energy per carbon atom in the buckling region relative to the unstressed state. We expect to be able to create strain energy in a quite localized region on a carbon nanotube and react selectively with given reactants, as a function of the mechanical load deforming the nanotube. This will be described in detail in the talk.

Electron Transfer and Phase Formation at Boron-Doped Diamond Electrodes

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Boron-doped diamonds electrodes have been examined in a variety of electrochemical circumstances permitting some generalizations about their behavior in the semi-metallic regime. The inertness of the hydrogen-terminated surface appears to dominate the electron transfer properties and, in addition, the lack of interaction with the atomically dense and hard surface determines the physical and electrochemical characteristics of both cathodic and anodic deposition on this material. A summary of the experiments leading to these conclusions will be given. Many questions remain, particularly when the semiconductive properties of diamond are of influence.

Single-Crystal, Polycrystalline, and Chemically Modified Diamond Electrodes: A Voltammetric Comparison

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Boron-doped, polycrystalline and single-crystal diamond electrodes were studied by voltammetry. A reversible redox couple at +1.7 V vs. SHE was detected on the polycrystalline electrodes but was absent on the single-crystal electrodes. The results strongly suggest that the couple is associated with reactivity at the grain boundaries, perhaps from non-diamond, sp^2, carbon. Plasma fluorination of polycrystalline diamond electrodes using CF_4 in an RF plasma also eliminated the reversible redox couple at +1.7 V, but did not alter the potential range of water stability. Anodic polarization of as-grown, polycrystalline diamond electrodes caused addition of oxygen to the surface and made the surface hydrophilic. Additional voltammetry studies of pretreated electrodes, both graphitized or chemically etched, indicate further that the redox couple may arise in part due to the reactivity of sp^2 carbon in the grain boundaries.

The Electrochemical Properties of Boron-Doped Diamond Thin Film Electrodes: New Uses in Electroanalysis

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The use of semiconductive and conductive diamond and diamond-like carbon thin films in electrochemical systems has only recently been reported. As a result, the relationship between the physical, chemical and electronic properties of the material and the observed electrochemical performance is not well understood. The interest in diamond and diamond-like carbons as novel electrodes has emerged because of the materials' unique properties: chemical inertness, corrosion resistance, hardness and thermal stability. Such properties are desirable for many electrochemical applications. Also, electrochemistry represents one application that could utilize the rough, polycrystalline films commonly produced by CVD-growth methodologies.

Some of diamond's interesting electrochemical properties have been found to include the following: (i) a low and stable voltammetric background current, (ii) superb corrosion resistance in acidic fluoride media, alkaline media and acidic chloride media at elevated temperatures and high current densities, (iii) a wide working potential window in aqueous electrolyte solutions (2.5 - 3V) with large overpotentials for hydrogen and oxygen evolution, (iv) resistance to the adsorption of organic macromolecules like anthraquinone-2,6-disulfonate, (v) reversible to quasireversible electron transfer kinetics for the redox analytes $Fe(CN)_6^{-3/-4,}$ $IrCl_6^{-2/-3}$, $Ru(NH_3)_6^{+2/+3}$, N_3^- and aliphatic diamines without any conventional surface pretreatment, (vi) enhanced S/B ratios for these analytes in voltammetric and flow injection analysis measurements because of the low and stable background current, and (vii) resistance to deactivation as some films have been observed to exhibit a relatively unchanging ΔE_p for $Fe(CN_6^{-3/-4}$ during a one month period of exposure to the laboratory atmosphere. The latter would appear to be a unique property of diamond because often other carbon-based materials deactivate quickly upon exposure to the laboratory atmosphere and subsequently require some form of pretreatment in order to overcome sluggish electron transfer kinetics. These observations demonstrate that electrochemical measurements can be made using boron-doped thin film electrodes. Continued research is needed to determine that specific electrochemical systems diamond's excellent electrochemical properties are best suited for.

The basic electrochemical properties of highly doped (> 1 x 10^{19} cm^{-3}) diamond think films will be discussed and two electroanalytical applications highlighted: the oxidative detection of dissolved inorganic azide anion and aliphatic diamines in aqueous media.

Characterization Diamond Films Grown by Chemical Vapor Deposition

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The quality of diamond grown by chemical vapor deposition (CVD) can vary from highly defective to material better than natural diamonds. The properties or quality required for particular applications is controlled by both the intrinsic properties of diamond and the impact of the defects on the material properties. A complete spectrum of defects is observed in CVD diamond, ranging from extended defects (e.g., stacking faults, dislocations, grain boundaries) to point defects (e.g., vacancies, impurity atoms). This presentation will touch upon the characterization of these defects and their role in the growth processes and morphology of the material.

A Comparative Study of Electrochemical Behavior of Single Crystal and Polycrystalline Boron-Doped Diamond

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Capacitance and potentiodynamic measurements were conducted on single crystal (homoepitaxial) and polycrystalline thin-film boron-doped diamond electrodes. The impedance characteristics and kinetic data in the $Ce^{3+/4+}$ redox system appeared to be similar for the two kinds of diamond electrodes. Whereas kinetics of redox reactions on crystalline diamond and amorphous diamond-like carbon films differs significantly. These data as a whole lead to a tentative conclusion that electrochemical behavior of polycrystalline diamond is determined by diamond crystalline proper, rather than by disordered carbon of intercrystallite boundaries.

Remarkable Properties of Newline Carbon Nanotubes

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The present status of research on the remarkable properties of carbon nanotubes is briefly reviewed and the future outlook is considered. Particular emphasis is given to the recent high activity generated by the availability of bundles of single-wall carbon nanotubes with a narrow distribution of diameters and chiralities. Areas where interesting and challenging research problems remain are suggested. The first experimental report by Iijima on the discovery of a carbon nanotube related to fullerenes stimulated a great deal of theoretical effort worldwide. The early experimental work, including the pioneering work of Iijima, was on multi-wall carbon nanotubes. Theoretical calculations, however, focused on smaller (less than 1-nm diameter) single-wall carbon nanotubes, which were predicted to show fascinating 1D quantum phenomena in their electronic, lattice, transport and mechanical properties. For example, nanotubes were found to be either metallic or semiconducting, merely depending on the diameter of the nanotube and the angle of principal axes of the hexagons on the nanotube surface relative to the nanotube axis. These remarkable electronic properties arise from the corresponding properties of a single cylindrical tube of graphite, one atomic layer thick, with very few atoms in the circumferential direction. The basic model for the electronic structure of graphite is thus used to describe carbon nanotubes which are approximately 1 nm in diameter and several microns in length. The experimentalists met the first challenge of the theorists with an experimental demonstration of single-wall carbon nanotubes in 1993 by Iijima at NEC in Japan, and independently by Bethune at IBM Almaden in the US. However, the small quantity (<1%) of available single-wall nanotubes and their lack of purity with regard to other carbon phases (e.g., carbon nano-spheres), diameter and chirality made it difficult to carry our systematic studies of the structure and properties of the single-wall carbon nanotubes. A big breakthrough in carbon nanotube research came from Smalley's group at Rice University early in 1996 when they succeeded in preparing bundles of single-wall carbon nanotubes with relatively high yield (>70%), and with a small distribution of nanotube diameters and chirality. The availability of these single-wall carbon nanotube bundles to the research community opened the possibility for experimental study of the 1D quantum phenomena in the electronic structure, transport phenomena, and lattice mode structure that had been predicted theoretically. This talk will review the remarkable electronic and lattice mode properties of carbon nanotubes. Recent results on the Raman spectra for single wall nanotubes show the beautiful interplay between the singular properties of the one-dimensional density of electronic states and the diameter dependent frequency of the radial breathing mode of the carbon nanotubes. The strong coupling between the 1D resonant density of electronic states and the lattice vibrations through the electron-phonon coupling enable the observation of unique one-dimensional quantum effects in the Raman spectra. Analysis of such resonant Raman spectra confirm the validity of the theoretical models and lead to evaluation of the band parameters governing the electronic structure of carbon nanotubes.

Fast-Scan Cyclic Voltammetry at Carbon Fiber Electrodes

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Microelectrodes fabricated from carbon fibers have been shown to be useful as concentration sensors for neurotransmitters in the mammalian brain as well as to investigate hormone secretion from individual cells in culture. Normally, we employ these electrodes with fast-scan cyclic voltammetry using scan rates of 300 V/s or greater. This allows acquisition of a single cyclic voltammogram in less than 10 ms, and allows repetition rates of 100 ms to be employed. In this way, concentration changes can be monitored with subsecond resolution. The chief problems with these electrodes arise from shifts in the background signal that occur when rapid (300 V/s) scan rates are employed. The background current has two components: a capacitive portion and a portion that appears to originate from functional groups on the carbon surface. These surface species promote adsorption of the desired analyte molecules such as dopamine, a neurotransmitter, and the location of the surface waves is sensitive to the pH of the solution. The cylindrical surface of the fibers and the polished cross-sectional area both exhibit similar surface properties. However, we have found that removal of the surface functional groups by polishing the electrode surface in cyclohexane removes both of these contributions. The decreased signal obtained for dopamine following this treatment can be partially restored by coating the electrode surface with Nafion, a perfluorinated ionomer that accumulates cations such as dopamine at the sensor tip.

Highly Oriented Pyrolytic Graphite

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Highly oriented pyrolytic graphite (HOPG) is a product obtained by heat-treating pyrolytic carbon under stress, usually compression. It was first made about 35 years ago. Though polycrystalline, HOPG exhibits many of the properties of ideal graphite and is used extensively in research on graphite and graphite intercalation compounds. HOPG also has valuable properties for application as monochromators for x-rays and thermal neutrons, and as substrates for scanning tunneling microscopy. The historical development, structure, properties and applications of HOPG are reviewed and illustrated with examples of research carried out using this material.

Modification of Carbon Surfaces with Biopolymers: Effects of Electrochemical or Laser Activation

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Recently, we have shown that it is possible immobilize proteins to micron-sized domains on a carbon surface using maskless photolithographic techniques and a photoactivatable form of biotin (photobiotin). Maskless photolithographic techniques utilizing an interference pattern generate with a UV laser can be used to attach photobiotin to micron-sized stripes on the carbon surface. Avidin-conjugated enzymes can subsequently be attached to this spatially-patterned biotin with essentially no loss in spatial resolution. Another approach to spatially pattern the biosensor is to cover the microelectrode surface completely with the enzyme of interest, then selectively remove it from specific regions of the surface. Since the laser activation of the electrode surface can also be performed with an interference pattern, this might be the simplest way to activate the able pattern. The laser-activated carbon surface has been show to be cleaned as well as roughened with visible cracks and defects (edge sites) and the rate of electron transfer was increased by or several model redox systems.

Lithiated Carbon-Electrolyte Interfaces

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Carbon intercalated compounds of lithium should be very reactive toward electrolyte components. Spontaneous formation of a layer of reaction products on the carbon surface during the initial stages of electrochemical insertion of lithium allows the carbon to take up the full content of lithium in a first stage intercalation compound (C_6Li). Further deintercalation and intercalation of lithium occurs with only a slight further reaction of electrolyte as the electrode is cycled. The details of the passivation reaction and the extent of other reactions are important to the understanding of the negative electrode of the lithium-ion battery. The author will review work done at Energizer and other laboratories on HOPG graphite as a test material and how this contrasts with commercial graphite. The state of knowledge concerning the reaction products will also be reviewed.

The Graphite-Lithium Electrode: Passivation Phenomena and Chemical Stability in Liquid Electrolytes

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The passivation of the carbon-lithium negative electrode takes place during the its first cathodic reduction in liquid, gelled or solid state electrolytes. Such reaction is predicted by the thermodynamics and results from the electron back donating from freshly deposited lithium on the electrode surface to the electrolyte. Both solvent(s) and the lithium anion salt contribute to overall electrolyte decomposition which is irreversible in nature, that is lithium is irreversibly consumed and as result the capacity of the battery is reduced. Many efforts have been devoted with aim to lower the amount or lost capacity by appropriately selecting the electrolyte composition, the type of active carbon, the rate of first charge (battery formation), etc. We have undertaken a series of physico-chemical characterizations of the passivating film grown on the surface of pre-lithiated graphitized carbon fibers. Such fibers were allowed to react with EC-$LiPF_6$. We show unambiguously and for the first time that in addition to the inorganic phases (Li_2CO_3 and LiF) and to the organic-inorganic one $(RO-Li)_2$ reported in the literature, the film is composed of organic polymers such as polycarbonates and polyoxides of ethylene. $LiPF_6$ is also reduced since the FT-IR spectra show some new lines attributed to P-F vibrational modes different from those characteristic of the PF_6^- anion. The polymerization is probably of anionic type (1 electron/EC) with concomittant decomposition of the EC-unit to ethylene oxide and CO_2. The second part concerns the stability of lithiated HOPG (golden color LiC_6 phase) with several $LiPF_6$-based electrolytes with a single or mixed solvents. Though the exfoliation is obviously observed in PC and DME single solvents, the presence of EC is shown to significantly reduce the rate of such irreversible decomposition.

Carbon in Fuel Cells – A Review

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This review deals with the current state of the art of carbon technology and its application to fuel cells, with special emphasis to PEM fuel cells. Carbon in a variety of forms finds application in different types of fuel cells. Carbon is used in fuel cells in three important areas:

- Catalyst (alkaline fuel cells)
- Catalyst support (both acid and alkaline fuel cells)
- Construction materials: End plates (carbon-carbon composites), Bipolar plates (graphite and carbon-carbon composites), Gas distributor/current collector (carbon paper, carbon cloth)

Light weight, good structural properties, benign corrosion products and an extraordinary corrosion resistance in both acid and alkaline media make this material unique for the long life requirements of present day fuel cells. This review will give a brief outline of carbon's unique macro- and micro-structural properties and its historic development as a fuel cell material. More detailed account of improvements to catalyst support, different problems associated with bipolar plate construction and the role of composites as construction material will be given. The role of carbon as catalyst support in PEM fuel cells will be examined and contrasted with the developments in phosphoric acid fuel cells. An extensive survey of recent patent literature will be provided. The coverage will include both patent and open literature.

Carbon Nanofiber Structures for Electrochemical Capacitors

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There has been considerable interest in the properties and potential applications of nanostructured materials, particularly carbon. However, electrochemical applications of these materials have been lacking. In this presentation, we will discuss the synthesis and properties of carbon nanofiber structures prepared by the pyrolysis of hydrocarbon gases on metallic catalysts. The electrochemical performance of these materials can be tailored for a specific application through control of the process variables used to grow the carbon nanofibers. Insight into strategies used to prepare electrode structures for electrochemical capacitors will be given.

High-Rate Carbon Double Layer Capacitors

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High-energy-density capacitors have been identified as an enabling technology for electric and hybrid gas-electric vehicles. Recent capacitor development efforts have focused primarily on electrochemical capacitor (EC) technology. ECs, sometimes referred to as supercapacitors or ultracapacitors, appear well suited for these applications since they offer extraordinarily high volumetric capacitance density. This advantage is derived from the use of high-surface-area electrodes, usually carbon, with double layer charge storage, pseudocapacitor charge storage, or a combination of both mechanisms. Since capacitors are not a net energy contributor to vehicular propulsion in this application, charge/discharge energy efficiency is critically important. Well-engineered ECs usually have negligible static energy losses but can have significant dynamic losses. Besides the reduced efficiency, high dynamic losses lead to self heating and often the need for thermal management hardware, thus an unwanted reduction in the system energy density. EC dynamic losses depend primarily on the physical structure of the electrode material, the electrode thickness, and the electrical conductivity of the electrolyte. This paper discusses each of these issues. Commercial and prototype developmental ECs are examined as to their cycle efficiency in vehicle applications. Recent carbon development work for this high-rate application is reported.

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