

Electrochemical and Spectroscopic Evaluation of Lithium Intercalation in Tailored Polymethacrylonitrile Carbons

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Abstract

Disordered polymethacrylonitrile (PMAN) carbon monoliths have been studied as potential tailored electrodes for lithium ion batteries. A combination of electrochemical and surface spectroscopic probes have been used to investigate irreversible loss mechanisms. Voltammetric measurements show that Li intercalates readily into the carbon at potentials 1V positive of the reversible Li potential. The coulometric efficiency rises rapidly from 50% for the first potential cycle to greater than 85% for the third cycle, indicating that solvent decomposition is a self-limiting process. Surface film composition and thickness, as measured by x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS), does not vary substantially when compared to more ordered carbon surfaces. Li⁺ profiles are particularly useful in discriminating between the bound states of Li at the surface of solution permeable PMAN carbons.

Introduction

A primary goal in the development of Li ion batteries is to minimize the irreversible losses in the intercalating host matrix to maximize energy density. Mechanisms of irreversible loss include solvent decomposition and subsequent solid electrolyte interphase (SEI) formation which contains bound ionic lithium, surface deposition of lithium followed by solvent reactions and entrapment with the carbon matrix. Focus is currently being placed on synthetically derived carbon materials as potential anodes (1-3). The goal is to either take advantage of intrinsic properties in a given carbon or to try to tailor the properties by altering the synthesis process. The overall degree of disorder, as well as other microstructure features like open porosity, can be altered with the potential for achieving capacities in excess of that found for ordered graphite. Polymer derived carbonized polymethacrylonitrile represents one material that appears well suited for use as an optimized, tailored carbon (4).

Successful development of PMAN electrodes requires an understanding of how irreversible loss processes correlate with carbon surface activity and structure. Voltammetry, x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) have been used to study the process of solvent decomposition, Li intercalation and Li deposition on monolithic PMAN electrodes. A contiguous method has been developed to couple solution and vacuum environments to minimize the contamination and secondary chemistry that is intrinsic to ex situ analysis methods. The basal plane of highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC) have been included as examples of more highly ordered, non-intercalating, non-porous carbons for comparison purposes.

Experimental

The carbon electrodes were electrochemically treated in a contiguous cell attached directly to the ultrahigh vacuum system. This cell, shown in cross-section in Figure 1, is mounted in a separate vacuum cell that is pressurized with UHP Ar during the electrochemical experiments. Carbon electrodes are transported on an electrically isolated manipulator and placed face down, immersed in the electrolyte meniscus that is formed at the top of the TFE cell. An approximate area of 0.5 cm² is immersed using this approach. Lithium is used as both reference and counter electrodes. The reference electrode is an annular ring that is placed on line with the top of the cell to minimize the working-reference spacing (< 1mm). The counter is a planar disk that is parallel to the working electrode surface, to ensure a uniform primary current density, and separated by 1.5 cm. The cell is alternately

filled with a 1M LiPF₆ ethylene carbonate, dimethyl carbonate (1:1 vol., 11 mS/cm, Merck) electrolyte or pure DMC (98%, Aldrich) as a rinsing reagent. The electrolyte and rinse solutions are stored in gas tight syringes and are supplied to the cell by a TFE manifold and metering valves. The entire manifold is kept under vacuum until solution is required. A PAR 273 potentiostat was used for electrochemical control and measurement. The cell is mounted in a UHV compatible chamber added to the end of a Vacuum Generators ESCALAB 5 spectrometer. XPS measurements were made with a 300 W Mg(K α) source using a pass energy of 20 eV. SIMS measurements were made with a Balzer QMA400 quadrupole with a three lens optic system for energy separation. Secondary ion emission was stimulated using 4 keV Xe.

The materials included in this study were glassy carbon (GC, Alpha AESAR, type II), a ZYB graphite crystal oriented to the basal plane (HOPG, Advanced Ceramics) and carbonized methacrylonitrile/divinylbenzene co-polymers (PMAN, Sandia). Glassy carbon disks were spark cut to size from either sheet or rod stock, polished and cleaned by sonication in o-xylene, followed by soxhlet extraction in isopropanol and a final o-xylene rinse. The graphite crystal was cut to size using a razor blade. PMAN monoliths were pressed from 3:1 (vol.) methacrylonitrile/divinylbenzene powder mixtures and carbonized at 1100°C in an Ar atmosphere (4). The resulting monoliths are permeable to the electrolyte with geometric densities of 0.54 g/cm³ and strut densities of 1.86 g/cm³. The average interlayer spacing, $d[002]$, was found to be 3.74 Å compared to values of 3.35 and 3.48 Å for HOPG and GC, respectively. The glassy carbon and graphite samples were also annealed in a 5% H₂/Ar atmosphere at 800°C for a period of 2 hours. After processing, samples were transferred under Ar to a glove box and stored under Ar until use to minimize contamination.

Results and Discussion

The initial carbon samples are relatively contaminant free. We find that all three types of carbon show varying degrees of surface oxygen. HOPG surfaces were the least contaminated surfaces yielding a value of 1.4 at% while PMAN monoliths gave values of 2.2 at%. The glassy carbon surfaces show the greatest oxygen concentrations on the order of 9.8 at%. CHNO analysis of these carbons produced O values at less than 0.8 at%, indicating that atmospheric exposure leads to measurable O adsorption. The PMAN surfaces show residual traces of nitrogen in the 1.0 at% range, consistent with bulk chemical analysis results that yielded a value of 1.7 at%.

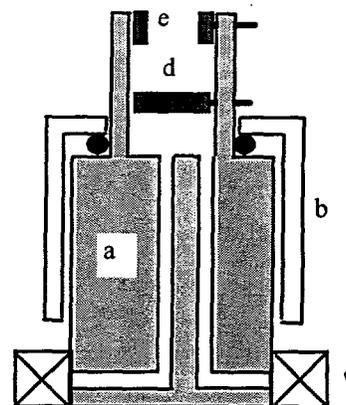


Figure 1: Cross-section View of Contiguous Electrochemical Cell - a) TFE cell body, b) polished stainless steel vacuum sealing surface, c) TFE metering valves, d) Li counter electrode, and e) Li reference electrode

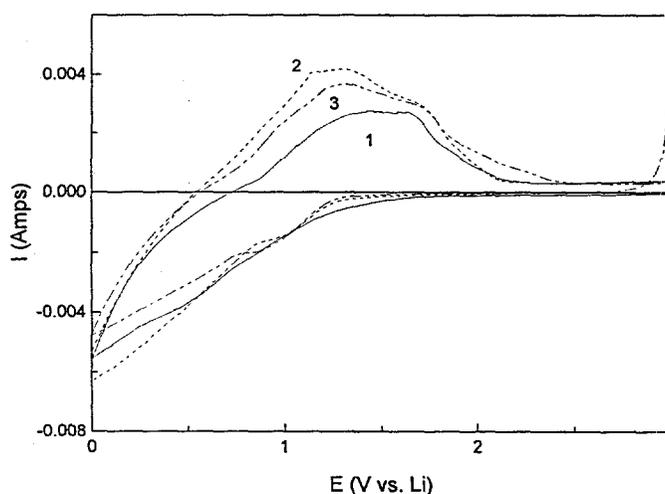


Figure 2: Cyclic Voltammetric Response of a PMAN Electrode in 1M LiPF₆ EC/DMC at 1 mV/s - cycle numbers are designated

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The similarity of these values argues that the surface is not appreciably enriched with N. SIMS measurements show that all of the carbons contain some quantity of surface oxygen with the glassy carbon yielding the highest levels. These three surfaces can also be distinguished by the width of their respective C(1s) transitions with the HOPG yielding the most narrow value of 1.04 eV while PMAN yields a value of 1.45 and GC of 1.24 eV.

The PMAN carbon shows clear evidence of lithium intercalation at potentials above 0V. Figure 2 shows a series of voltammetric scans from initial open circuit (ca. 3.1 V) to 0V at 1 mV/s. The first cycle voltammogram shows a cathodic current threshold at approximately 1.5 V, followed by a rapidly increasing current as 0V is approached. The return first cycle shows significant recovery of charge with de-lithiation (efficiency = 49%). De-intercalation is characterized by a broad band of current with several inflection points, indicating that the process of Li release is occurring in stages. Subsequent cycles show a decrease in the potential of cathodic current threshold to 1.2 V and an overall decrease in cathodic current levels to 0V. The higher currents of cycle 2 are an artifact of a meniscus fluctuation. The shift in threshold and lower currents indicate that intercalation and solvent decomposition are occurring simultaneously. The efficiency rapidly climbs during the first several cycles reaching a value of 85% after three cycles. These electrochemical results are very similar to what we observe for PMAN fully immersed in the same electrolyte using an alternate electrochemical cell design. Comparison of the meniscus and fully immersed techniques indicate that capacities of 29 mAh/g are achieved in these 1 mV/s cycles and that only 26 % of the total monolith mass, or 9.4 mg, is being accessed using this meniscus method. Full immersion of the PMAN electrode also appears to produce a more rapid rise in efficiency with cycle number (> 95% for second cycle).

Table 1: Variation in Surface Composition for Electrochemically Pretreated Carbon Electrodes
Concentration (at. %)

Sample	Li	F	O	C	P
HOPG cycled to 0V	38.3	47.2	5.0	7.5	2.0
GC cycled to 0V	52.8	33.2	8.4	2.1	3.5
GC cycled and held at -0.3V	54.5	33.9	5.6	3.8	2.3
PMAN cycled to 0V	43.7	28.2	6.9	19.4	1.8
PMAN cycled and held at 0V	43.2	26.0	13.1	15.3	1.9

The structure of the solid electrolyte interphase (SEI) layer appears to be comprised of two components. XPS measurements indicate that the outer layer of the SEI is predominantly comprised of Li and F, as shown in the data of Table 1. Considerably lower levels of both C and O are measured along with trace levels of P. The position of the Li(1s) is subject to considerable surface potential induced shifting. We find a consistent energy difference of 26.1 eV between the Li(1s) and the F(2s) indicating a similar LiF outer layer composition for the films formed on all carbon types explored. The position of the F(1s) is consistent with a surface LiF species. This predominance of surface F indicates that residual moisture is present and may be responsible for HF-based modification of the SEI layer (6). The outer surface also shows a broad, asymmetric O(1s) with a

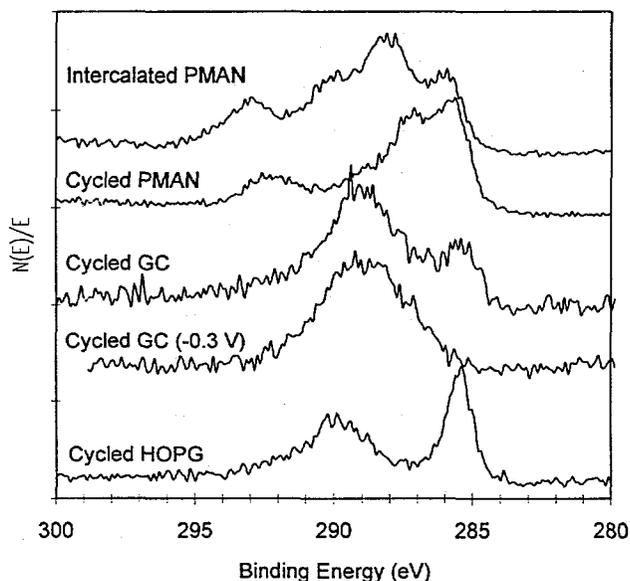


Figure 3: Variation in C(1s) Lineshape with Carbon Type and Electrochemical Pretreatment

halfwidth typically of 3 eV indicative of multiple states of surface O. C(1s) spectra show a variety of forms of carbon. Representative spectra are shown in Figure 3. We find evidence for aliphatic carbon in the range of 285 to 286 eV, carbon bound to oxygen in the range of 286 to 289 eV, and carbonate and alkylcarbonate at 290 eV (5). The very high binding energy species observed on PMAN at 293 eV most likely results from a CF complex and is not always observed. All of the carbons are seen to possess some level of near-surface carbonate. HOPG shows the lowest overall degree of product carbon build-up with its substrate transition (full width at half maximum - 1.05 eV) still easily detectable. The fact that a product layer is observed in SIMS analysis suggests that the surface film on HOPG may be discontinuous, resulting in electrolyte decomposition and product nucleation and growth at select sites on the surface.

SIMS data are consistent with the XPS results. Representative positive and negative ion spectra for PMAN cycled to 0V are shown in Figure 4. We find a series of positive ions separated by 26 amu starting at 33 amu and extending up to 137 amu. We attribute these ions to a series of $\text{Li}_{x+1}\text{F}_x$ species. Negative ion spectra show the predominance of F^- . Additional positive ions are detected at 37, 47 and 56 amu in substantially lower yields than the $\text{Li}_{x+1}\text{F}_x$ ions. We attribute these ions as being due to LiCH_2O^+ , CH_3O_2^+ or $\text{C}_2\text{H}_4\text{F}^+$, and $\text{C}_3\text{H}_4\text{O}^+$, respectively. Additional negative ions are detected at 35, 38, 45 and 71 amu. Possible assignments for these ions are LiCO^- , F_2^- , CHO_2^- and $\text{C}_4\text{H}_7\text{O}^-$, respectively. These observed $\text{LiCH}_n\text{O}^{\pm}$ ions may result from carbonate or they may be derived from alkylcarbonates. We do not detect CO_3^{2-} directly. We find that an Li_2CO_3 standard (powder pressed into In foil) yields predominantly Li^+ , O^- , LiO^+ , Li_2O^+ , LiCO^- and $\text{LiCH}_2\text{O}^{\pm}$ ions, indicating that the inert gases are not effective at generating appreciable carbonate ion yields. We do observe higher order (C_2 or greater) alkoxy ions on PMAN, but do not detect analogs complexed with Li. We also observe low intensity emission consistent with C_2H_n , C_3H_n and C_4H_n ions, that may indicate the possibility for some degree of polymerization of ethylene carbonate. In addition, emission of a series of PO_n^- ions (63 and 79 amu) is detected in negative ion spectra. These same ions are detected on a reference PMAN surface that is kept in the vacuum system specifically for tracking the adsorption of volatile species. P, along with F, appear to be ubiquitous contaminants within our system. Large scale differences in SIMS spectra are not observed between carbon types, despite the differences observed in the photoemission spectra. We see the same series of positive and negative ions for graphite and glassy carbon surfaces with only minor differences in abundance.

The composition of the SEI below this surface layer can be evaluated by ion sputtering. SIMS has been used to track both the composition of the surface film as well as the Li profile into the carbon bulk. The spectra displayed in Figure 5 show the relative secondary ion intensities as a function of

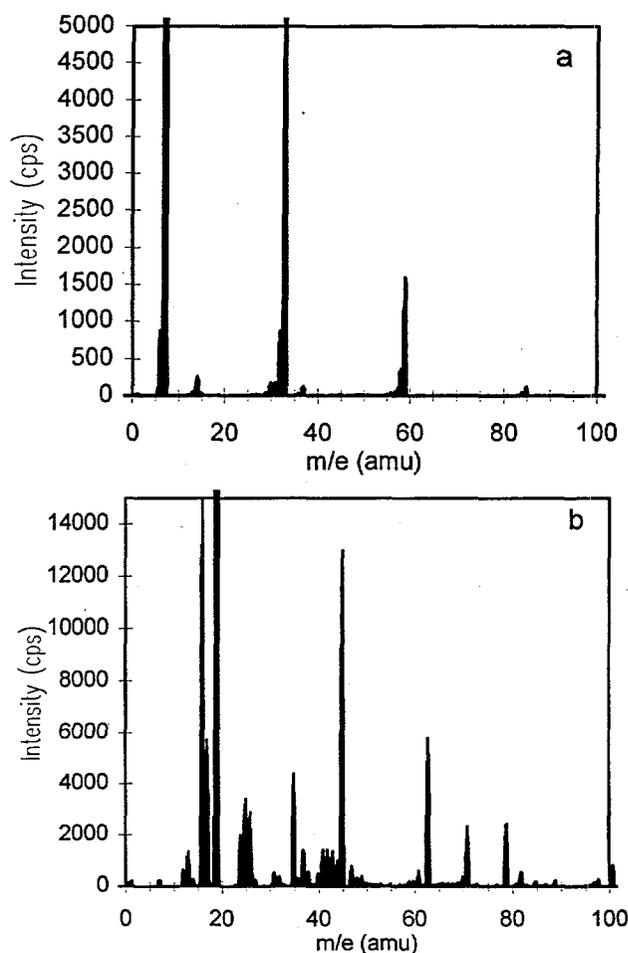


Figure 4: Positive (a) and Negative Ion (b) Spectra of PMAN Cycled to 0V

sputtering time for glassy carbon. The glassy carbon possesses a clear interface between substrate and surface film because of its lack of porosity. The positive ion profile shows an immediate decay for CH_3O_2^+ ions, an initial increase, maximum and eventual decrease for Li_2F^+ and LiCHO^+ , and a similar but extended response for Li. The negative ion profile shows that P is rapidly removed from the surface, followed by a maximum signal for both oxygenated and fluorinated forms of carbon, and the eventual rise of the substrate signals. This data argues that F^- , in various forms, is distributed throughout the film along with LiCO^- ions that may be derived from either carbonate or alkylcarbonates. The mismatch in the LiCO^- and LiCH_2O^+ profiles suggests two different molecular sources of these ions or a significant change in local chemical environment resulting in varying ion production probability. The cause of the extension in time of the Li signal is unknown. Sequential 0 to 200 amu spectra were acquired at increments of 200 seconds for the first 1000 seconds of sputtering. No unique positive or negative ions were detected. Possible interpretations of this data could include either an aliphatic layer adjacent to the glassy carbon substrate or preferential ion mixing of Li with the substrate and a resulting ion yield change. Support for the latter explanation can be found in a more narrow profile for Li^- when compared to Li^+ . We have calibrated our sputter rate using polydimethylsiloxane films ranging in thickness from 20 nm to 100 nm, spin cast onto Si wafers. An average sputter rate of 0.08 nm/s was calculated for this thickness regime. Based on the inflection point for the product ion curves in these sputter profiles, we estimate a mean film thickness of approximately 70 nm ($\pm 10\%$) for glassy carbon.

The profiles generated on PMAN substrates are more difficult to interpret due to the permeable nature of this material and the lack of a reference plane to define the substrate/surface film interface. However, the same general trends are observed. We find that Li is preserved well into the bulk of the film, after the decay of surface fluoride and alkylcarbonate derived species. Similar mean film thicknesses of 70 nm are measured using ion emission from the film. The primary difference in the profiles is the continued presence of surface product long after the appearance of ions derived from the substrate. We find no significant change in the ion distribution, indicating that what forms on the outer surface of the monolith is very similar to what forms on the internal surface.

The SIMS profiles can be used to detect Li intercalation into PMAN monolith electrodes. Figure 6 shows a series of Li^+ distribution curves for both PMAN and glassy carbon subjected to different electrochemical pretreatment. Comparison of these profiles shows the retention of a relatively high Li signal for PMAN due to the porous nature of the monolith, as previously discussed. Comparison of Li profiles from PMAN cycled from open circuit to 0V and back to open circuit versus PMAN cycled to 0V and emersed, show a greater relative signal, indicating Li has intercalated into the monolith. We can

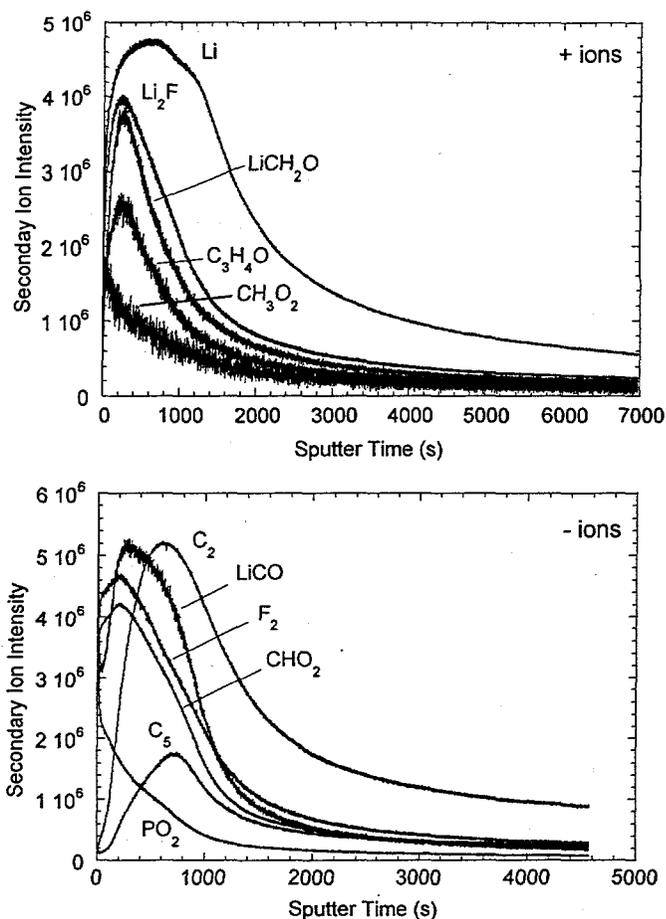


Figure 5: SIMS Profiles for Glassy Carbon Cycled to 0V - intensities have been adjusted for display purposes

distinguish between intercalation and substrate surface deposition by comparing the previous profiles with that generated from a glassy carbon surface cycled to -0.3 V and emersed. This profile shows a discrete region of additional Li that extends the maximum ion yield portion of the curve by approximately an additional 500 seconds, but rapidly decays. Based on previous metal and semi-metal sputtering studies, we estimate the mean Li underlayer thickness to be approximately 34 nm. The Li profiles for PMAN show that where the Li intensity from the cycled

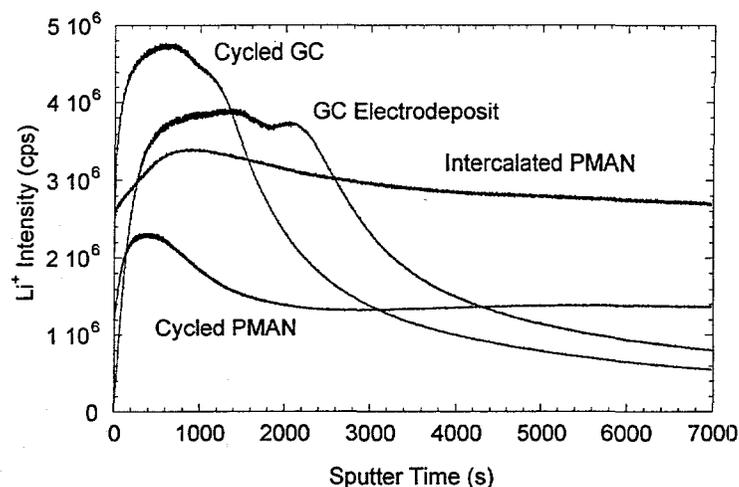


Figure 6: Variation in Li^+ Secondary Ion Sputter Profiles with Carbon Type and Electrochemical Treatment

PMAN eventually stabilizes at a nearly constant value, the intercalated PMAN signal gradually decays with sputter time. This behavior would be expected for the cell design used because the region of the monolith immediately adjacent to the bulk solution should be in contact with the highest local concentration of Li and would be expected to yield a higher extent of intercalation, provided solution diffusion constraints are as rate limiting as intercalation kinetics.

Conclusions

The response of monolithic PMAN electrodes has been studied using a combination of electrochemical and surface spectroscopic probes. We find that Li intercalation occurs at 1.2 V positive of the reversible Li potential. Solvent decomposition occurs with initial intercalation below this threshold potential. The initial efficiency of the monolith can be as low as 50% and rapidly rises to 85% with the third full cycle (higher values are seen for full electrode immersion). XPS analysis demonstrates that the near-surface of the SEI that forms is predominately LiF, indicating moisture contamination in the solution phase treatment of these electrodes. Evidence for hydrocarbon, carbonate and alkylcarbonate formation in the surface film are found with combined XPS and SIMS analysis. The chemical identity of the film is not strongly dependent on the carbon type. We find that these films are approximately 60 to 80 nm in thickness and show some compositional variation. Li distribution profiles generated by dynamic SIMS can be used to discriminate between surface film formation, Li surface deposition and intercalation, even for the electrolyte permeable PMAN carbons.

Acknowledgments

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