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The Effects of Silicon Doping on the Performance of PMAN Carbon Anodes in Li-Ion Cells

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Abstract

Carbons derived from polymethylacrylonitrile (PMAN) have been studied for use as intercalation anodes in Li-ion cells. The effect of Si doping upon the electrochemical performance of PMAN carbons was studied using tetravinylsilane (TVS) and tetramethysilane (TMS) as sources of Si during the formation of the PMAN precursors. The carbons were characterized by galvanostatic cycling, cyclic voltammetry, and complex impedance. The presence of 9 to 11 w/o Si in the PMAN lattice greatly increased the irreversible capacity of these materials.

Introduction

A considerable effort has been expended worldwide in trying to maximize the capacities and improve the rates of Li-ion carbons for rechargeable applications. These carbons are disordered in structure and are only partially graphitized. The maximum degree of intercalation that is theoretically possible for pure graphite is LiC_6, which is equivalent to 372 mAh/g. A number of the disordered carbons have capacities well above that but much of this capacity is not reversible; i.e., a fair amount of the Li inventory is permanently tied up in a passivation film that forms on the surface of the carbon during the first intercalation of Li^+.

Compositional modifications have been examined by various researchers to improve performance. Wilson and Dahn studied Si doping of carbons derived from benzene using $SiCl_4$ and dimethyldichlorosilane [$(CH_3)_2Cl_2Si$] as sources of Si.[1] These carbons were formed by vapor pyrolysis of the reactants using conventional chemical-vapor-deposition (CVD) techniques. They reported an increase in the reversible capacity from 300 mAh/g to near 500 mAh/g at a Si level of 11 a/o.

In this paper, we report on the performance of carbons derived from PMAN doped with ~4 a/o Si using TVS and TMS. The doped PMAN carbons were characterized by galvanostatic cycling, cyclic voltammograms, and complex impedance.

Experimental Procedures

Materials - PMAN carbons are typically prepared by an inverse-emulsion technique, using divinylbenzene (DVB) as a crosslinking agent.[2,3] In this study, the silicon species was incorporated into the mixture in the form of an oil-phase-soluble species (TMS) or an oil-phase co-monomer (TVS) at a nominal concentration of ~4 a/o. The surfactant used in the emulsification process was reasonably effective in partitioning the silanes from the water phase of the emulsion.

The samples were cured under argon at 65°C for 16 hours with ammonium persulfate as a free-radical initiator. In the case of TVS, the initial mole ratios were MAN:DVB:TVS=2:1:1; the corresponding ratios for TMS were MAN:DVB:TMS=2:1:1.5. The materials were ground, washed, and stabilized in air at 240°C for 12 hours before pyrolysis. The resulting polymer precursor powder was pyrolyzed under Ar/5% H_2 with a heating rate of 2°C per minute and held at 700°C for 5 hours to establish an equilibrium microstructure. The Si content of the TVS PMAN carbon was 9 w/o while that for the TMS PMAN carbon was 11.3 w/o. This was determined by combustion of the carbon to CO_2 and measurement of the amount of SiO_2 that formed.

The electrolyte solution for the characterization tests was 1M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC), in a 1:1 volume ratio. The water content of the solution, as measured by Karl-Fischer titration, was typically <40 ppm. Li foil (Foote Mineral) was used for the counter and reference electrodes.

Cells - The three-electrode system used to test the carbons has been previously described.[4] The anode was made with carbon powder, 15 w/o polyvinylidene fluoride (PVDF) as a binder, and 5 w/o Super 'S' carbon as a conductive additive and was pasted onto a Cu substrate. The anode discs were 1.27 cm or 0.63 cm in diameter (1.27 cm^2 and 0.32 cm^2 area, respectively) and were separated from the 0.25-mm thick Li counter electrode by Celgard 2500 separators. A Li flag was used as a reference electrode. The mass of active carbon ranged from 2 mg to 6 mg. Cell assembly was conducted in a dry room maintained at a dew point of less than -60°C. The cells were evacuated and backfilled with electrolyte solution in a glove box where the moisture and oxygen content were <10 ppm each. After filling, the cells were allowed to stand overnight before testing.

Apparatus - Galvanostatic testing of the cells was performed using an Arbin Corp. Battery Test System.

DISCLAIMER

undoped carbon (inset in Fig. 4) was considerably different, however. It showed a semicircle of ~10 ohms but with a significant inductive component (portion above the *x* axis). (The corresponding resistance for a 0.63-cm-dia. anode–the same diameter as for the Si-doped carbons–would be 40 ohms.) This behavior has been repeatedly observed for PMAN carbons pyrolyzed between temperatures of 700° and 1,100°C.[4] It is attributed to the formation of reactive surface species on the carbon during the first reduction below potentials of 0.5 V–especially at 0.01 V. These species are associated with solvent-reduction processes that lead to formation of the passive film. The inductive behavior is no longer observed after four or five cycles, after a more coherent passive film has been formed.

The TMS-doped carbon showed a single semicircle with a diameter of ~30 ohms in its impedance spectrum at 0.01 V (Fig. 5), with a pseudo-Warburg tail. The corresponding spectrum for the TVS-doped carbon showed a much larger semicircle–with a diameter three times that for the TMS carbon–plus the beginning of a second semicircle. The spectrum for the undoped carbon (insert in Fig. 5) showed the same inductive behavior that it did at 0.5V, with a similarly sized semicircle. After four or five cycles, the carbons show a second, low-frequency semicircle along with the original high-frequency semicircle.

The high-frequency semicircle is associated with charge-transfer reactions with the passive film. The much larger semicircle for the TVS carbon indicates the charge-transfer kinetics are not as facile as for the TMS carbon. The smaller, low-frequency semicircle for the TVS carbon is associated with charge transfer during Li^+ intercalation of the carbon to form LiC_6–the normal electrochemical process at this potential. The low frequency semicircle becomes better defined after four or five cycles. The Warburg tail associated with diffusion is not present for the TVS sample; it only becomes evident at frequencies below 10 mHz.

Discussion

The performance data for our Si-doped PMAN carbons are in marked contrast with those reported by Wilson and Dahn.[1] They observed an increase in the reversible capacity from 300 mAh/g to near 500 mAh/g at a Si level of 11 *a/o*. The difference does not appear to be related to the lower level of Si (~4 *a/o*) in our samples. Wilson and Dahn reported a reversible capacity of 433 mAh/g at even 3.1 *a/o* Si.

Our Si-doped carbons were prepared by pyrolysis at 700°C of liquid PMAN-DVB precursors doped with TMS and TVS. Wilson and Dahn prepared their Si-doped carbons by CVD at 950°-1,050°C. The major differences in the precursors used and considerably different pyrolysis conditions are felt to be responsible for the observed differences in the electrochemical characteristics. The actual distribution or location of the Si in the carbon structure is not known. NMR tests are planned to shed light on this issue.

Conclusions

Between 9 and 11 w/o Si can be incorporated into PMAN carbon by using TVS and TMS during the formation of the precursor emulsion. The presence of Si in the carbon lattice has only a small effect on the reversible Li-ion capacity of the carbon but dramatically increases the irreversible capacity and, to a lesser extent, the capacity fade during cycling. The passive film that forms is not as protective or as complete as for undoped PMAN and results in a lower coulombic efficiency during cycling. The cyclic voltammograms for the TVS-doped PMAN corroborates the low first-cycle efficiency noted during galvanostatic cycling. Film formation is initiated at 1.14 V for undoped PMAN and at 1.33 V for the TVS-doped PMAN.

Complex-impedance spectra for the Si-doped PMAN carbons show a large semicircle at 0.5 V and a pseudo-Warburg tail during the first reduction. They lack the inductive loop that is normally observed under these conditions for undoped PMAN. The diameter of the semicircle for the TVS material is greater than that of the TMS material at 0.01 V, indicating the charge-transfer kinetics are as not as facile. In general, Si doping reduces the charge-transfer kinetics. Even at 0.01 V, there is no evidence for any inductive behavior for the Si-doped PMAN carbons, in marked contrast to the undoped material. The Si doping has a profound impact upon the formation of reactive species during solvent reduction (passive-film formation) in the first reduction step.

References

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3. Delnick, F. M., W. R., Even, Jr., A. P Sylwester, J. C. F. Wang, and T. Zifer, **U.S. Patent 5,426,006**, June 20, 1995.
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The test profile consisted of galvanostatic cycling at 0.50 mA/cm^2 between 2 V and 0.01 V for 20 cycles. An open-circuit wait of 600 s was imposed between charge and discharge. The nominal open-circuit voltage (OCV) of a fresh cell was ~3.25 V.

Cyclic voltammograms were generated using a Princeton Applied Research Model 263 potentiostat. The cell was scanned between voltage limits of 3 V and 0.01 V at a sweep rate of 1 mV/s.

Complex-impedance measurements were performed using a Solartron Model 1250 Frequency Response Analyzer coupled to a Solartron Model 1286 Electrochemical Interface. The impedance spectra were normally taken over a frequency range of 65 kHz to 100 mHz. Complex-impedance spectra of the carbon samples during galvanostatic cycling were taken at open circuit before intercalation and under OCV conditions at 2 V, 0.5 V, and 0.01 V during the first intercalation. Similar measurements were taken at 2 V, at the end of one complete intercalation/deintercalation cycle.

Results

Galvanostatic Cycling - Typical first-cycle charge/discharge curves for a standard (undoped) and the two Si-doped PMAN carbons are shown in Figure 1. The maximum theoretical capacity of 372 mAh/g that is possible with the formation of LiC_6 for a graphitic material is indicated.

The Si-doped materials showed a more gradual decrease in voltage with extent of intercalation than did the undoped PMAN carbon. The capacities for all the carbons were much greater than that for LiC_6 formation, with the Si-doped carbons showing the largest capacities. Unfortunately, the amount of irreversibility was also increased by Si doping, as shown by the cycling data in Table 1.

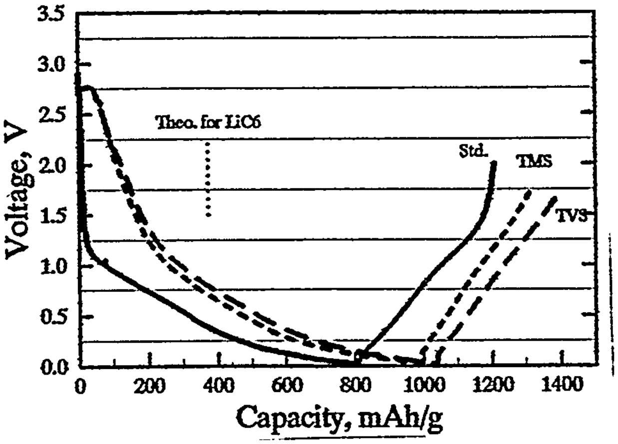

Figure 1. Typical First-Charge/Discharge Cycle for Undoped and Si-Doped PMAN Carbons.

Q_{tot} is the total capacity observed on the first intercalation. Q_{rev} is the reversible capacity observed during the first deintercalation. The reversible capacities were similar for the undoped and Si doped carbons. The fade, however, was more severe with the Si-doped samples. Q_{irr} is the difference between Q_{tot} and Q_{rev} and represents the irreversible capacity that is associated with the formation of a passive film. This results from reduction of solvent during the first reduction (intercalation). The addition of Si to the PMAN carbon had a detrimental effect on the irreversible capacity–especially for the TVS-doped material.

The addition of Si to the PMAN considerably reduced the first-cycle efficiency for both TMS and TVS doping. Smaller reductions in efficiencies were

Table 1. Summary of Electrochemical Performance of Undoped and Si-Doped PMAN Carbons During Galvanostatic Cycling.[a]

Sample	1st Cycle				20th Cycle			
	Q_{tot}, mAh/g	Q_{rev}, mAh/g	Effic., %	Q_{irr}, mAh/g	Q_{tot}, mAh/g	Q_{rev}, mAh/g	Effic., %	Fade,[b] mAh/g-cycle
TVS-doped	965.4	363.8	37.7	601.6	272.3	263.1	96.6	-1.83
TMS-doped	971.3	394.8	40.8	576.5	286.1	278.5	97.3	-1.77
Undoped	675.5	328.7	48.6	346.8	218.8	214.9	98.3	-1.40

[a] Average of two data points per test (1.27-cm diameter anodes).

[b] Fade = (Q_{rev} at cycle 20 - Q_{rev} at cycle 11)/10

observed by the 20th cycle, but were still greater for the Si-doped PMAN carbons. This indicates that the passive film is not as as well formed or complete, or that is film is more porous when Si is introduced into the carbon.

Cyclic Voltammetry - The results of cycling voltammetry tests with the undoped PMAN carbon are summarized in Figures 2.

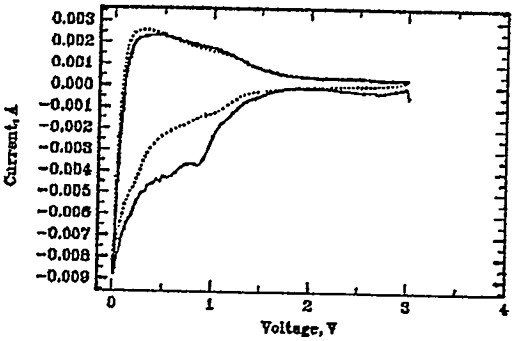

Figure 2. Cyclic Voltammogram for Undoped 700°C PMAN Carbon. Solid line is 1st cycle; dotted line is 2nd cycle. (Scan rate = 1 mV/s.)

On the first reduction, the undoped PMAN showed major peaks at 0.84 V and 0.56 V, with much smaller peaks at 1.14 V and 0.20 V. Only a single broad peak at 0.28 V was observed during the oxidation step. The two major reduction peaks are associated with solvent-reduction (film-formation) processes, since they were not reversible. The overall coulombic efficiency for the first cycle was only 53.0%. This increased to 91.7% on the second cycle.

The results of cyclic voltammetry tests with the TVS Si-doped PMAN carbon are shown in Figure 3. This material showed a broad peak at 0.50 V with a second weak peak at 1.33 V. No peaks were observed during the subsequent oxidation. The presence of Si greatly increased the irreversibility of the reduction processes, with the first-cycle coulombic efficiency being only 26.0%; this increased to 69.5% on the second cycle–much less than for the undoped PMAN.

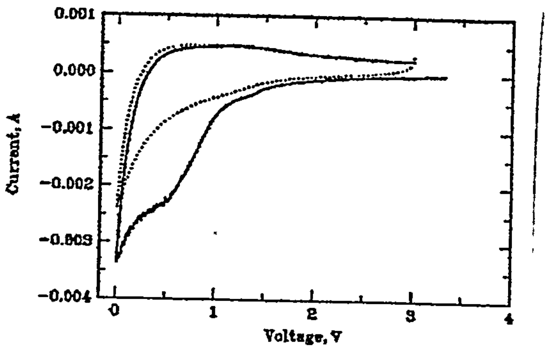

Figure 3. Cyclic Voltammogram for TVS Si-Doped 700°C PMAN Carbon. Solid line is 1st cycle; dotted line is 2nd cycle. (Scan rate = 1 mV/s.)

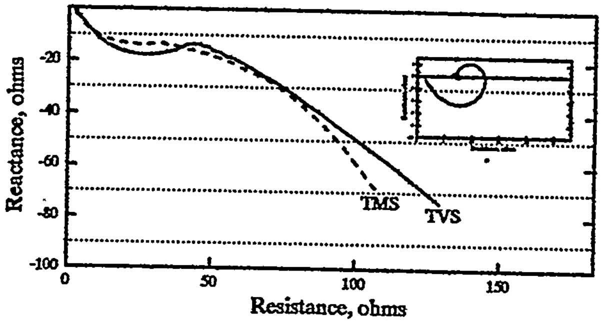

Figure 4. Complex-Impedance Spectra for TMS and TVS Si-Doped PMAN Carbons at 0.5 V. The Inset Shows the Corresponding Spectrum for Undoped PMAN (25 Ohms Full Scale X Axis).

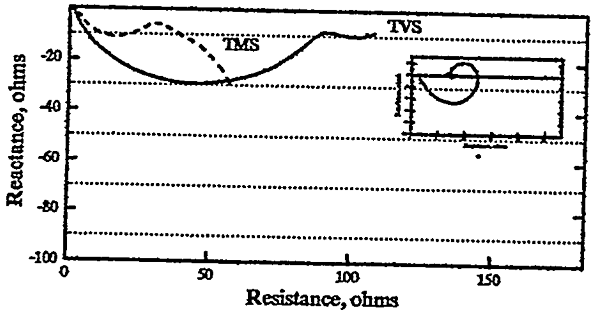

Figure 5. Complex-Impedance Spectra for TMS and TVS Si-Doped PMAN Carbons at 0.5 V. The Inset Shows the Corresponding Spectrum for Undoped PMAN (25 Ohms Full Scale X Axis).

Complex Impedance - The complex-impedance spectra for both the doped and undoped carbons were similar at open circuit and at 2 V during the first reduction, basically showing capacitive behavior. The corresponding spectra at 0.5 V and 0.01 V, however, differed markedly. The impedance spectra for the Si-doped carbons at a potential of 0.5 V during the first reduction are shown in Figure 4 for 0.63-cm-dia. discs. They show a semicircle with a diameter of ~43 ohms (associated with charge-transfer processes) and a Warburg tail (associated with diffusion processes). (A pure diffusion process will result in a line at an angle of 45° to the *x* axis.) At this potential, lithiation is just starting, as the formation of the passive film was initiated at 1.33 V for Si doped PMAN (Fig. 3) and 1.14 V for undoped PMAN (Fig. 2) during the first reduction. The two impedance spectra are quite similar.

The corresponding impedance spectrum for the