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Temperature Effects on the Performance of PMAN-Derived Carbon Anodes in 1M $LiPF_6$/EC-DMC Solution

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Abstract

The effect of temperature on the reversible and irreversible capacities of disordered carbons derived from polymethacryonitrile (PMAN) and divinylbenzene (DVB) copolymers was studied in 1M $LiPF_6$/ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 v/v) solution by galvanostatic cycling. The kinetics of passive-film formation were examined by complex-impedance spectroscopy. Temperatures of 5°, 21°, and 35°C were used in the study.

Introduction

A considerable research effort is underway to utilize carbon and graphite materials as anodes for use in rechargeable Li-ion cells. During the first intercalation, however, solvent-reduction processes take place which irreversibly tie up part of the Li^+ in a passive film. This film is a solid-electrolyte interface (SEI) that is conductive to Li^+.[1] The nature and composition of the film is a function of the type of solvent and supporting electrolyte used. It is desirable to minimize the extent of passive-film formation while maintaining a high reversible capacity for intercalation.

To gain an understanding as to the kinetics of passive film formation, the intercalation process was examined as a function of temperature for disordered carbons derived from PMAN-DVB copolymers. The disordered carbons are of interest because they frequently have reversible capacities well in excess of the 372 mAh/g possible with graphites. Both the irreversible and reversible capacities were measured during galvanostatic cycling experiments with 1M $LiPF_6$/EC-DMC at temperatures of 5°, 21°, and 35°C. Complex-impedance spectra were taken as a function of voltage during intercalation to derive kinetic information of the intercalation and passive-film processes.

Experimental

Materials – PMAN carbons were prepared by an inverse-emulsion technique, using DVB as a crosslinking agent with methacrylonitrile.[2,3] The materials were 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. The electrolyte solution for the characterization tests was 1M $LiPF_6$ in EC-DMC in a 1:1 volume ratio (Merck). The water content of the solution was typically <40 ppm as measured by Karl-Fischer titration. 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) (Kynar 461) 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 in diameter (1.27 cm^2 area) and were separated from the 0.25-mm thick Li counter electrode by two Celgard 2500 separators. A Li flag was used as a reference electrode. The mass of active carbon ranged from 3 to 6 mg. Cell assembly was conducted in a dry room maintained at a dew point of less than -60°C. The polypropylene 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. The cells were cycled galvanostatically at 0.50 mA/cm^2 (C/2 to C/3 rate) between 2 V and 0.01 V for 20 cycles, with a 10-min wait between charge and discharge.

Complex-impedance measurements were performed using a Solartron Model 1250

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Frequency Response Analyzer coupled to a Solartron Model 1286 Electrochemical Interface. The impedance spectra were normally generated over a frequency range of 65 kHz to 100 mHz with a 10 mV peak-to-peak sine wave. Complex-impedance spectra of the carbon samples during galvanostatic cycling were taken at open circuit (~3.25 V) before intercalation and 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. Spectra were also taken after multiple cycles. Cells were equilibrated in a temperature-controlled chamber for the tests at 5°C and 35°C. The tests at 21°C were performed at ambient.

Results and Discussion

Galvanostatic Cycling Tests – The galvanostatic cycling data are sumamrized in Table 1. ("Load" refers to intercalation and "unload" refers to deintercalation.) Between 21°C and 35°C, there was little difference in the reversible capacities and coulombic efficiencies for the first cycle. At 5°C, however, the reversible capacity was cut to almost half of that at the higher temperatures and the efficiency was also reduced. The fade (loss in capacity upon cycling) was highest for the highest temperature. The reversible capacities for the 20th cycle increased with temperature, although the coulombic efficiencies were similar. The fade was the highest at the highest temperature.

Impedance Tests – The complex-impedance spectra for the first reduction is shown in Figure 1 for a potential of 2 V (all values are reported vs. Li/Li^+). The impedance spectrum shows mainly a line tilted at 64° to 74° from the horizontal axis for all temperatures. (The line for the 35°C test is not visible, having an inductance of only –10 ohms.) For a purely diffusional process, the Warburg angle would be 45°. There is also a small semicircle at the highest frequencies evident for the test at 5°C.

The impedance spectra at 0.01 V shown in Figure 2 are drastically different and reveal a major inductive component. This inductive component is first noted near 0.5 V and is believed to be a consequence of the presence of oxygenated surface species on the PMAN carbon which undergo reduction during the first several galvanostatic cycles. The inductive behavior disappears after four or five cycles and is replaced by two semicircles and a Warburg-like tail, after formation of the SEI layer becomes well established.[4] The inductive response is not observed with typical graphitic materials that have a much lower surface area, where sorption of oxygen is less important.

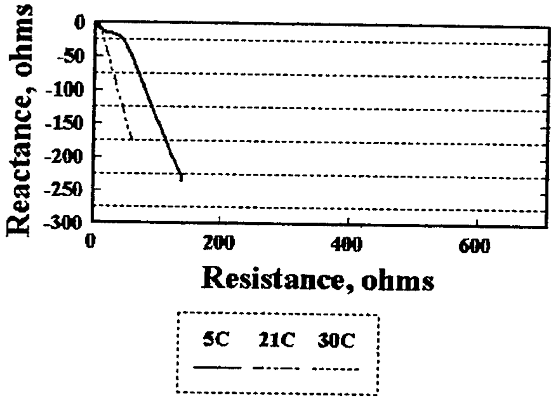

Figure 1. Complex-Impedance Spectra as a Function of Temperature at a Potential of 2 V.

Table 1. Effect of Temperature on Performance of 700°C PMAN Carbon#

	First Cycle				20th Cycle			
Temp., °C	Load, mAh/g	Unload, mAh/g	Effic., %	Q_{irr}, mAh/g	Load, mAh/g	Unload, mAh/g	Effic., %	Fade,* mAh/g-cycle
35	435.4	212.9	48.7	222.5	141.4	139.3	98.5	-0.90
21	484.0	213.8	47.8	252.2	130.3	126.6	97.2	-0.69
5	282.4	120.0	42.5	162.4	101.0	99.3	98.3	-0.62

Data are the average of two cells. * Fade = (20th-cycle capacity – 11th-cycle capacity)/10.

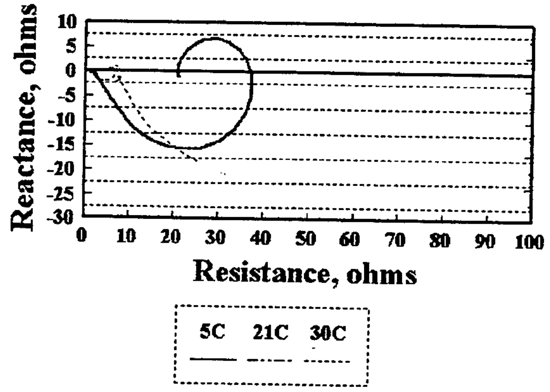

Figure 2. Complex-Impedance Spectra as a Function of Temperature at a Potential of 0.01 V.

The spectra were modeled using Equivalent Circuit (EG & G PARC), using constant-phase-elements (CPE):

$$Y_{CPE} = Y_c\omega^n\cos(n\pi/2) + jY_c\omega^n\sin(n\pi/2)$$

where n = 1 for a pure capacitor, 0.5 for Warburg behavior (diffusion), and –1 for a pure inductor.[5] The equivalent circuit is shown in Figure 3.

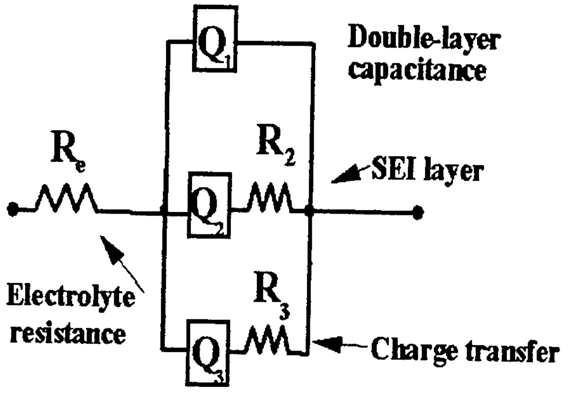

Figure 3. Equivalent Circuit Used to Model Response of PMAN Electrode at 0.01 V.

The final electrical analog circuit is shown in Figure 4. The fitted data are compared to the experimental data in Figure 5 and the overall model results are summarized in Table 2. R_{lf} is the low-frequency intercept; R_e is the electrolyte resistance (defined by the high-frequency intercept); C_{dl} is the double-layer capacitance; C_{ct} is the charge-transfer capacitance; n_{dl} and n_{SEI} are the fitting parameters used. (The values of n_{dl} and n_{SEI} reflect the fact that these do not represent either pure capacitance and diffusion or pure inductance, respectively.)

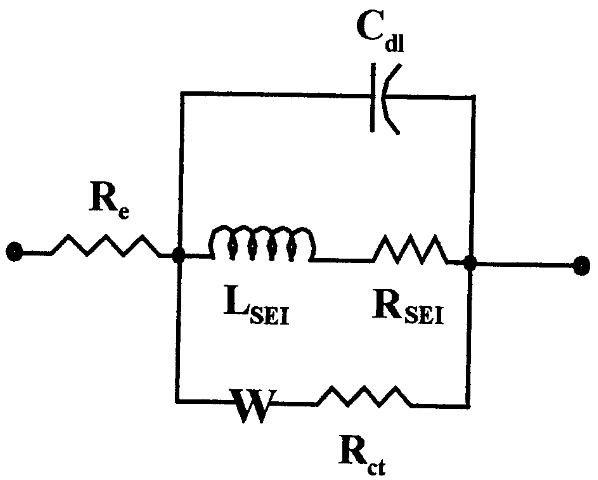

Figure 4. Final Electrical Circuit for Li^+ Intercalation at 0.01 V.

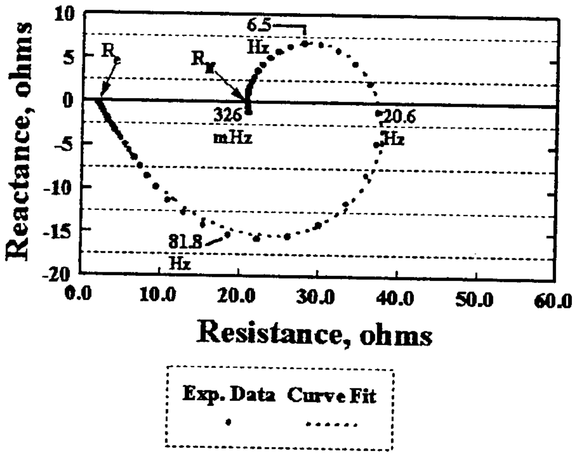

Figure 5. Comparison of Experimental Data to Results of Modeling.

The ionic resistivity of the electrolyte behaves as one would expect, decreasing with increase in temperature. (This could also act to shift the true potential at the electrode-electrolyte interface due to increased IR losses in the electrolyte.) The resistance of the SEI layer behaves similarly. The charge-transfer resistance decreases substantially as the temperature increases. This reflects the kinetics of the reduction processes are much enhanced at the elevated temperatures.

At 5°C, for example, the charge-transfer resistance is 16 times larger than at 35°C. The enhanced reduction kinetics are similarly reflected in the reduced reversible capacity when the temperature is reduced below 21°C (Table 1). The reduction kinetics are so much slower at 5°C that the inductive loop that is a small component of the impedance spectra at 0.01 V at 21°C and 35°C totally dominates the spectrum at 5°C (Figure 2). At 35°C, the beginning of a possible second charge-transfer semicircle is also evident.

Conclusions

Temperature has little effect during the first reduction on the reversible capacity of a carbon derived from a PMAN/DVB copolymer at temperatures between 21°C and 35°C; the capacity at 35°C is only slightly less. However, at 5°C, both the reversible capacity is reduced to slightly more than half that of higher temperatures. The irreversible capacity is similarly reduced. The coulombic efficiencies are comparable over the temperature range by the 20th cycle.

Complex-impedance spectroscopy was used to study the kinetics of the reduction processes that occur on the surface of the PMAN carbon during passive-film formation during the first reduction. These processes most likely involve the reduction of oxygenated species on the carbon surface that give rise to a large inductive component in the spectra at potentials below 0.5 V vs. Li/Li$^+$. It is in the potential region where intercalation processes become important, along with solvent/electrolyte reduction. The inductive behavior is especially pronounced at 0.01 V at 5°C, where the kinetics of solvent/electrolyte reduction are less favorable, and is totally absent at 35°C where the kinetics are faster.

The inductive behavior and charge-transfer processes were modeled using an equivalent circuit consisting of three parallel complex elements: a double-layer capacitor, a Warburg element with a charge-transfer resistance, and an inductive element in series with a passive-film resistance. The resistances of the electrolyte and the passive-film decrease with increase in temperature. The charge-transfer resistance behaves similarly, as the kinetics become more facile at elevated temperatures.

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Table 2. Results of Modelling of Equivalent Circuit for Intercalation Process with PMAN Carbon

Temp., °C	R_{ct}, Ω	R_{tf}, Ω	R_{SEI}, Ω	R_e, Ω	C_{dl}, mF	n_{dl}	n_{SEI}	L_{SEI}, H	Warburg, S*
35	5.0	N.A.	6.0	1.10	0.280	0.75	N.A.	N.A.	0.055
21	48.1	18.8	29.3	1.49	0.614	0.58	-0.65	2.26	0.0061
5	81.2	21.8	59.4	1.92	0.531	0.67	-0.77	0.77	0.015

* n = 0.5.

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