Plasma-Polymerized Carbon Disulfide Thin-Film Rechargeable Batteries

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This paper discusses the results on deposition conditions, rates of polymerization, and properties of carbon disulfide films prepared by two techniques, viz., plasma polymerization and argon-plasma-assisted polymerization of carbon disulfide. A higher rate of polymerization and sulfur content was obtained for carbon disulfide films prepared by the plasma-polymerization technique. A Li/LiClO$_4$ propylene carbonate/PPCS cell was assembled using lithium foil, 2 M LiClO$_4$/PC electrolyte with polyolefin separator, and PPCS deposited on Pt foil. The electrode area was 1.3 cm^2. The cell cycled reversibly between 1 and 3 V and retained its capacity (5 mA h/g) well over 12 cycles.

Introduction

There has been a significant research work done in the recent past in the development of thin solid-state lithium polymer batteries in which the conventional liquid electrolyte has been replaced by an ion-conducting polymer.[1] This development has eliminated the hazards associated with the combination of lithium with an organic liquid. Another recent development has been the use of solid redox polymerization electrodes as positives in these film batteries. For example, thin-film solid-state batteries consisting of lithium foils, amorphous PEO separators, and solid redox polymerization electrodes, such as 2,5-dimercapto-1,3,4-thiadiazole have been prepared by Doeff et al.[2]

The objective of this work was to prepare thin-film solid-state batteries using plasma-polymerized carbon disulfide as the cathode material. The carbon disulfide polymer has been made chemically in the past.[3] In this paper we give the details of preparation of poly(carbon disulfide), conductivity measurement, structural and morphological features, and the rechargeable battery performance of the plasma polymerized carbon disulfide (PPCS) films.

Some of our previous work[4,5] includes preparation of insulating, metal containing and conducting plasma polymerized films. Asano[6,7] has studied the plasma-polymerized carbon disulfide and metal containing carbon disulfide films for optical recording applications. Gazicki[6,7] and Yasuda[8] have studied the dielectric properties of plasma polymerized carbon disulfide films. Hirotsu[9] has compared the gas-phase reactions in the

plasma polymerization of carbon disulfide and carbon dioxide. In all these studies, the plasma-polymerized films were prepared by depositing the films in the high rf flux-density region, which generally causes significant structural and compositional changes in the polymer as compared to the starting monomer. The objective of our work was to prepare polycarbon disulfide films by two techniques using plasma. In the first method, poly-(carbon disulfide) film is prepared away from the high rf flux density area in the reactor. An inert gas passes through the plasma zone, and its excited species are used in initiating the polymerization of carbon disulfide. In the second method of regular plasma polymerization, carbon disulfide passes through the high rf flux density zone. The rate of deposition, conductivity, morphology, composition, and structure of the films prepared by two methods are compared. Performance of the rechargeable battery using plasma deposited carbon disulfide film as an active material has been evaluated.

Experimental Section

Plasma polymerization was carried out in an inductively coupled tubular reactor composed of a reactor chamber made of Pyrex glass (100 cm long × 7 cm diameter), rf power source (operating at 13.56 MHz frequency), matching network, vacuum systems, and leak valves. The substrates (glass slides, NaCl IR crystals, partially masked glass slides for thickness measurements, platinum electrode) were placed in the reactor at several positions. The reactor was evacuated to about 1 mTorr. The polymer deposition was carried out in two ways:

(a) The reactor geometry and the flow of gases in this procedure are shown in Figure 1. Argon was introduced from the end and passed through the high rf flux density region, while carbon disulfide was introduced downstream of the high flux density region within the reactor as shown in Figure 1. Other conditions of polymerization are summarized in Table 1. This method of polymerization is referred to as "plasma-assisted polymerization" in this paper.

(b) The reactor geometry and the flow of carbon disulfide used in this deposition procedure were altered. The monomer carbon disulfide was introduced at one end of the reactor without a carrier gas (argon). The monomer carbon disulfide passes through the high rf flux density region (RF coils). The conditions used for polymerization are summarized in Table 2. This method of polymerization is referred to as "plasma polymerization" in this paper.

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.
(1) Ratner, M. A.; Shriver, D. F. *Mater. Res. Soc. Bull.* **1989**, *9*, 39.
(2) Doeff, M. M.; Visc, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1992**, *139*, 1808.
(3) Liu, M.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1992**, *138*, 1891.
(4) Sadhir, R. K.; James, W. J. *ACS Symp. Ser.* **1984**, *242*, 533.
(5) Sadhir, R. K.; Schoch, K. F., Jr. *Thin Solid Films* **1993**, *223*, 154.
(6) Asano, Y. *Thin Solid Films* **1983**, *105*, 1.
(7) Asano, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, 1618.
(8) Gazicki, M.; Yasuda, H. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1984**, *38*, 35.
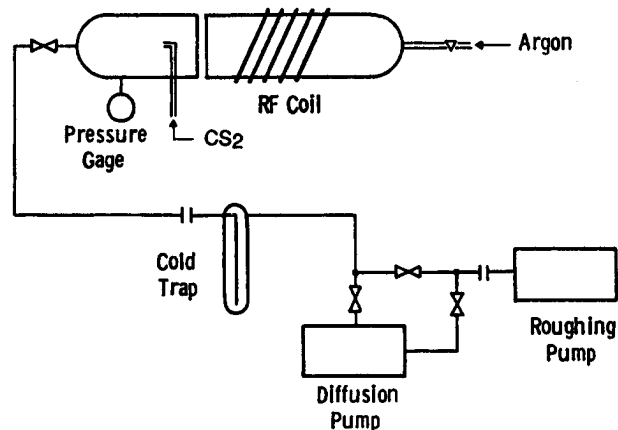(9) Hirotsu, T. *J. Macromol. Sci., Chem.* **1981**, *A16*, 1217.

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Figure 1. Tubular reactor for plasma-assisted polymerization.

Table 1. Conditions Used for Plasma-Assisted Polymerization of Carbon Disulfide

initial pressure = 1 mTorr
pressure with argon = 31 mTorr
flow rate of argon = 1.815×10^{-2} cm³ s⁻¹ (STP)
flow rate of CS_2 = 1.16×10^{-2} cm³ s⁻¹ (STP)
combined pressure of argon and CS_2 = 65 mTorr
combined flow rate = 4.465×10^{-2} cm³ s⁻¹ (STP)
rf power = 5 W
rf frequency = 13.56 MHz
duration of polymerization = 173 min
maximum rate of deposition = 42.6 Å/min

Table 2. Condition Used for Plasma Polymerization of Carbon Disulfide

initial pressure = 1 mTorr
pressure with carbon disulfide = 30 mTorr
flow rate = 1.573×10^{-2} cm³ s⁻¹ (STP)
rf power = 5 W
rf frequency = 13.56 MHz
duration of polymerization = 95 min
maximum rate of deposition = 134.3 Å/min

The thickness of the films were determined by a Sloan Dektak thickness monitor. The surface topography of the films was determined by SEM (Cambridge Stereo Scan 150 Mkz). Electrical conductivity (dc) was measured by a two-probe method using parallel silver paint contacts on opposite edges of the films. Ohmic behavior was observed in all samples over the current and voltage ranges investigated: 0–10 V, 0–200 nA. The bulk conductivity was calculated using the measured resistance and film thickness determined by profilometry.

The composition of the plasma-deposited carbon disulfide films was determined by ESCA (ESCA Lab MK-2 from VG Scientific). An Mg Kα X-ray source with 1253.6 eV energy line was used and C_{1s}, S_{2s}, S_{2p}, O_{1s}, and N_{1s} signals were analyzed to determine the composition.

Cyclic voltammetry measurements were made using an Electrosynthesis Corp. 630 potentiostat and a Keithley 230 programmable voltage source. The voltage was swept at 100 mV/s between −3 and +4 Vs Li/Li⁺. Polymer samples were deposited on clean Pt foil strips of ¹/₂ in. × 2 in. In addition to the polymer working electrode, the test cell contained an 80% Li/20% Al foil reference electrode and a Pt foil counter electrode.

Bipolar electrochemical cells were prepared by stacking 1.27 cm² disks of 99.99% Li foil (Cypress-Foote) anode, Celgard 5501 separator (Hoechst-Celanese) previously impregnated under vacuum with 2 M LiClO₄ in propylene carbonate and the polymer cathode. We chose a bipolar cell construction in order to give the most complete contact to the electrode materials. This is especially important in the case of a low-conductivity material. Nickel current collectors were used for each electrode. A Li-foil reference electrode was inserted along the edge of the stack. All components were rigorously dried and handled under argon. The cell was assembled and tested in an argon-filled drybox. Cell tests were performed as follows.

Table 3. Thickness of the Plasma-Assisted Polymerization of Carbon Disulfide Films at Various Positions in the Reactor (Figure 1)

sample	position of the substrate (cm)	deposition thickness (μm)	rate (A/min)	conductivity
1	24.0	0.4650	26.88	7.8×10^{-7}
2	35.5	0.4835	27.90	7.6×10^{-8}
3	46.0	0.7370	42.60	
4	63.5	0.7085	40.95	
5	71.0	0.5375	31.07	

The cell test system has a constant-current power supply (Keithley 225) with the output going through an ammeter (Keithley 177) and a coulometer, into a relay (Hewlett-Packard 59511A) which isolates the cell from the power supply during open circuit stand. An 84-Ω resistor is used as the load through which the cell is discharged. The voltages in the cell are monitored at regular intervals throughout the test via a voltmeter (Keithley 195A) with the input selected by a scanner (Keithley 705/7055). The system is controlled by a PC using Lotus Measure to run the experiments and record the data directly into a Lotus 1–2–3 spreadsheet. The software permits selection of voltage cutoffs on charge and discharge, intervals at which data are recorded, and duration of open-circuit stands. During the experiments reported here, cells were discharged to 1.0 V and charged to 3.0 V at various currents, given in the discussion section.

For comparison purposes, poly(carbon disulfide), PCS, was also prepared by anionic polymerization as follows.

After the procedures given by Tsukamoto and Takahashi[10] produced a low yield using toluene or DMF as the solvent, we settled on a modification of the procedure provided by Moltech.[11] A sodium dispersion (2.00 g) was prepared in xylene (15.0 mL, Aldrich, ACS reagent grade, distilled from CaH₂ under N₂) and added to a solution of CS_2 (5.0 mL, Aldrich, 99%, anhydrous, under N₂, as received) in NMP (50 mL, Fisher, purified grade, distilled from NaOH, under N₂) over a period of an hour while the flask was held at −3 to 0 °C. The mixture was then permitted to warm up slowly and stirred for 2.5 days at room temperature. After the xylene and NMP were removed under vacuum, the residue was reacted with water and then acidified with 100 mL of 1 M HCl. The residue was then washed with water and acetone, producing a very dark red solid. The solid was dried in a vacuum oven at 55 °C for 24 h. The yield was 3.5686 g.

Results and Discussion

Deposition. The thickness and rate of film deposition of carbon disulfide polymers at various positions in the reactor by plasma-assisted polymerization technique are given in Table 3. The maximum rate of polymerization was observed slightly before the monomer inlet position in the reactor. On both sides of that position, the deposition rate decreased. Argon entering from the right side of the reactor (Figure 1) goes through the high-flux density area and produces excited species, such as ions and electrons. Carbon disulfide is introduced downstream in the reactor. In this scenario, we are using the excited species of argon to initiate the polymerization of carbon disulfide. The rate of polymerization of carbon disulfide will depend upon the monomer concentration and the concentration of excited species of available argon in that area. In addition, the polymerization rate will depend upon the diffusion of neutral carbon disulfide toward the plasma zone and its transport through the excited argon species, which is opposite to the pumping direction.

(10) Tsukamoto, J.; Takahashi, A. *Jpn. J. Appl. Phys.* **1986**, *25*, L338.
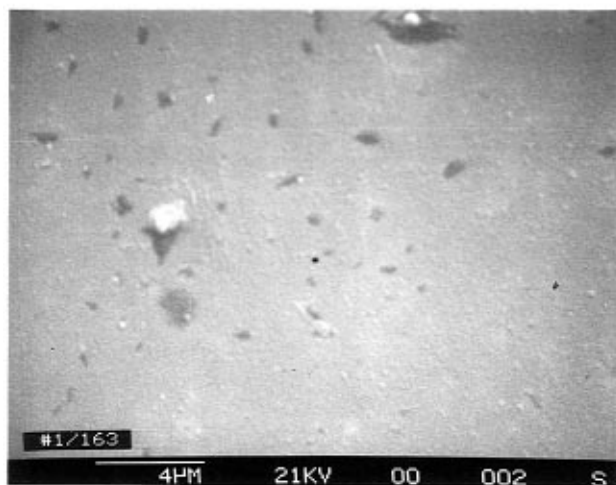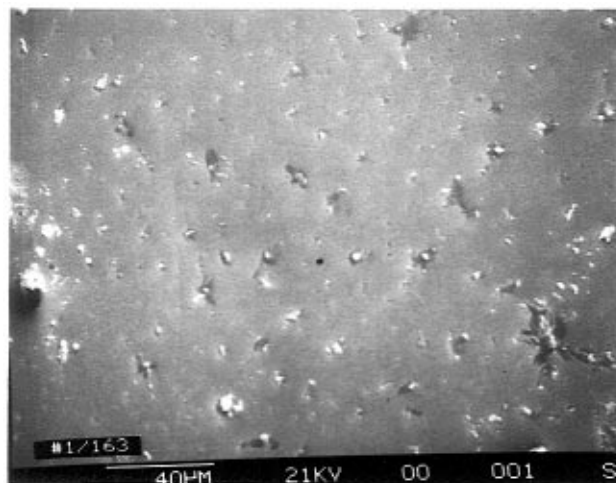(11) Prasad, S., private communication, 1992.

Figure 2. SEMs of plasma-assisted polymerization of carbon disulfide (position 24.0 cm).

Figure 3. SEMs of plasma-polymerized carbon disulfide films (position 44.5 cm).

Table 4. Thickness of the Plasma-Polymerized Carbon Disulfide Films at Various Positions in the Reactor (Figure 2)

sample	position of the substrate (cm)	deposition thickness (μm)	rate (A/min)	conductivity
6	3.8	1.2590	132.5	1.04×10^{-7}
7	23.0	0.5757	60.6	
8	44.5	1.2760	134.3	
9	66.0	1.2750	134.2	

The thickness and rate of film deposition of plasma-polymerized carbon disulfide at various positions in the reactor are given in Table 4. The rate of polymerization under these sets of conditions (i.e., where carbon disulfide monomer passes through the plasma zone) was higher than in the case of plasma-assisted polymerization. Part of the reason for the higher deposition rate is the slightly higher flow rate of the monomer. Second, a higher concentration of carbon disulfide converts into excited species due to their passage through the plasma zone. At about 25 cm from the monomer inlet, the thickness of the film was found to be minimum, which happens to be the point of highest flux density (center point of the rf coil). On both sides of this position, the film thickness was uniform.

Morphology. The morphology of the films deposited at various positions in the reactor by two methods was found to be similar. Figure 2 shows the micrographs of the films deposited at 24 cm position in the reactor
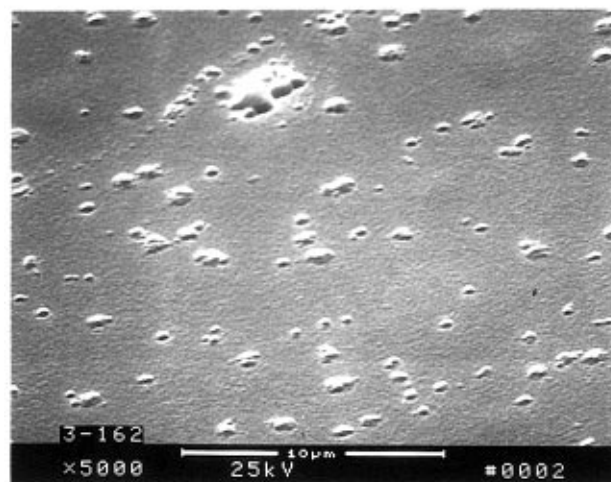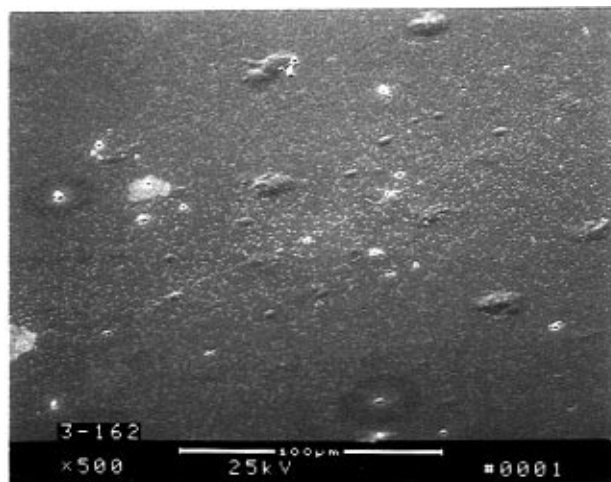
during argon plasma-assisted polymerization of carbon disulfide. This micrograph shows a continuous film with crystallite formation on the surface. The micrographs of the films at 46 cm position in the reactor were generally smooth with fine crystallite, having dendritic growth on the surface. The micrographs of the plasma-polymerized carbon disulfide are shown in Figure 3. The films were found to be generally smooth with some texture to them. Also at the surface some scattered globular structure was detected.

Electrical Conductivity. The conductivity of the films deposited at various positions by two methods are shown in Tables 3 and 4. The conductivity was determined by a two-probe method. The range of electrical conductivity, irrespective of the method of deposition, was found to be 1×10^{-7}—7.6×10^{-8} S/cm. The samples for measurement of conductivity were not placed at all positions in the reactor. Therefore the conductivity values are given only for a limited number of samples in the tables. The conductivity of the films deposited by the plasma methods was found to be comparable to the electrical conductivity of polymeric carbon disulfide prepared by chemical and high-pressure techniques.[10]

Composition and Structure. The infrared spectra of the plasma-polymerized carbon disulfide and polymer prepared by conventional chemical reactions are shown in Figure 4. The absorption peaks due to C=S in polycarbon disulfide at 1060 cm^{-1} and other absorption peaks at 1245, 1365, 1415, and 1440 cm^{-1} confirm the
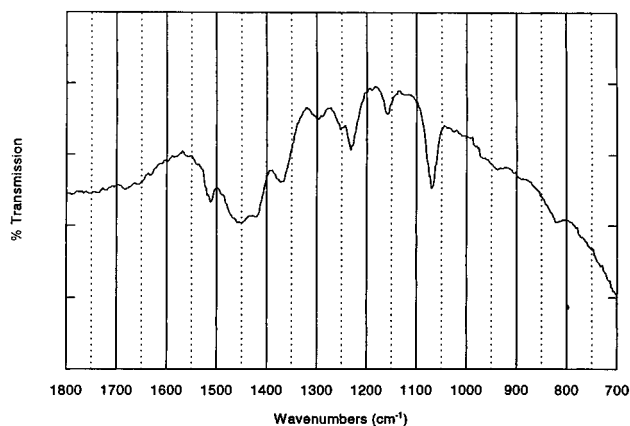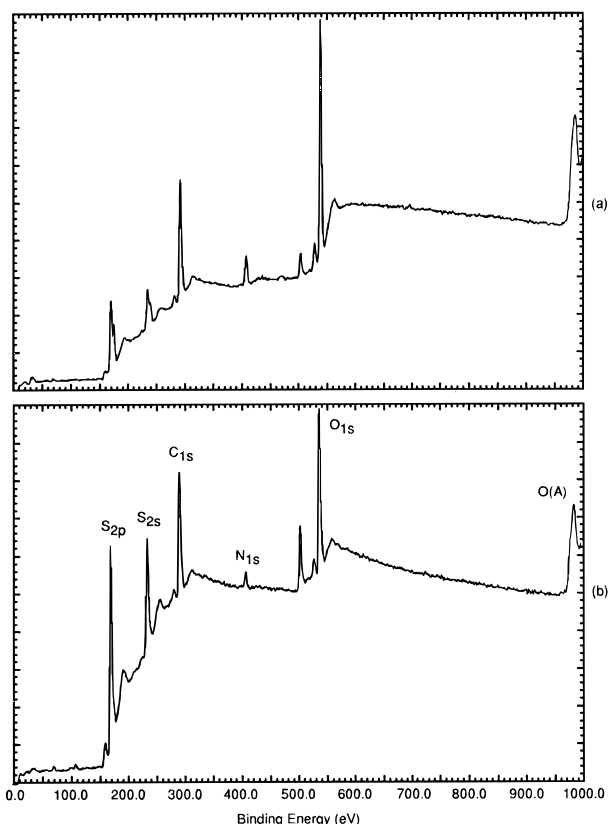
Figure 4. Infrared spectra of PPCS.

Figure 5. ESCA spectra of the films prepared by argon-plasma-assisted polymerization of carbon disulfide: (a) 24.0 cm; (b) 71.0 cm.

Figure 6. ESCA spectra of the plasma-polymerized films of carbon disulfide: (a) 3.8 cm; (b) 66.0 cm.

production of poly(carbon disulfide) in the plasma.[12] Similar absorption peaks were obtained for argon-plasma-assisted polymerization of carbon disulfide. No carbonyl absorptions were observed in either case, indicating that oxygen observed in the ESCA spectra (discussed below) was due to surface oxidation.

The composition of the films was determined by ESCA. The ESCA spectra of the polymerized carbon disulfide at two places in the reactor and prepared by two methods are shown in Figures 5 and 6. In the following discussions, the peak positions have been reduced by 8.4 eV due to the charging from the sample substrate. Peaks at 284, 230, and 163 eV are assigned to C_{1s}, S_{2s}, and S_{2p}, respectively. The composition of the film on the surface may be different from the composi-
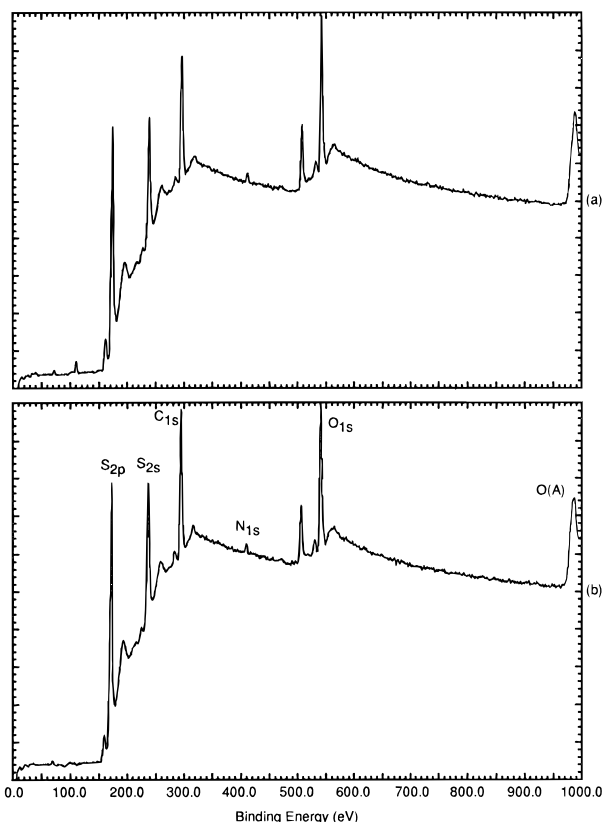
tion of the bulk, especially the oxygen concentration. After the deposition of the film, when the reaction was stopped, there remained some free radical traps and these active sites were capable of reaction with the environment (e.g., O_2, N_2, CO_2, etc.). The observation of peaks of oxygen that contain functional groups and hydrocarbon contamination in the plasma-polymerized films of fluorocarbons have been documented by Clark and Shuttleworth.[13] In addition peaks corresponding to oxygen, nitrogen, silica, and sodium were also detected due to minor air leakage into the system and etching of the glass reactor walls. The atomic concentration of C, S, O, N, Na, and Si determined on the surface of the films at various positions in the reactor in two experiments are summarized in Table 5. The films prepared by argon-plasma-assisted method contained slightly higher amounts of oxygen and nitrogen, mainly due to a slightly higher concentration of air leakage into the reactor chamber. A higher atomic percent of sulfur was obtained for plasma polymerization. The binding energies for the core level spectra of S2p of various deposited films are shown in Figure 7.

The spectra extended from 4 to 7 eV, and their full width at half-maximum (fwhm) from 2 to 3.0 eV. The spectral evidence indicates that there are more than two species having different binding energies. The S2p peak for the film deposited at 24.0 cm by argon-plasma-assisted polymerization shows two distinct peaks at 163.7 eV with a shoulder at 164.0 and at 168.8 eV. The line at 168.8 eV corresponds to S bonded to two oxygen atoms. Two lines at 163.7 and 164.0 eV correspond to

(12) Chan, W. S.; Jonscher, R. K. *Phys. Status Solidi* **1969**, *32*, 749.

(13) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 27.

Table 5. ESCA Surface Compositions of Carbon Disulfide Plasma-Polymerized Films

sample	method of polymerization	sample position in reactors (cm)	atomic %					
			C	S	O	N	Na	Si
1	argon-assisted plasma	24.0	43.42	14.37	33.96	6.41	1.85	
5	argon-assisted plasma	71.0	41.40	28.92	23.50	3.69	1.06	1.43
6	plasma polym	3.8	40.44	31.93	23.42	1.31	0.38	2.51
9	plasma polym	66.0	45.55	32.51	20.15	1.39	0.40	

$C=S$ and $C-S-C$, respectively.[10] The S_{2p} core level ESCA spectra of the films deposited at other positions and by the plasma polymerization method has a negligible line corresponding to $S-O$ bond (168.8 eV).

Electrochemistry. The results of cyclic voltammetry (CV) on PPCS are shown in Figure 8. Initially there was a large reduction wave at 1.8 V vs Li/Li^{+}. With each succeeding cycle the wave broadened up to the eighth cycle and then disappeared completely after 13 cycles. It thus appeared that the polymer was undergoing irreversible chain scission during the redox cycles. Other workers have reported on CV of chemically prepared PCS but have not specifically addressed the issue of cycle life.[14]

Electrochemical cells were prepared using both chemically polymerized CS_2 (PCS) and plasma-polymerized CS_2 (PPCS) as described in the Experimental Section. These cells were cycled while under Ar at rates of 0.02–0.5 mA/cm^2.

Discharge curves for the two types of cells are given in Figures 9 and 10. The chemically polymerized material has a more stable voltage during discharge than the plasma polymerized material. Apparently the PCS (Figure 9) depolymerized during the first discharge cycle and never recovered. As seen in Figure 9, when the load was removed the cell potential immediately returned to 2.4 V, but no added capacity during subsequent charging was observed as the cell voltage immediately rose to 2.7 V. The electrolyte was observed to be intensely colored after the first cycle. The cell containing PPCS behaved more favorably with respect to reversibility, although the usable capacity was much reduced after the first discharge (Figure 10). It is likely that the PPCS has a more highly cross-linked structure than does PCS, which would reduce the amount of depolymerization during the discharge cycle. As expected, when the current was reduced, there was an increase in usable capacity for the first two cycles after the change.

Figure 11 shows the change in capacity of the cells during several cycles. These charts show even more clearly that the PCS cell had negligible charging capacity even in the first cycle. The PPCS cell had much greater charging capacity, particularly at low rates. Direct comparison of these curves is difficult, however, because the PCS electrode has much more active material available (54 mg) than does the PPCS electrode (0.423 mg). Nevertheless, each material has advantages and disadvantages. The PCS has more total capacity and better performance but cannot be recharged, and PPCS has much less total capacity but can be recharged.

Conventionally prepared poly(carbon disulfide) is shown to be chemically reversible with moderate electron-transfer rates. Cyclic voltammetry on that material is reportedly consistent with a material having various
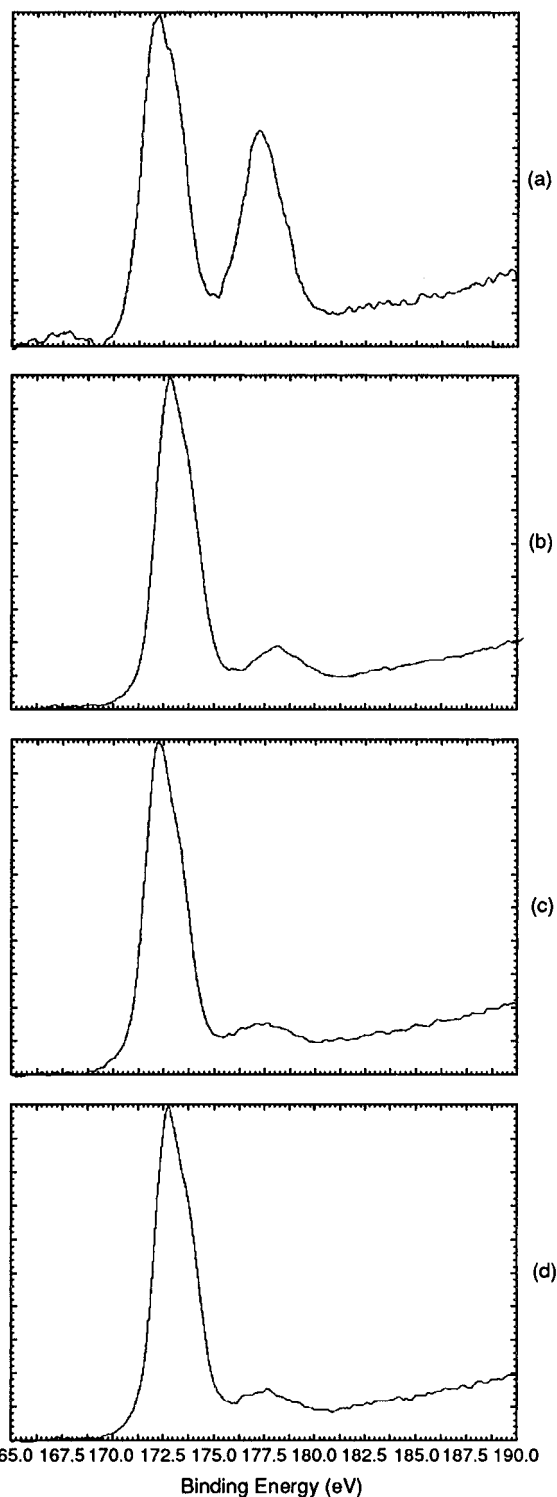

Figure 7. S_{2p} core level spectra of plasma-deposited carbon disulfide films. (a) Ar-plasma-assisted polymerization of CS_2 at 24.0 cm in the reactor. (b) Ar-plasma-assisted polymerization of CS_2 at 71.0 cm. (c) PPCS$_2$ at 3.8 cm. (d) PPCS$_2$ at 66.0 cm in the reactor.

(14) Geng, L.; Lee, H. S.; Xu, J.; McBreen, J.; Prasad, S.; Skotheim, T. A. *Mater. Res. Soc. Symp Proc.* **1993**, *293*, 185.
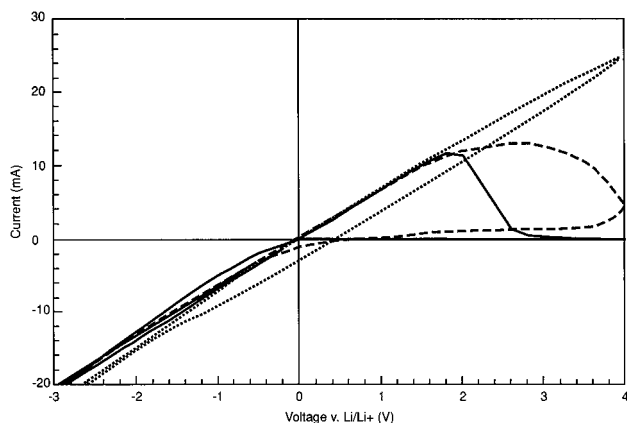
repeat units.[14] Since plasma polymerization causes

Figure 8. Cyclic voltammetry of PPCS in 2M LiClO₄/PC: initially (—); after eight cycles, 1 h (- - -); and after 13 cycles, 6.5 h (···).
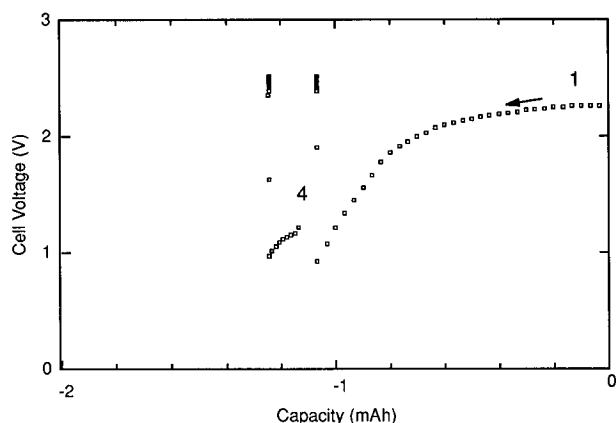

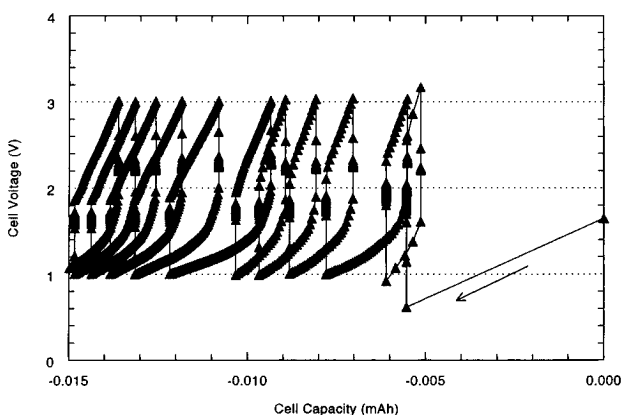**Figure 9.** Performance of a 1.27 cm² Li/LiClO₄−PC/PCS cell during cycles 1 and 4.

Figure 10. Performance of a 1.27 cm² Li/LiClO₄−PC/PPCS cell.

some disruption of the structure, we may have domains where the chemical structure of the polymer is close to the conventional polymer, whereas there may be structures where higher cross-linking and lower sulfur
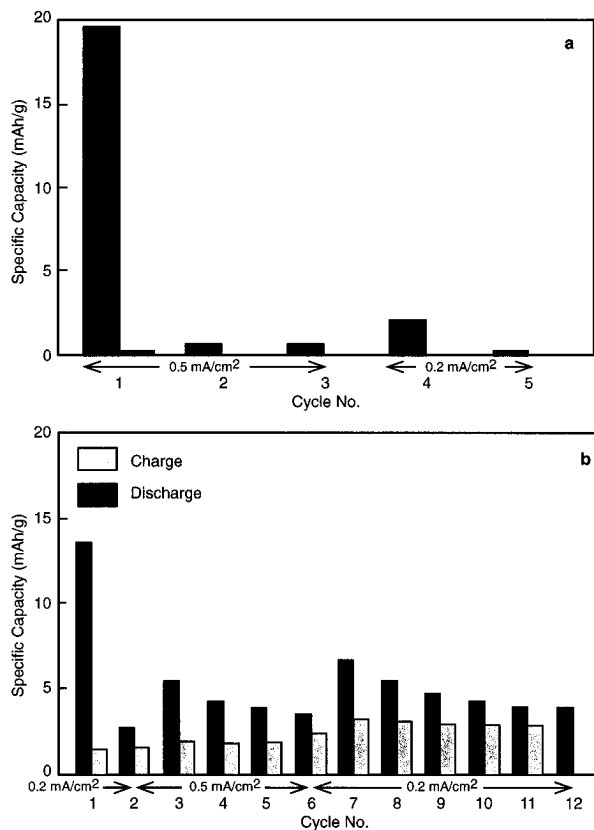

Figure 11. Specific capacity of 1.27 cm² cells: (a) Li/PCS; (b) Li/PPCS.

content could be present. This kind of polymer structure will have lower electron-transfer rates and lower current densities which are observed in the cell prepared from this material.

Conclusions

Plasma polymerization and plasma-assisted polymerization have been proven effective for prepared polymerized CS_2 thin films. Infrared and ESCA evidence indicates the presence of C=S and C−S moieties. The deposited films show electrochemical activity in cells vs Li/Li⁺. Compared to poly(carbon disulfide) prepared by chemical means, cells having the plasma-polymerized CS_2 have improved cycle life because the plasma-polymerized material does not depolymerize as readily.