Voltammetric Studies of Poly(carbon disulfide)

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ABSTRACT

Poly(carbon disulfide) was studied by cyclic voltammetry using glassy carbon and platinum macro- and microdisk electrodes. The electron transfer kinetics is significantly faster at glassy carbon electrodes than at Pt electrodes. It is chemically reversible with moderate electron transfer rates. Voltammetric results of poly(carbon disulfide) are in good agreement with our battery testing data. The k^0 value measured at a Pt microdisk electrode is 7×10^{-3} cm/sec. Electrochemical data suggest that PCS can be a potential cathode material for low current density lithium batteries.

Introduction

Organosulfur compounds have been used as cathode materials in lithium polymer batteries due to their high capacity, long cycle life, low toxicity and low cost. In recent years, various organosulfur compounds have been synthesized and tested in several research laboratories^{1,2}. As a cathode material, an important parameter is the sulfur/carbon ratio which often dictates the capacity and the energy density. Among various organosulfur compounds, poly(carbon disulfide) has the highest sulfur/carbon ratio and excellent chemical stability. Our laboratory studies have shown that it is a potentially useful cathode material for lithium batteries³. It is important to understand the structure and the electron transfer characteristics of the cathode material since these properties will determine the current density, cycle life and energy efficiency of the battery.

Although poly(carbon disulfide) (PCS) was first synthesized in 1941⁴, electrochemical studies of PCS have not yet been reported. Several proposed variants of the structure are shown in Figure 1^{5,6}. It is clear that the resulted polymer structure is significantly different from the CS₂ monomer, due to the carbon-sulfur single bond formation. The polymer is a black, solid material while CS₂ is a colorless liquid. IR studies showed that the PCS synthesized under high pressure and high temperature conditions predominately has the structure of B in Figure 1⁵. However, XPS studies revealed that poly(carbon disulfide) synthesized under atmosphere pressure and low temperature is a mixture of both the linear (Figure 1, B) and crosslinked (Figure 1, A) structures⁶. The cyclic voltammetric measurements of CS₂ have been reported, and the current vs. potential responses are significantly different from PCS^{7,8,9,10}.

Experimental

1. Chemical and Materials

Poly(carbon disulfide) was synthesized under atmospheric pressure according to literature procedures⁶ with minor modifications. Elemental analysis showed the S/C ratio is between 1.7 to 1.9. Poly(ethyleneglycol dixanthate) was also prepared according to literature procedure¹¹. Anhydrous methyl sulfoxide (DMSO), dimethyl formamide

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Figure 1 Idealized chemical structures of poly(carbon disulfide). (From references 5 and 6)

(DMF) and LiClO_4 were purchased from Aldrich and used as received. Tetraethylammonium tetrafluoroborate (TEABF_4) was purchased from Fluka and used without further purification.

2. Electrochemical Measurements

Cyclic voltammetry was carried out on a PAR 173 potentiostat driven by a PAR 175 universal programmer, whose output was recorded by a Graphtek WX2400 X-Y recorder. A standard three-compartment cell was used for both the cyclic voltammetry and bulk electrolysis. Solutions were degassed for at least 10 min before measurements. The platinum and glassy carbon working electrodes were constructed by shrouding Teflon around a 2 mm diameter Pt disk or a 3 mm diameter vitreous carbon rod. The glassy carbon disk electrode was polished on a fine sand paper each time before use to physically renew the surface and remove any adsorbed species. Carbon disk microelectrodes and Pt microelectrodes were constructed by sealing a piece of carbon fiber (10 μm diameter) or platinum fiber (25 μm diameter) into the end of a capillary tube. A microdisk electrode was obtained by polishing the sealed capillary end. A home made preamplifier was used together with a PAR 173 potentiostat for microelectrode voltammetry for both 3-electrode and 2-electrode cell configurations. Prior to the cyclic voltammetry experiment, PCS was dissolved in methyl sulfoxide solution containing electrolyte, 0.1 M LiClO_4 or TEABF_4 .

Bulk electrolysis was carried out using a PAR 273 potentiostat with a digital coulometer. A Pt gauge working electrode was used together with a Pt wire counter electrode and a Ag wire reference electrode. The solution was degassed before electrolysis. During the electrolysis, N_2 was continuously running through the solution which was constantly stirred by a magnetic stir bar.

Results and Discussion

Voltammograms of poly(carbon disulfide) at a glassy carbon disk electrode and at a platinum disk electrode in $\text{DMSO}/0.1 \text{ M TEABF}_4$ are shown in Figure 2. Experimental results showed that cyclic voltammetric measurements were almost identical in 0.1 M TEABF_4 and 0.1 M LiClO_4 , implying no significant ion pairing effect.

Three reductive electron transfer peaks were observed. The first electron transfer cathodic peak that occurred at -440 mV vs. saturated sodium calomel electrode (SSCE) appeared electrochemically reversible under low scan rates, with cathodic and anodic peaks separated by 60 mV. When the potential scan was reversed before the second electron transfer peak, however, the anodic current (Figure 2, dashed line) was significantly smaller than the cathodic current, and the shape of the anodic curve resembles that of $[(C_2H_5)_4N]_2C_2S_4$ ¹², suggesting the possible existence of $-S_2C-CS_2-$ structure in this polymer material (Figure 1, C). This conclusion also supports the results of the elemental analysis.

The plateau anodic peak shape is also an indication of high charging current, characteristic of electronically conducting polymers such as poly(pyrrol) and poly(aniline). It is reasonable to say that the reduced form of poly(carbon disulfide) probably has conjugated electronic structures. For comparison purpose, the cyclic voltammetry of poly(ethyleneglycol dioxanthate) was carried out in DMSO/0.1 M LiClO₄ (Figure 3). The electrochemical properties of poly(ethyleneglycol dioxanthate) differs from PCS in several aspects, although it has the $-CS-S-$ unit which is the building block of poly(carbon disulfide). First, the cathodic peak potential

strongly depends on the scan rate suggesting very slow electron transfer kinetics. In contrast, the first reduction peak potential of PCS is only slightly dependent on the potential scan rate. Secondly, the cathodic to anodic current ratio is also dependent on the potential scan rate, implying an electrochemical-chemical reaction whose kinetics falls into the time scale of cyclic voltammetry. The cathodic reduction peak potential (at 10 mV/sec sweeping rate) is -410 mV vs. SSCE compared to -440 mV of PCS. It is evident that in PCS, each $(CS_2)_2$ unit is not acting independently as in poly(ethyleneglycol dioxanthate).

Bulk electrolysis of PCS was carried out at the potential of the first electron transfer peak in DMF/0.2 M LiClO₄. When the solution containing PCS was completely electrolysed, the color of the PCS/DMF solution changed from dark brown to dark green. The data showed one electron was transferred for each carbon disulfide

Figure 2 Cyclic voltammograms of PCS in DMSO/0.1 M TEABF₄ at (A) glassy carbon electrode (3 mm diameter) and (B) platinum disk electrode (2 mm diameter). Scan rate = 50 mV/sec.

Figure 3 Cyclic voltammogram of poly(ethyleneglycol dioxanthate) at a glassy carbon disk electrode (3 mm diameter) in DMSO/0.1M LiClO₄. Scan rate = 5mV/sec.

unit. In comparison, electronically conducting polymers, for instance, poly(pyrrole) and poly(aniline) are not completely accessible electrochemically. Therefore, it is reasonable to assume that, in solution, PCS probably exists mainly in the non-crosslinked form. When PCS is reduced, the negative charge is shared among the complete CS₂ unit rather than localized at a specific atom, which implies a polymer backbone with delocalized electronic structure (Figure 4).

Two more reductive electron transfer reaction at about -0.9 and -1.1 volts vs. SSCE occur, respectively (Figure 2). The peak current of these two reductions were smaller than the first reduction, indicating less than one electron transfer for each CS₂ unit. The third wave showed reversible feature on glassy carbon

electrodes. The second reduction appeared irreversible with no corresponding anodic current peak near the second redox peak potential. Cyclic voltammetric data showed that the reoxidation of the product of the second reduction actually occurs at the onset of the first anodic peak.

Bulk electrolysis at the third peak potential confirmed that the number of electrons transferred is less than one for each CS₂⁻ unit, which is in agreement with the smaller peak current. There are two possible explanations for this phenomenon. Firstly, the PCS synthesized is not a polymer with a single chemical structure⁵. Instead, the polymer chain probably consists of several different forms of CS₂ derivatives. In other words, the PCS synthesized under atmosphere pressure is a complicated copolymer. Secondly, based on our previous argument, after the first reduction, PCS have certain characteristics of a conjugated electronic conducting polymer. Therefore, a certain percentage of the redox sites are not directly accessible electrochemically, analogous to poly(pyrrole) and poly(aniline).

Voltammograms of PCS on Pt disk electrodes (Figure 2. B) are significantly different from those on glassy carbon electrodes. Under low potential scan rates, the first reduction peak at a Pt electrode is 50 mV more cathodic than at a glassy carbon electrode. As the scan rate increased, the cathodic peak shifted to -600 mV vs. SSCE which is 70 mV more cathodic than at a glassy carbon electrode under the same experimental conditions.

In addition, at the platinum surface, the redox peaks of the first electron transfer showed significantly greater ΔE_p values than on glassy carbon. In fact, the first reductive peak was shifted more cathodic by 100 mV while the anodic peak was shifted

Figure 4 Schematic diagram for the reductive electron transfer of PCS.

90 mV more anodically. The greater ΔE_p values at Pt electrodes suggest that PCS has a higher electron transfer activation energy at Pt than glassy carbon.

Another characteristic of the voltammogram at Pt electrodes, which differs from the one at glassy carbon electrodes, is that the distance between the third and the first reduction peaks are smaller (Figure 2). The third electron transfer occurs at Ca. -1.15 and -1.2 volts for glassy carbon and platinum, respectively, i.e. the third peak was shifted less than the first peak. The surface-PCS⁻ interactions may, therefore, not be as significant for the third reduction as for the first electron transfer. However, it is also possible that both carbon and Pt surfaces have approximately identical effect on PCS⁻.

Figure 5 shows voltammograms of PCS at Pt and glassy carbon microdisk electrodes DMSO/0.1 M TEABF₄. Ideally, a microdisk should give a steady state current response under normal potential sweep rates. In our experiment, the current response of a Pt microdisk electrode is potential independent, as expected. The hysteresis is an indication of possible surface modification. The steady state current of the second plateau is less than the first, which is consistent with the result of macroelectrodes.

The voltammograms at carbon microdisk electrodes, has certain distinguishing characteristics. The large charging current is a characteristic of the large surface area due to the microporous nature of the glassy carbon. The voltammogram showed properties of surface adsorption since both the current and the peak shapes are sweep rate dependent. In addition, the reverse scan peak clearly indicates that PCS⁻ was still adsorbed on the carbon surface.

The faster kinetics at the glassy carbon surface, therefore, is possibly due to the adsorption of poly(carbon disulfide) molecules on carbon. It is not yet understood why the adsorption of PCS on carbon speed up the electron transfer process. Probably the adsorption aligns the molecular orbital of the PCS and the carbon, which lowers the activation barrier. It is also possible that an intermediate was formed as the product of PCS adsorbed on carbon. Then, this intermediate species act as a catalyst between PCS and the carbon.

For a pseudo-reversible electron transfer reaction, the electron transfer rate constant at a microdisk electrode can be expressed as $k^0 = (4D\lambda)/(\pi r)$, where λ is a parameter dependent on the values of $E_{3/4}$, $E_{1/2}$, and $E_{1/4}$, which can be obtained from the steady state voltammogram, and r is the radius of the microdisk electrode¹⁴. Assuming $D_p n = D_0$, where D_p is the average polymer diffusion coefficient and n is

the average polymer chain length, and D_0 is the diffusion coefficient of CS_2 , a k^0 value of 7×10^{-3} cm/sec is obtained for the electron transfer of CS_2 at Pt microdisk electrodes.

Conclusion

The poly(carbon disulfide) synthesized under atmospheric pressure and room temperature probably consists of several different structures. Electrochemical studies showed that it is a potentially useful cathode material for low current density battery applications with high capacity. It is also evident that the electron transfer rate of this material is faster at a carbon surface than that at a Pt surface.

Figure 5 Cyclic voltammograms of PCS at a 25 μm diameter Pt microdisk electrode (A) (scan rate = 20 mV/sec); and a 10 μm diameter carbon microdisk electrode (B) (scan rate = 50 mV/sec).

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References

1. S. J. Visco, C. C. Mailhe, L. C. De Jonghe, and M. Armand, *J. Electrochem. Soc.*, **136**, 661(1989).
2. M. Liu, S.J.Visco, and L.C.De Jonghe, *J. Electrochem. Soc.*, **137**, 750(1990).
3. S. Prasad, H.S. Lee, J. McBreen and T.A. Skotheim, Extended Abstract, 182 Electrochemical Society Meeting, p63, Toronto, Canada, 1992.
4. P.W. Bridgman, *Proc. Am. Acad. Arts Sci.* **74**, 399(1941).
5. E. Whalley, *Can. J. Chem.*, **38**, 2105(1960).
6. J. Tsukamoto and A. Takahashi, *Jap. J. Appl. Phys.*, **25**, L338(1986).
7. S. Wawzonek and S. M. Heilmann, *J. Org. Chem.* **39**, 511(1974).
8. M. F. Hurley and J. Q. Chambers, *J. Org. Chem.*, **46**, 778(1981).
9. P. Jeroschewski, F. Pragst, *J. Electroanal. Chem.*, **149**, 131(1983).
10. S. Wawzonek, H-F. Chang, W. Everett, and M. Ryan, *J. Electrochem. Soc.*, **130**, 803(1983).
11. M.R. Hunt, G. Winter, *Australia J. Chem.*, **25**, 417(1972).
12. P. Jeroschewski, F. Pragst, *J. Electroanal. Chem.*, **149**, 131(1983).
13. G. Bontempelli, F. Magno, Gian-Antonio Mazzocchin, and Renato Seeber, *J. Electroanal. Chem.*, **63**, 231(1975).
14. M. V. Mirkin and A. J. Bard, *Anal. Chem.*, **64**, 2293(1992).

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