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Polysiloxane Pyrolysis

A. M. Wilson,[†] G. Zank,[‡] K. Eguchi,[‡] W. Xing,[§] B. Yates,[||] and J. R. Dahn*,[§]

Department of Physics, Simon Fraser University, Burnaby, BC, Canada V5A 1S6, Dow-Corning Asia Ltd., Yamakita, Kanagawa, Japan, Department of Physics, Dalhousie University, Halifax, NS, Canada B3H 3J5, Canadian Synchrotron Radiation Facility, University of Wisconsin, Stoughton, Wisconsin 53589-3097

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Different polysiloxanes were pyrolyzed to make silicon oxycarbide glasses which have been shown to be possible candidates for anode materials of Li-ion batteries. The decomposition process during pyrolysis was studied using a thermal gravimetric analyzer connected to a residual gas analyzer for three representative polymers. No silicon- or oxygen-containing gases were observed during pyrolysis. The stoichiometry of all of the final chars was measured and found to agree well with predictions calculated using the initial polymer stoichiometry, the ceramic yield, and the fact that only carbon and hydrogen atoms were eliminated during pyrolysis. For three chars with identical stoichiometry at 1000 °C, prepared from three different polymers, the local chemical environment of the silicon was studied as a function of pyrolysis temperature by X-ray absorption (XAS) near the silicon K-edge. As the samples are heated, the XAS spectra eventually become identical, once the different labile species have been eliminated, suggesting that the properties of the char are dependent mainly on its stoichiometry and not on the initial composition of the polymer precursor. The bulk properties of these three chars prepared at 1000 °C were also studied by X-ray diffraction and by electrochemical methods which showed them to be identical.

Introduction

Silicon polymers are commonly used in the production of silicon carbide and silicon oxycarbides.[1,2] We have experience in the pyrolysis of siloxane polymers for possible use as anode materials in Li-ion cells.[3−6] In ref 6, we showed how the capacity of the pyrolyzed polymers for lithium depends strongly on the stoichiometry of the silicon oxycarbide. Some of the pyrolyzed materials showed reversible capacities of 900 mAh/g, which is more than twice that of the graphite anodes (372 mAh/g) currently used in commercial Li-ion cells, so there is good reason to be interested in silicon oxycarbide chars. Considering the stoichiometry of the material desired, one chooses appropriate polymers and pyrolysis parameters. At sufficiently low temperatures, one does not expect to break the Si−O linkages in the polymer. Therefore, the stoichiometry of the resulting char depends on the stoichiometry of the initial polymer. Above about 1300−1500 °C, the Si−O bonds are reduced and silicon carbide will be produced upon pyrolysis.[1−3]

Siloxane polymers differ in the number of oxygen atoms per silicon and in the chemical composition of the ligands. Initially, it was not obvious to us how the stoichiometry and properties of the pyrolysis products should be related to that of the initial polymer. Therefore, we always used chemical analysis[6] to determine the stoichiometries of the ceramic products and other techniques to determine their properties. Here, we show that the stoichiometry of pyrolyzed siloxanes is easily estimated based on the initial polymer composition and the char yield, provided that the initial polymer is highly cross-linked or branched such that the parent backbone does not "unzip" and evaporate during heating.

Chars of the same final stoichiometry can be prepared from polymers of different initial composition. For example, phenyl-containing polymers might be expected to give chars of different properties than those of vinyl- or methyl-containing polymers, even if the final stoichiometries of the chars are identical. Here, we address this question as well by examining three highly cross-linked polysiloxanes chosen, based on experience, so that they would produce roughly the same stoichiometry after pyrolysis to a sufficiently high temperature. This temperature was high enough to ensure complete decomposition of the polymers to produce silicon oxycarbide glasses (Si−O−C) of nearly the same stoichiometry but low enough that the oxygen was not driven out of the material, forming silicon carbide. Other recent work[7] has shown that the initial chemical environment around silicon in a siloxane polymer is only maintained up to about 500 °C. As those authors state: "Further heating results in a scrambling of the silicon environment". On the basis of this, one expects

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* Author to whom correspondence should be addressed.

[†] Simon Fraser University.

[‡] Dow-Corning Asia Ltd.

[§] Dalhousie University.

[||] University of Wisconsin.

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Table 1. Polymers Which Were Pyrolyzed To Make the Samples

sample no.[a]	polymer used
13	$(PhSiO_{1.5})_{0.75}(Ph_2ViSiO_{0.5})_{0.25}$
14	$(PhSiO_{1.5})_{0.76}(Me_2ViSiO_{0.5})_{0.24}$
15	$(PhSiO_{1.5})(Me_2ViSiO_{0.5})_{0.5}$
16	$(PhSiO_{1.5})_{0.5}(Ph_2ViSiO_{0.5})_{0.5}$
17	$(MeSiO_{1.5})(Me_2ViSiO_{0.5})_{0.5}$
18	$(MeSiO_{1.5})_{0.77}(Me_2ViSiO_{0.5})_{0.23}$
23	$(PhSiO_{1.5})_{0.76}(Ph_2ViSiO_{0.5})_{0.24}$:$(PhSiO_{1.5})_{0.75}(Ph_2HSiO_{0.5})_{0.25}$
24	$(PhSiO_{1.5})_{0.5}(Ph_2ViSiO_{0.5})_{0.5}$:$(PhSiO_{1.5})_{0.5}(Ph_2HSiO_{0.5})_{0.5}$
25	$(PhSiO_{1.5})_{0.75}(Me_2ViSiO_{0.5})_{0.5}$:$(PhSiO_{1.5})_{0.5}(Me_2HSiO_{0.5})_{0.5}$
27	$(PhSiO_{1.5})_{0.76}(Me_2ViSiO_{0.5})_{0.24}$:$(PhSiO_{1.5})_{0.75}(Me_2HSiO_{0.5})_{0.25}$
40	$(PhSiO_{1.5})_{0.22}(MeSiO_{1.5})_{0.55}(Me_2ViSiO_{0.5})_{0.23}$
41	$(ViSiO_{1.5})_{0.77}(Me_2ViSiO_{0.5})_{0.23}$
42	$(ViSiO_{1.5})_{0.66}(MeSiO_{1.5})_{0.09}(Me_2ViSiO_{0.5})_{0.25}$
43	$(PhSiO_{1.5})_{0.09}(MeSiO_{1.5})_{0.66}(Me_2ViSiO_{0.5})_{0.25}$
44	$(PhSiO_{1.5})_{0.38}(MeSiO_{1.5})_{0.39}(Me_2ViSiO_{0.5})_{0.23}$
45	$(PhSiO_{1.5})_{0.5}(MeSiO_{1.5})_{0.23}(Me_2ViSiO_{0.5})_{0.27}$
46	$(PhSiO_{1.5})_{0.66}(MeSiO_{1.5})_{0.08}(Me_2ViSiO_{0.5})_{0.26}$
47	$(PhSiO_{1.5})_{0.13}(ViSiO_{1.5})_{0.64}(Me_2ViSiO_{0.5})_{0.2}$

[a] From ref 6.

these three materials pyrolyzed at 1000 °C to show similar properties.

We have examined the characteristics of these three materials in some detail. The decomposition process was studied by thermal gravimetric analysis coupled with residual gas analysis to determine the gases of pyrolysis. The structure of the pyrolysis products was probed by powder X-ray diffraction (XRD) measurements. The chemical environment of the silicon atoms was investigated by X-ray absorption at the silicon K-edge. The behavior of these materials upon electrochemical insertion of lithium was also studied using lithium metal coin cells since this electrochemistry has been shown to be strongly dependent[6] on char composition and structure.

Experiment

The electrochemical behavior of many of these samples has been described in a previous publication of ours.[6] Since they are the same samples, to make connection with the previous publication, we have used the same sample numbers in Tables 1 and 2 as in ref 6.

The following is a description of the preparation of polysiloxane 43, which was pyrolyzed to make sample 43. Phenyltrimethoxysilane (77.0 g), methyltrimethoxysilane (742 g), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (192 g), trifluoromethanesulfonic acid (5.0 mL), and deionized water (50 g) were heated to reflux for 2 h. Toluene (1.5 L) and deionized water (410 mL) were added to the mixture and heated to reflux for an additional 2 h. Calcium carbonate (10 g) was added, and solvent was distilled until the vapor head temperature increased to about 85 °C. Aqueous 3 wt % potassium hydroxide (50 mL) was added, and the water was azeotropically removed using a Dean-Stark apparatus. After the reaction mixture was dry of water, reflux was continued for 8 h, the mixture was cooled to about 50 °C, and chlorodimethylvinylsilane (50 mL) was added to cap the remaining Si−OH groups of the polymers. After being stirred at room temperature for 3 days, the mixture was filtered through a Buchner funnel containing Celatom filter-aid and the solvent removed using a rotary evaporator, giving a quantitative yield of a clear, colorless viscous fluid. The other polymers were prepared by a similar method. Table 1 contains a summary of the stoichiometries of the polysiloxanes made, determined by NMR. (Stoichiometries determined by the weights of the reactants used were generally in very good agreement.)

All polymers were cured (cross-linked) by mixing with 1% by weight of Lupersol 101 and heating to between 150 and 175 °C for 20−45 min.

Table 2. Predicted and Measured Stoichiometries of the Samples Pyrolyzed at 1000 °C

sample no.[a]	yield (%)	predicted (at. %) final C	predicted (at. %) final Si	predicted (at. %) final O	experiment (at. %) C	experiment (at. %) Si	experiment (at. %) O
13	67	66.3	15.0	18.7	66	17	16
14	71	57.9	18.7	23.4	62	15	24
15	62	51.0	24.5	24.5	62	16	21
16	53	66.5	16.7	16.7	71	12	17
17	60	14	43	43	37	27	36
18	79	27.2	32.4	40.5	33	31	36
23	73	68.2	14.1	17.6	67	13	21
24	66	72.1	14.0	14.0	73	12	15
25	78	57.7	21.1	21.1	60	18	23
27	75	58.2	18.6	23.2	61	15	24
40	76	44.5	24.4	31.0	47	24	30
41	86	45.1	24.2	30.7	45	25	30
42	83	44.9	24.5	30.6	45	25	30
43	75	30	31	39	39	26	34
44	79	50.6	21.7	27.6	54	20	26
45	76	54.6	20.4	25.1	59	19	23
46	77	60.1	17.8	22.1	63	16	20
47	85	48.7	22.8	28.6	50	22	28

[a] From ref 6.

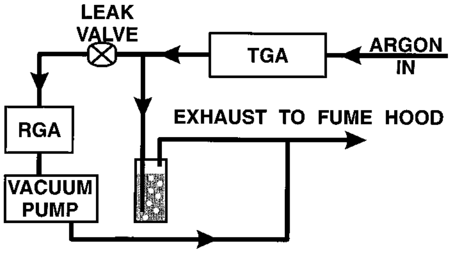

Figure 1. Schematic representation of the apparatus used for thermal gravimetric and residual gas analysis.

Polysiloxane pyrolysis took place under constant purging with ultrahigh purity argon (Linde, 99.999%) gas. The purge rate maintained was sufficient to prevent the decomposition and redeposition of vapors released during polymer decomposition. The samples were held in an alumina boat and placed inside the reaction tube at 100 °C. The tube was sealed from the atmosphere and flushed with a volume of argon sufficient to fill the reaction tube 20 times. The temperature was raised at a rate of 5 °C/min to the maximum temperature. The maximum temperature was maintained for 60 min. Cooling to 100 °C was at a rate of approximately 4 °C/min. Samples were weighed before and after pyrolysis to obtain the char yield. The material was reclaimed and reduced to a powder by grinding in an automatic mortar and pestle for 20 min. As shown in Table 2, 18 samples were made from the listed polysiloxanes at a temperature of 1000 °C. In order to study changes in the silicon K-edge with heat treatment temperature, samples 40, 41, and 42 were also pyrolyzed to a maximum of 600, 800, and 1100 °C.

The decomposition process of the polysiloxane was studied using a TA Instruments model 51 thermal gravimetric analyzer (TGA) connected to a Leybold Quadrex 200 residual gas analyzer (RGA, mass spectrometer), as shown in Figure 1. Ultrahigh purity argon (Linde, 99.999%) flowed at 25 cm^3/min over the polymer samples (between 50 and 70 mg) as they were heated. The argon stream exited the TGA and passed to the atmospheric pressure inlet of the RGA. A Vacoa (Vacuum Corporation of America, Bohemia, New York) leak valve was used to sample a small amount of the TGA exhaust and pass it to the mass spectrometer chamber. The base pressure of the RGA chamber is near 5×10^{-8} Torr, and we operated near 3×10^{-5} Torr with the leak valve open. Thus, the signal from the gases evolved during polymer decomposition overwhelms those from the chamber alone. All gas flow lines were heated above 100 °C to facilitate the transport of evolved water, benzene, and other residual vapors which otherwise might condense in the hoses at ambient room temperature. After the sample was loaded in the TGA, argon was flushed through

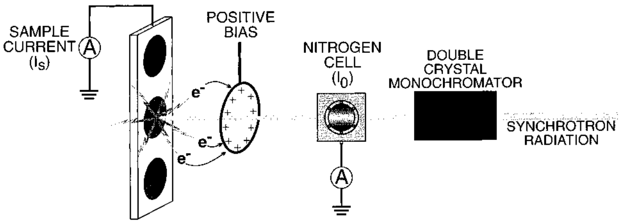

Figure 2. Schematic representation of the apparatus used to measure the X-ray absorption.

the system until the base pressure in the RGA stabilized. Then the samples were heated at a rate of 10 °C/minute to 950 °C while the sample weight and evolved gases were monitored.

Elemental analyses of the materials discussed were performed by employees of Dow Corning Corp. (Midland, MI). CHN analysis were done on a Perkin Elmer 2400 analyzer. Oxygen analysis was done on a Leco oxygen analyzer (model R0-316) equipped with an oxygen determinator 316 (model 783700) and an electrode furnace EF100. Silicon analysis was determined by a fusion technique which consisted of converting the solid to a soluble form and analyzing the solute for total silicon by Arl 3580 ICP-AES (inductively coupled plasma atomic emission spectroscopy) analysis. Typically, the sum of the experimentally derived carbon, silicon, hydrogen, and oxygen weight percentages were within 5% of 100%. We are most confident of the carbon, hydrogen, and silicon analyses, so in the tables reported below, the oxygen content is calculated from the difference between 100 wt % and the sum of the C, H, and Si weight percentages.

A Siemens D5000 powder X-ray diffractometer, equipped with a Cu target X-ray tube and a diffracted beam monochromator, was used to characterize all the samples. Samples were prepared by filling a 25mm × 16mm × 2mm deep well in a stainless steel plate with the powdered sample, followed by a smoothing of the surface.

X-ray absorption measurements were performed at the Canadian Synchrotron Radiation Facility double-crystal monochromator beam line, located at the Synchrotron Radiation Facility in Stoughton, Wisconsin. The operational details of the double-crystal monochromator have been explained elsewhere.[8] Figure 2 shows a schematic of the apparatus used. Samples under a vacuum, not exceeding 1×10^{-6} Torr, were exposed to monochromatic synchrotron radiation. The electrons excited from the material were collected by a loop of wire biased at 136 V located in front of the sample. To maintain electrical neutrality, a current, I_S, flowed from ground through a Keithley 427 current/voltage converter to the sample. The value of the sample current, I_S, is proportional to the total electron yield. The absorption measurements were made by measuring I_S, which resulted from the total electron yield. A 1 Torr nitrogen gas cell is used to measure the beam strength, I_0, which reaches the sample. The final K-edge signal is determined by dividing I_S by I_0 and is hereafter referred to as the X-ray absorption signal.

Coin cells of these materials with lithium metal foil were made to test the behavior of these materials upon the electrochemical insertion of lithium. The details of this cell construction have been explained elsewhere.[6] The electrolyte used was 1 M $LiPF_6$ dissolved in a 70/30 volume percent (v/o) mixture of ethylene carbonate and diethyl carbonate. All cells were cycled using a constant current of 18.6 mAh/g.

Results

Parts a, b, and c of Figure 3 show, respectively, the decomposition of polysiloxanes 40, 41, and 42 as measured by TGA and RGA. The bottom frame in each part (3a–c) shows the weight (as a percent of the original weight) and the derivative of the weight with respect to the temperature (dW/dT) plotted versus temperature. The frames above this show the RGA signal for a number of masses. There is no measurable amount of oxygen- or silicon-containing gas species in the decomposition stream. Mass 28 could be CO or C_2H_4, but considering that mass 27 shows a virtually identical signal and that no signal is observed for mass 44 (CO_2), we believe mass 28 is C_2H_4 and mass 27 is C_2H_3. The phenyl groups in polysiloxane 40 can be clearly seen leaving as masses 78 and 52.

The RGA data suggests that only carbon- and hydrogen-containing species are leaving the polysiloxane during decomposition to a maximum of 1000 °C. On the basis of the initial stoichiometries of the polysiloxanes, it is straightforward to calculate the resulting weight percentages of silicon, oxygen, and carbon that should be in the resulting silicon oxycarbide glasses. We assume that the entire weight loss is due to carbon and hydrogen and that all of the hydrogen leaves the material. What follows below is a sample calculation for sample 40, based on the initial stoichiometry of polysiloxane 40.

sample calculation:

Polysiloxane 40 stoichiometry: $C_{2.79}H_{4.82}SiO_{1.27}$

weight percent carbon = 38.6%, weight percent H = 5.5%

total weight loss observed: 19.0%

percentage weight loss due to carbon (= total weight lost − wt % H) = 13.5%

Carbon lost per formula unit = $2.79(13.5/38.6) = 0.98$

remaining carbon = $2.79 - 0.98 = 1.81$

final predicted stoichiometry, $C_{1.81}SiO_{1.27}$; at. % C = 44.5%, at. % Si = 24.5%, at. % O = 31.0%.

Table 2 contains a summary of the atomic percentages (at. %) of Si, O, and C predicted in all the pyrolyzed polymers as calculated by the method shown above. Experimental compositions (believed to be accurate to ±3%) are also given. Considering that the weight percentages by elemental analysis do not close on 100% and the discrepancy associated with that, the agreement between the experiment and the calculation is very good for all but three of the polymers. This suggests that our model for the pyrolysis of these polysiloxanes is correct. In addition, it is clear that polymers containing phenyl groups instead of methyl or vinyl (e.g. compare samples 13 and 14) groups add more carbon to the chars as has been previously reported.[9–11]

The experimental stoichiometries of samples 15, 17, and 43 do not agree well with the predicted values. Of these, sample 17 is the worst, and there was black, tarry material deposited at the cool end of the pyrolysis tube during its production. This suggests some evaporation of "unzipped" fragments and a breakdown of the our model. On the other hand, sample 43 was observed to have fragmented violently during pyrolysis, and it could have had a low yield due to our inability to recover all

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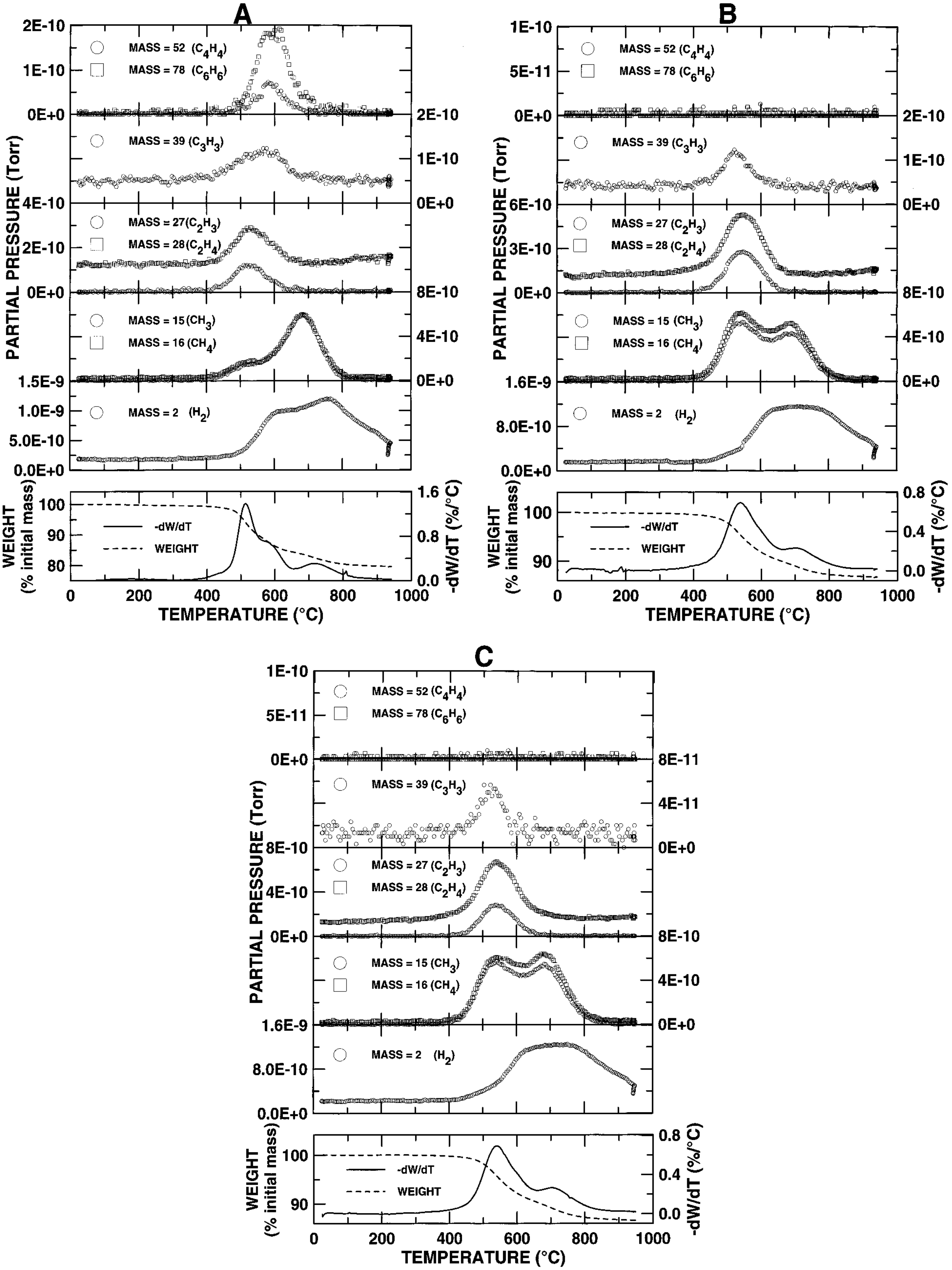

Figure 3. Thermal decomposition of the polysiloxanes. The TGA data is presented in the bottom panel for each. The upper panels are partial pressures of the masses shown, as measured by the RGA. Parts a, b, and c, respectively, show the results for samples 40, 41, and 42.

the fragments from within the tube. For this sample, and for sample 15, the experimental stoichiometries can be well-matched if the measured yields are increased by about 11%. This treatment does not work for sample 17 at any value of the yield, presumably because of the unzipping.

The powder X-ray diffraction profiles for samples 40, 41, and 42 are shown in Figure 4. Broad features

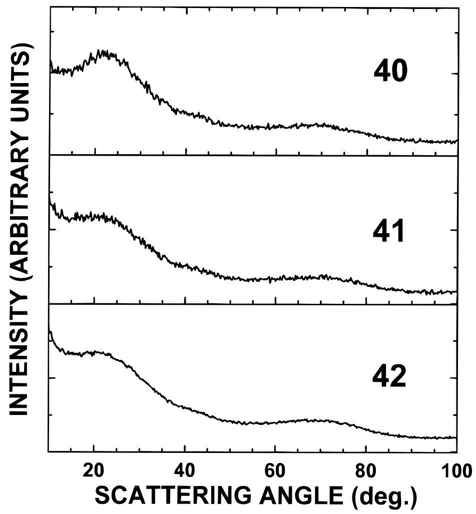

Figure 4. XRD profiles for samples 40, 41, and 42, pyrolyzed at 1000 °C.

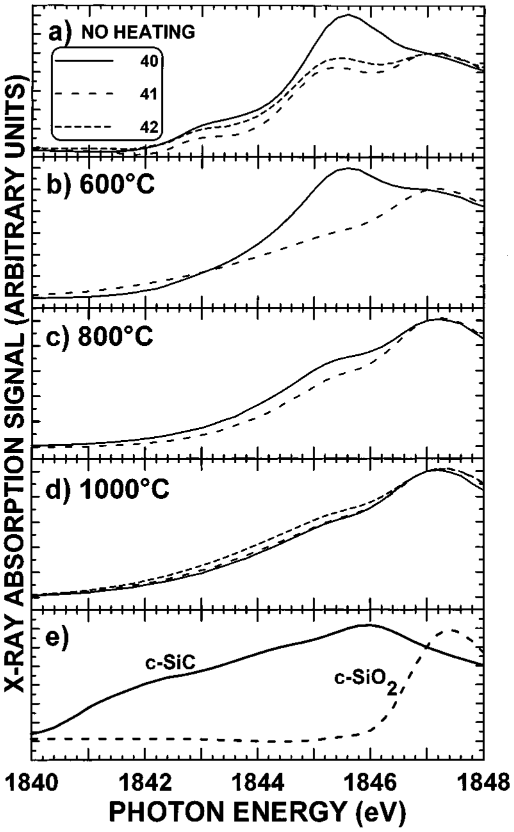

Figure 5. Silicon K-edge for (a) polysiloxanes 40, 41, and 42 without any heat treatment, (b) polysiloxanes 40 and 41 heated to 600 °C, (c) polysiloxanes 40 and 41 heated to 800 °C, (d) samples 40, 41, and 42 heated to 1000 °C, and (e) SiC and SiO_2. All spectra were normalized at 1847 eV.

identified as networked glass peaks (due to their similarity to peaks found in a-SiO_2) are centered near 23° and 73°. A slight feature at 43° may be due to the presence of a small number of single graphene sheets, as we have stated elsewhere.[4,6] However, the weakness of this peak makes it difficult to identify. The XRD profiles for the three samples are almost identical. For sample 40, the 23° peak is somewhat more intense and narrower.

Figure 5 summarizes the X-ray absorption measurements of the silicon K-edge for samples 40, 41, and 42.

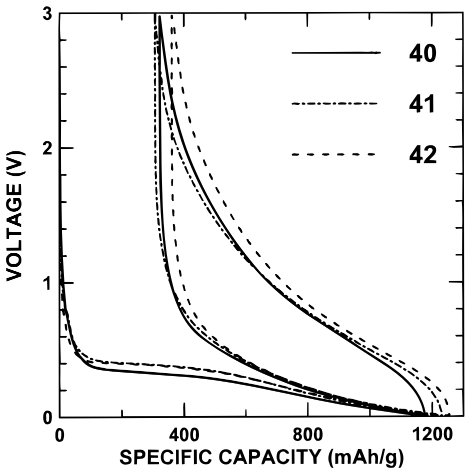

Figure 6. Voltage profiles for samples 40, 41, and 42 heated to 1000 °C.

Figure 5a shows the profiles for the unheated polysiloxanes 40, 41, and 42. Figure 5b,c shows the profiles for materials made by heating polymers 40 and 41 to a maximum of 600 and 800 °C, respectively. The profiles for samples 40, 41, and 42 heated to 1000 °C are shown in Figure 5d. For reference purposes the c-SiC and c-SiO_2 silicon K-edges were measured and are shown in Figure 5e. All the spectra (I_S/I_0) in Figure 5 have been normalized at 1847 eV.

All the profiles in Figure 5a−d show features near 1845.5 and 1847.2 eV which, by comparison to the spectra for c-SiC and c-SiO_2, we attribute to silicon−carbon and silicon−oxygen bonding, respectively. Sample 40, which is the only one which initially contained phenyl groups, differs at low temperatures from the others. As the maximum pyrolysis treatment temperature increases, the intensity of the 1845.5 eV feature decreases relative to the 1847.2 eV feature. Between 600 and 800 °C, most of the labile phenyl groups leave sample 40 (see Figure 3a), and the X-ray absorption (XAS) spectrum begins to resemble that of sample 41, which did not contain phenyl groups initially. By 1000 °C the spectra are almost identical, implying that the local chemical environment of the silicon atoms in samples 40, 41, and 42 is the same. If this is true, other bulk measurements should also give identical results. To confirm this, we made electrochemical cells and studied the reversible reaction of lithium with these materials.

Figure 6 shows the first discharge, first charge, and second discharge of electrochemical cells made with materials 40, 41, and 42. Each of these materials reacts reversibly with over 800 mAh/g of lithium. The differences between the profiles are within expected experimental discrepancies. Thus, the electrochemical behavior upon the insertion and deinsertion of lithium into these materials is the same. This suggests that it is the final char stoichiometry, not the precise nature of the starting polymer, which controls the bulk properties of the Si−O−C glasses.

In recent work[12,13] the local environment of the Si atom in chars has been studied with Si^{29} magic angle spinning NMR. There it is shown that local environ-

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ment of the Si is determined by the Si−O ratio in the char, which is related to that in the initial precursor. This, however, does not mean that the overall structure of the char only depends on the Si−O ratio. For example, in ref 6, we have prepared series of materials with the same Si−O ratio but with different amounts of carbon. These materials have different diffraction patterns and have different electrochemical behavior, which are controlled by the overall stoichiometry of the char and not by the local environment around Si, which is probably the same.

Conclusions

We have developed a simple method for estimating the chemical composition of chars prepared from highly cross-linked polysiloxanes. The method relies on two inputs and one assumption: (1) the initial polymer stoichiometry, (2) the char yield, and (3) that only C and H atoms evolve during pyrolysis. On the basis of this model, the predicted stoichiometries of 15 and 18 chars were found to agree well with experimentally determined stoichiometries. We believe that these rules can serve as a useful "rule of thumb" for those working on chars and ceramics prepared from pyrolyzed polysiloxanes.

The pyrolyzed materials 40, 41, and 42, prepared from different polymers, have the same final stoichiometry and were shown to have similar XRD, XAS, and electrochemical signatures. Therefore, we believe it is the final char stoichiometry, not the initial polymer structure or composition, which dominates the properties of the char. This fact may have importance for those wishing to optimize the synthesis of a particular char or ceramic by moving to less expensive initial polymers which give the same char stoichiometry.

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