Thermal Stability in Air of Pt/C Catalysts and PEM Fuel Cell Catalyst Layers

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The durability of PEM fuel cell materials is essential to application longevity. This research explores the limits of thermal stability of platinum/Vulcan XC 72 catalysts and a 46 wt % Pt/Vulcan XC 72/Nafion catalyst layer. The thermal stability of Pt/Vulcan XC 72 catalysts and the PEM fuel cell catalyst layer is studied by thermal gravimetric analysis (TGA) in air. The products of decomposition are analyzed with TGA coupled with mass spectrometry (TGA−MS). Low temperature (100−200 °C) carbon combustion in the presence of platinum is confirmed. The high precision and sensitivity of TGA allows differentiation of two oxidative/mass loss regimes for 46% Pt/C. The presence of surface protective groups raises the activation energy for the low-temperature/low-conversion ($\leq$5%) oxidation of 46% Pt/Vulcan XC 72 (197 $\pm$ 13 kJ/mol) compared to a higher temperature/higher conversion level (10−30%) process (140 $\pm$ 10 kJ/mol). In PEM fuel cell catalyst layers, the thermal decomposition temperature of Nafion is lowered by about 100 °C to 300 °C in the presence of Pt/C catalysts. As a result of the above studies it was found that TGA is convenient for the determination of Pt wt % in catalyst-coated membranes.

Introduction

Development of carbon-supported platinum catalysts was one of the major steps to commercialization of PEM fuel cells. Advantages of such catalysts under fuel cell operation conditions include high surface area, sufficient electronic conductivity, and slow catalyst agglomeration.[1] Due to increased surface area of Pt/C catalysts, Pt loading in fuel cell cathodes can be reduced 20−40 times compared to Pt black catalysts while achieving similar fuel cell performance.[2]

While gaining economy, carbon-supported Pt catalysts have significant shortcomings. In air, platinum catalyzes the oxidation of the carbon support.[3] Carbon corrosion would clearly jeopardize the long-term operation of fuel cells for demanding terrestrial and space applications.

To mimic PEM fuel cell operating conditions, Stevens et al. conducted extensive isothermal weight loss studies in dry air for a wide range of platinum catalysts (5−80 wt % Pt) supported on BP2000 high surface area carbon.[3] It was shown that Pt facilitates carbon oxidation even at moderate temperatures (125−195 °C). Increasing both the temperature (in the given range) and Pt loading resulted in increasing of the rate of carbon combustion. From 150 to 195 °C carbon combustion was described by a first-order kinetic model. The carbon combustion rate decreased at temperatures lower than 150 °C. The authors suggested that protective surface functional groups might inhibit carbon combustion at lower temperatures.

Contemporaneously, low-temperature carbon corrosion was identified under conditions close to PEM fuel cell environments.[4,5] Using on-line mass spectrometry, Roen et al. detected increased CO_2 emission at cathodes with higher Pt loadings.[5]

Platinum also accelerates thermal decomposition of Nafion, another component of the PEM fuel cell catalyst layer, at high temperatures.[6] Samms et al. investigated the thermal stability of a catalyst layer consisting of 20% w/w Pt black and 80% of Nafion by TGA−MS. They found that Pt lowers the decomposition temperature of Nafion by 40 °C.

Due to increased interest in higher temperature PEM fuel cells (100−200 °C), it is important to explore the limits of thermal stability of carbon-supported Pt catalysts and PEM fuel cell catalyst layers. Here, we report the application of TGA and TGA−MS to facilitate evaluation of Pt/C catalysts. We find that TGA is a time-efficient method for evaluation of thermal stability and that TGA−MS provides identification of volatile species during catalytic decomposition processes. The results confirm the existence of a low-temperature oxidation process between 100 and 200 °C, which is a desirable operation range. In addition, the Pt-catalyzed decomposition of Nafion is further explored.

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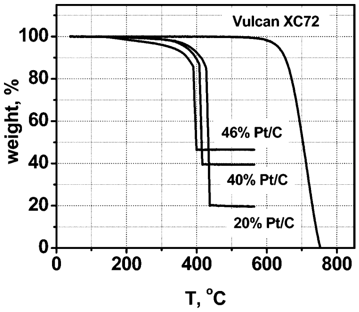

Figure 1. TGA data of 20%, 40%, and 46% Pt/C in air; heating rate 20 °C/min.

Experimental Section

Materials. Pt/Vulcan XC 72 from E-TEK (20 and 40 wt % Pt) and 46 wt % Pt/Vulcan XC 72 (Tanaka KK) were used in these studies. Nafion 112 membrane was purchased from Ion Power Inc. and cleaned[7] to obtain the acid form of membrane.

Materials Processing. The catalyst layer was obtained by electrospraying Pt ink onto Nafion 112 membrane.[7] The ink composition was ~40 wt % of Nafion ionomer (equivalent weight 1100, Aldrich) and ~60 wt % of 46 wt % Pt/Vulcan XC 72 (dry base). The catalyst layer was sampled for TGA by carefully scraping a small amount from the Nafion 112 substrate.

Thermal Analysis. Thermogravimetric analyses (TGA) utilized a Q500 TGA (TA Instruments-Waters, LLC). Platinum pans were used in all measurements. Heating rates from 0.1 to 20 °C/min were employed under dry air (100 mL/min). Before thermal analysis, to eliminate mass loss due to adsorbed water, samples were heated at 20 °C/min to 100 °C, dried for 1 h at this temperature, and cooled to 40 °C under a dry nitrogen atmosphere. As a result, all weight loss in Pt/C samples is due to carbon oxidation and is not related to water desorption. To verify that the thermal stability of Nafion does not depend on the casting procedure, TGA data were obtained both for electrosprayed and commercial samples. No significant difference was detected.

TGA was coupled with mass spectrometry (Pfeiffer Vacuum Thermostar quadrapole mass spectrometer) to analyze products of catalyst layer decomposition, Nafion112, and Pt/C powders. The mass spectrometer was connected to the TGA furnace via a fused silica capillary heated to 200 °C. A heating rate of 10 °C/min was used. This is the lowest heating rate permitted when Q500 is coupled to the mass spectrometer. Mass spectra were collected in the range of 10−100 mass-to-charge (m/e) ratios; ion currents vs temperature curves for every observed m/e ratio were then obtained. Kinetic analysis of experimental data was performed using TGA Kinetics Analysis software based on the ASTM procedure that is part of the TA Advantage Specialty Library.[8]

Results and Discussion

Thermal Decomposition of Carbon-Supported Pt Catalysts. *Thermal Gravimetric Analysis (20 °C/min).* Figure 1 contains the weight loss vs temperature curves at 20 °C/min in air for carbon-supported Pt catalysts with different platinum loadings and Vulcan XC 72 carbon. There is no mass loss for Vulcan XC 72 up to 550 °C. Above 550 °C, the weight of sample decreases gradually until a precipitous mass loss occurs above 625 °C.

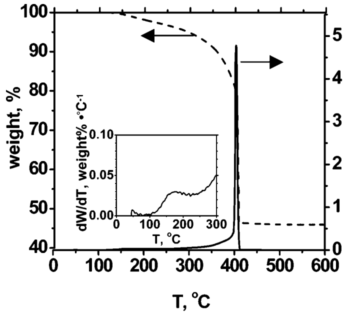

Figure 2. TGA and DTG data for 46% Pt/C in air. The inset shows DTG on a larger scale.

The weight change of Pt/C powders follows a pattern different from that of Vulcan XC 72. At 20 °C/min there are four distinctive mass loss regions. Between 40 and 200 °C little or no mass loss is observed for Pt/C (20−46% Pt). In the next section of this paper the mass loss in this temperature range at lower heating rates will be examined. Returning to Figure 1, oxidation occurs gradually in the second region from 200 to 400 °C with the exact range depending on composition (200−430 °C, 20%; 200−410 °C, 40%; 150−390 °C, 46%) An abrupt mass loss around 400 °C occurs in the third region. The onset temperature for sudden weight loss is inversely correlated with Pt loading. Finally, in the fourth region the sample reaches constant mass that reflects Pt weight percent. This final value provides a convenient confirmation of Pt loading (as received %/TGA %: 45.5/46.6, 40/39.5, and 20/20.3).

These observations indicate that Pt accelerates carbon decomposition in carbon-supported Pt catalysts. While oxidation of Vulcan carbon begins at 500 °C, the corresponding initial mass loss temperature for Pt/C ranges from 150 to 200 °C, a difference of 300−350 °C. The residue for Pt/C above 400 °C shows that Pt/C catalysts (20%−46% Pt) decompose quantitatively in air to Pt. Finally, the onset of both low-temperature mass loss (150−200 °C) and sudden mass loss at higher temperatures (390−430 °C) shifts to lower temperatures with increased Pt loading. Stevens observed a similar shift to lower decomposition temperatures at higher Pt loadings.[3] This shift is probably due to changing the total reaction rate because of the larger available Pt surface area at higher loadings.

TGA−Mass Spectrometry. Since Tanaka 46% Pt/Vulcan XC 72 is considered superior for the oxygen reduction reaction in PEM fuel cells,[9] its thermal behavior was analyzed in more detail both as a single component and as a part of a catalyst layer. Figure 2 shows weight loss and DTG (differential thermal gravimetry) for 46% Pt/C obtained at 10 °C/min.

Table 1 summarizes thermal stability of carbon functional groups in an inert atmosphere in the absence of catalysts. These data from the literature were obtained by a temperature-programmed desorption method.[10,11] The assignment of decomposition temperatures to particular functional groups

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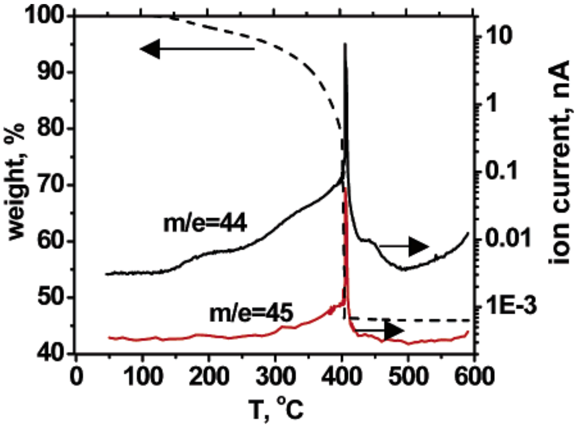

Figure 3. Mass signals for carbon dioxide (*m*/*e* = 44 and 45) superimposed on TGA data for 46% Pt/C; heating rate 10 °C/min.

Table 1. Thermal Stability of Carbon Functional Groups in an Inert Atmosphere[20]

functional group	decomp product	*T* (°C)	functional group	decomp product	*T* (°C)
carboxylic	CO_2	250[11]	anhydride	CO_2+CO	600[26]
		100−400[21]			627[11]
		200−250[22]			627[23, 24]
lactone	CO_2	627[23, 24]			350−400[22]
		350−400[22]	ether	CO	700[23]
		190−650[25]	quinone	CO	700−980[25]
phenol	CO	600−700[22]			800−900[22]
carbonyl	CO	700−980[25]			
		800−900[22]			

is not straightforward, but the general trend is that carboxylic groups are less thermally stable than other oxygen-containing functional groups. Considering this information, the presence of a small shoulder with an onset at 150 °C (Figure 2, insert) is assigned to decomposition of carboxylic groups on the carbon surface. It seems that Pt facilitates oxidation of these surface functional groups, since there are no features at this temperature for DTG of Vulcan XC 72.

Figure 3 shows mass signals at *m*/*e* = 44 (CO_2)[12] and 45 (probably HCO_2^+) for decomposition products of 46% Pt/Vulcan XC 72. The weight loss profile for the catalyst is depicted in the same figure. The curve for *m*/*e* = 44 mass signal has a small shoulder at ∼200 °C and a sharp peak at the temperatures where carbon combustion occurs. Thus, the mass loss process is unambiguously attributed to carbon dioxide generation. The presence of a small shoulder with an onset at 150 °C is again assigned to thermal decomposition of surface functional groups existing prior to the TGA experiment. The curve for *m*/*e* = 45 (Figure 3) closely follows the profile of *m*/*e* = 44 mass signal, indicating that both species originate from the same source. Mass signals observed at *m*/*e* = 48 and 64 (not shown) are due to SO_2.[12] Commercial carbon blacks typically contain sulfur as a contaminant.[13]

Both carbon monoxide and CO_2 are primary products from the reaction between carbon and oxygen.[13] In the presence of platinum, CO_2 is the primary product of carbon oxidation, along with residual traces of CO.[14] In our experiments with Pt/C, only CO_2 was detected by TGA−MS.

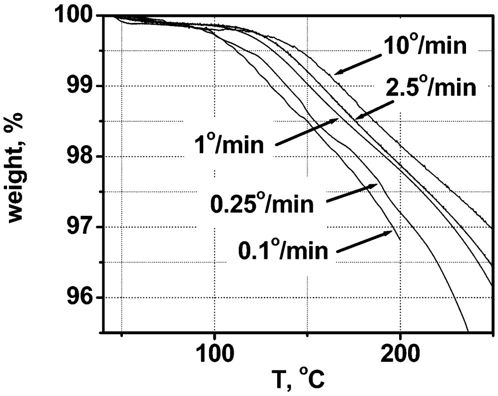

Figure 4. TGA data for 46% Pt/C measured at heating rates of 0.1, 0.25, 1, 2.5, and 10 °C/min.

TGA at Low Heating Rates: Kinetics of Decomposition. Careful examination of Figure 1 shows that mass loss for 46% Pt/C begins below 200 °C at 20 °C/min. To investigate low-temperature mass loss, the TGA of 46% Pt/C was examined at low heating rates. Figure 4 shows the TGA of 46% Pt/C at heating rates from 0.1 to 10 °C/min. As the heating rate decreases the percent mass loss increases, which is consistent with prior work that showed Pt catalyzed low-temperature oxidation of carbon by isothermal aging.[3]

To study the kinetics of carbon decomposition, TGA data were analyzed according to the method of Flynn and Wall[15,16] and standardized by ASTM.[8] This method, based on the Arrhenius equation, enables determination of activation energies from mass loss profiles measured at several heating rates. At a given conversion rate, the activation energy (E_a) can be found from a plot of log β vs 1/T according to eq 1[16]

$$E_a = -\left(\frac{R}{b}\right)\cdot\left(\frac{d(\log\beta)}{d(1/T)}\right) \qquad (1)$$

where β is a heating rate, R is the gas constant, and b is a parameter that is constant for first-order reactions. An approximate value of b (0.457) is used to obtain the initial activation energy from the slope of log β vs 1/T.[17] Once the initial value is determined, parameter b can be improved through a number of successive iterations.[16] Following the ASTM procedure, TGA data for kinetic analysis were collected at heating rates lower than 10 °C/min.

TGA curves were recalculated so as to normalize on initial carbon mass excluding Pt (Figure 5). With all mass loss due to carbon combustion and with an initial Pt fraction of 0.46, carbon weight loss vs temperature at a given heating rate was calculated according to eq 2,

$$m_c\,(\%) = \frac{m_T - 0.46m_o}{m_o - 0.46m_o}\cdot 100\% \qquad (2)$$

where m_o is the weight of the sample after drying in nitrogen at 100 °C for 1 h and m_T refers to the sample weight at a

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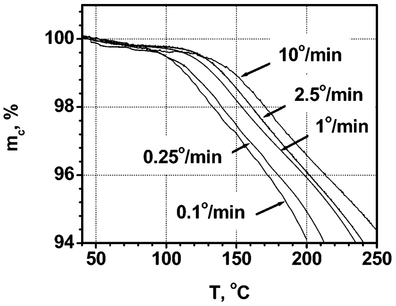

Figure 5. Carbon weight loss profiles calculated from TGA data (Figure 3) at heating rates of 0.1, 0.25, 1, 2.5, and 10 °C/min.

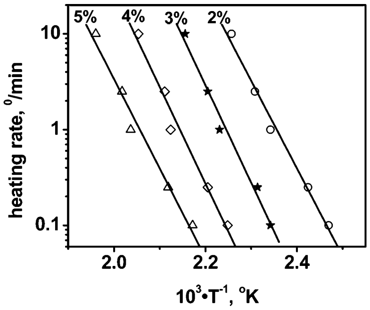

Figure 6. Heating rate vs 1/*T* in for carbon conversion levels of 2, 3, 4, and 5%.

Table 2. Activation Energies and Pre-Exponential Factors at Different Conversion Levels for Carbon Combustion in 46% (w/w) Pt/Vulcan XC 72 and Vulcan XC 72

	E_a (kJ/mol)		log(pre-exponential factor)	
conversion (%)	46% (w/w) Pt/C	Vulcan XC 72	46% (w/w) Pt/C	Vulcan XC 72
2	194 ± 10	159 ± 14	22.8	9.4
3	210 ± 13	157 ± 12	23.8	9.3
4	204 ± 15	157 ± 11	22.1	9.4
5	193 ± 14	158 ± 11	20.6	10.0
10	144 ± 12	170 ± 9	12.0	8.6
20	132 ± 9	173 ± 10	10.0	8.8
30	145 ± 10	176 ± 9	10.7	9.0
40[a]	−	175 ± 9	−	8.9
50	−	174 ± 8	−	8.9
60	−	173 ± 8	−	8.9
70	−	173 ± 10	−	8.9
80	−	173 ± 8	−	8.9
90	−	173 ± 8	−	9.0
99.9	−	172 ± 9	−	9.2

[a] For 46%(w/w)Pt/C plots of log B vs 1/*T* were nonlinear for conversion levels higher than 40%.

given temperature. At the lowest heating rate (0.1 °C/min) a carbon loss of 6% occurs at 200 °C (Figure 5). The cumulative mass loss to 200 °C attenuates at higher heating rates.

The high precision of TGA permits obtaining activation energies at low temperatures and low conversion levels (≤5%). From the weight loss profiles the temperatures of carbon decomposition were determined at conversion levels of 2, 3, 4, and 5% for different heating rates. The data obtained were used to plot log β vs 1/*T* dependencies at different conversion levels (Figure 6). The parallel arrangement of lines indicates that carbon combustion can be described as a first-order reaction.[16]

Plots of log β on 1/*T* were also examined for higher conversion levels (10−30%) at low heating rates (0.25−2.5 °C/min), where sample weight changed gradually over the entire temperature range. At conversion levels higher than 30% plots of log β vs 1/*T* were not linear. As a control, weight loss profiles for Vulcan XC 72 were measured at heating rates of 0.1−10 °C/min to obtain log β vs 1/*T* for different conversion levels. Activation energies calculated from slopes of log β vs 1/*T* along with log pre-exponential factors at different conversion rates for 46% Pt/C and Vulcan XC 72 are listed in Table 2.

An average activation energy of 197 ± 13 kJ/mol is obtained from kinetic analysis of thermal decomposition for 46% Pt/Vulcan XC 72. The low *T*/conversion process (≤5%) corresponds to the occurrence of a shoulder in the DTG assigned to CO_2 by TGA−MS (Figure 2). The high activation energy provides additional evidence for the existence of oxidation-inhibiting surface groups. The existence of "protective functional groups" was previously suggested by Stevens[3] to account for the slow rate of oxidation in the temperature range 125−170 °C.[3] As a control, the activation energy of Vulcan XC 72 was 158 ± 12 kJ/mol at low *T*/conversion (Table 2).

At higher conversion levels (≥10%) the relative order of activation energies changes (Table 2). For 46% Pt/Vulcan XC 72 at conversion levels 10−30%, an average activation energy of 140 ± 10 kJ/mol is obtained while for the Vulcan XC 72 control, E_a is 173 ± 9 kJ/mol (Table 2). The same average value for the Vulcan XC 72 control is obtained in the wide range of conversion levels from 10 to 99.9%.

Considering the different temperatures for low conversion (≤5%) compared to higher conversion (≥10%), different mechanisms of carbon oxidation in the presence of platinum must be operative. At higher *T*/conversion for 46%Pt/C, the presence of groups on the carbon surface do not "protect" carbon. At higher *T*/conversion the relative order of activation energies is in keeping with the lowering of the activation energy by the Pt catalyst.

The value for E_a for 46% Pt/Vulcan XC 72 at higher conversions (140 ± 10 kJ/mol) is marginally higher than that reported by Stevens for higher Pt loaded BP2000 (106 ± 17 kJ/mol).[3] Stevens obtained TGA data for BP2000 at 2.5 °C/min and found a rapid mass loss at ~500 °C.[3] At this heating rate we find that a precipitous mass loss for Vulcan XC 72 occurs at ~570 °C (similar in form to that shown in Figure 1 at 20 °C/min). Empirically, Vulcan XC 72 appears more thermally stable than BP2000. Additionally, BP2000 has a surface area[3] of 1365 m^2/g while the corresponding value for Vulcan XC 72[18] is ≈250 m^2/g. The higher surface area for BP2000 must account in part for both the lower temperature onset of rapid mass loss and the lower activation energy.

Thermal Decomposition of PEM Fuel Cell Catalyst Layer. Previous research demonstrated that the onset of Nafion decomposition was shifted to lower temperature by the presence of Pt.[6] We have found additional details concerning the catalytic decomposition of Nafion by Pt and report the results below.

TGA and DTG data were obtained for catalyst layers consisting of 46% Pt/Vulcan XC 72/Nafion ionomer (Figures

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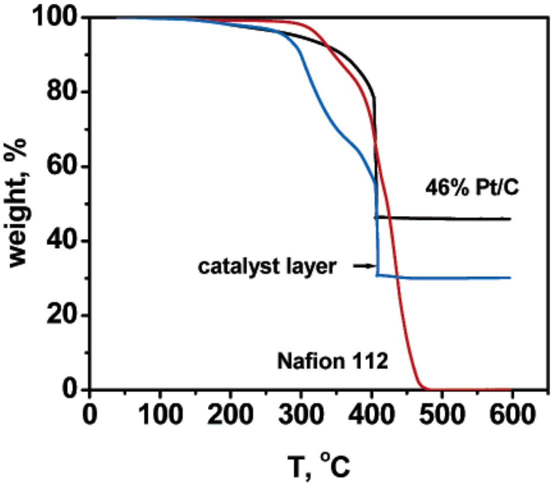

Figure 7. TGA data for 46% Pt/C, Nafion 112, and catalyst layer in air; heating rate 10 °C/min.

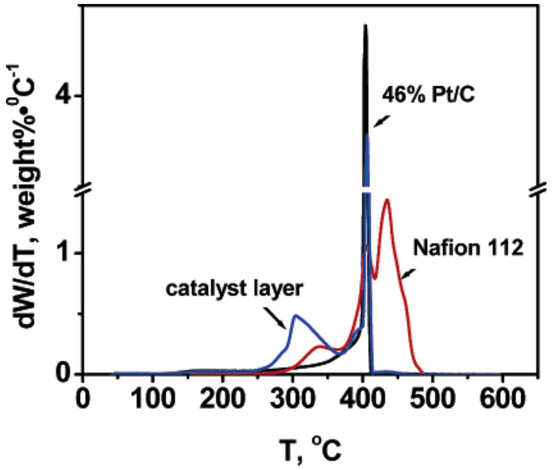

Figure 8. DTG data for 46% Pt/C, Nafion 112, and catalyst layer in air; heating rate 10 °C/min.

7 and 8). As controls, corresponding data were obtained for Nafion 112. The TGA of 46% Pt/Vulcan 72 is included in Figure 7 for reference. The TGA curve for the catalyst layer shows three distinct mass loss regions. A small mass loss (≈4%) is observed between 50 and 250 °C. This mass loss occurs over a broad range in comparison to higher temperature processes. The second loss process occurs between 250 and 360 °C, while the third one is between 360 and 410 °C. At 20 °C/min, assignment of these mass loss regions is not straightforward, since the third region is in the same temperature range for Nafion 112 decomposition (∼400 °C) and Pt-catalyzed carbon oxidation.

To resolve better the second and third regions for the thermal decomposition, a mass loss profile was obtained at a heating rate of 2.5 °C/min (Figure 9). In the first region mass loss is ∼3 wt %, while 37 and 30 wt % losses occur in the second and third range, respectively. As the measured amounts of Nafion and carbon in the catalyst layer are 38% and 31%, respectively, the second mass loss region is attributed to Nafion decomposition, while the third is due to carbon oxidation. This assignment is confirmed further with TGA−MS measurements.

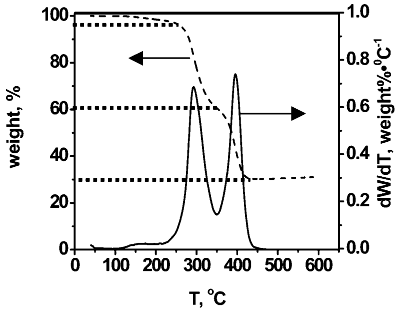

Figure 9. TGA and DTG data for catalyst layer in air; heating rate 2.5 °C/min.

Table 3. Mass Signal Assignments[6,12] for Some of the Decomposition Products of Nafion

sulfur dioxide		thionyl fluoride		carbonyl fluoride		carbon dioxide	
m/e	RA[a]	*m/e*	RA	*m/e*	RA	*m/e*	RA
64	1000	67	1000	47	1000	44	1000
48	493	86	556	66	548	28	98
32	104	48	233	28	136	16	96
16	52	32	76	31	45	12	87
66	49	69	46	12	26	22	19

C_3F_6O		$C_2F_4O_2$		C_2F_4		C_3F_6	
m/e	RA	*m/e*	RA	*m/e*	RA	*m/e*	RA
69	1000	44	1000	31	1000	31	1000
31	536	47	400	81	731	69	771
50	342	85	400	100	431	100	361
81	211	69	350	50	308		
100	199	66	250	69	36		

[a] RA is relative abundance.

Figure 10 presents mass signals (*m*/*e* range from 10 to 60) detected during Nafion 112 and catalyst layer decomposition in air. The mass signal with *m*/*e* = 48 observed during Nafion decomposition (Figure 10a) has a peak at ∼350 °C, indicating desulfonation of Nafion (see Table 3). The curves with mass signals 44 (CO_2 and $C_2F_4O_2$)[6] and 47 (COF_2 and $C_2F_4O_2$)[6] closely follow each other, which suggests a significant contribution from COF_2 and $C_2F_4O_2$. However, the ion current associated with the *m*/*e* = 44 peak is much stronger, indicating a major contribution from CO_2. The presence of the peaks at 350 °C on both curves suggests that the desulfonation process is accompanied by decomposition of a side chain of Nafion 112. The broad peaks at 450 °C are probably related to overlapping of two peaks (corresponding to the two peaks on DTG for Nafion 112 in Figure 8), one of which is related to decomposition of the side chain and the other to the polymer backbone.

The mass signal for *m*/*e* = 47 for the catalyst layer (Figure 10b) has only one well-pronounced peak at ∼300 °C, which suggests the presence of carbonyl fluoride in this temperature range. The mass signal with *m*/*e* = 44 probably presents superposition of ion currents produced by carbon dioxide and $C_2F_4O_2$ (Table 3). However, the fact that mass signals with *m*/*e* = 44 and 47 are no longer parallel indicates there is a significant contribution from CO_2 to the total ion current. The peak at 450 °C, followed by the *m*/*e* = 45 mass signal, can be attributed mostly to carbon dioxide. The small peak at ∼200 °C (*m*/*e* = 44) is probably due to the thermal decomposition of carboxylic groups on the surface of carbon black.

Figure 11 shows mass signals detected in the range of *m*/*e* from 60 to 100 for products of decomposition of Nafion and catalyst layer in air. The mass signal with *m*/*e* = 66 in Figure

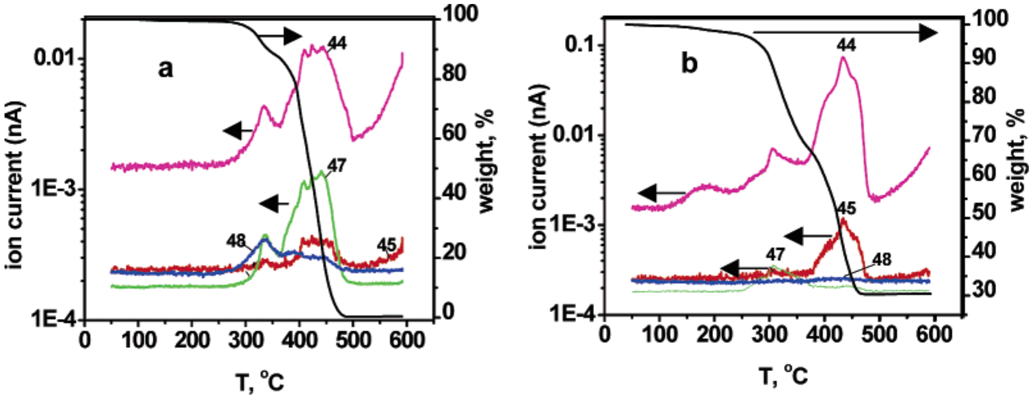

Figure 10. Mass signal data for *m*/*e* 44, 45, 47, and 48 obtained as decomposition products of (a) Nafion 112 and (b) the catalyst layer superimposed on TGA data for (a) Nafion 112 and (b) the catalyst layer; heating rate 10 °C/min.

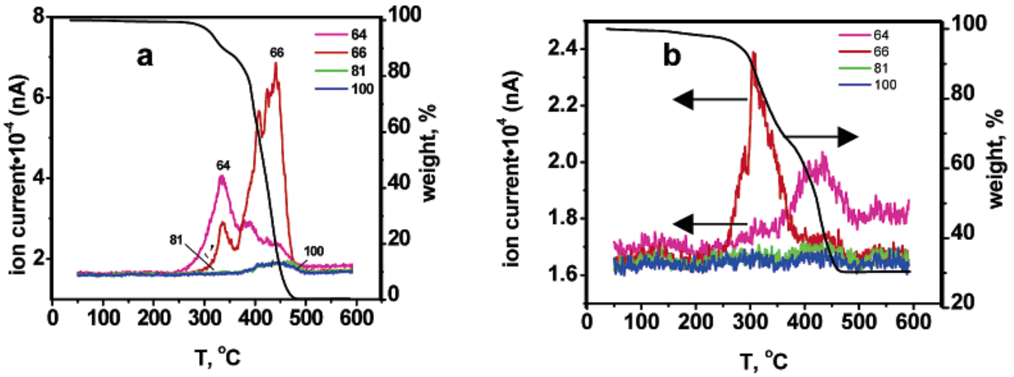

Figure 11. Mass signal data for *m*/*e* 64, 66, 81, and 100 obtained as decomposition products of (a) Nafion 112 and (b) the catalyst layer superimposed on TGA data for (a) Nafion 112 and (b) the catalyst layer; heating rate 10 °C/min.

11a has the same features as *m*/*e* = 47 mass signal in Figure 10a and can be attributed to fragments from COF_2 (see Table 3). For decomposition of the catalyst layer (Figure 11b) the peak for mass signal *m*/*e* = 66 is found at 300 °C. This fact confirms that Nafion decomposition occurs at lower temperatures in the presence of Pt in the catalyst layer. The shift in 150 °C for Nafion decomposition when switching from Nafion to the catalyst layer is much higher than the 40 °C observed by Samms.[6] This difference can be explained by a higher Pt:Nafion ratio in our experiments (~30:40 instead of 20:80[6]).

The mass signal *m*/*e* = 64 in Figure 11a with a sharp peak at ~350 °C and two shoulders at ~375−500 °C is parallel to the *m*/*e* = 48 mass signal in Figure 10a and can be attributed to sulfur dioxide. In contrast to the shift to lower temperature for the process that produces COF_2 (Figure 11), the mass signal for SO_2 (*m*/*e* = 64) shifts *up* in temperature to 450 °C for the catalyst layer. It is not possible to comment on the *m*/*e* = 48 SO peak (Figure 10b), as it is too weak. Perhaps Pt reacts with the sulfonate groups in some fashion to form an intermediate that decomposes at the higher temperature. Samms also observed that the nature of Nafion decomposition changed in the presence of Pt.[6]

Mass signals *m*/*e* = 81 and 100 with a broad maximum at 450 °C are typical both for C_3F_6O fragments and C_xF_y (Table 3). A possible mechanism of $C_xF_yO_z$ formation during Nafion decomposition was proposed by Samms.[6]

Conclusions

The high precision and sensitivity of TGA facilitated confirmation of a low-temperature, Pt-catalyzed carbon oxidation process previously observed isothermally.[3] The surface protective groups act to raise the activation energy for the low-temperature/low-conversion (≤5%) oxidation of 46% Pt/Vulcan XC 72 (197 ± 13 kJ/mol) compared to a higher temperature/higher conversion level (10−30%) process (140 ± 10 kJ/mol). Pt/Vulcan carbon catalysts decompose quantitatively in air to Pt at ~400 °C compared to >700 °C for Vulcan XC 72. At higher Pt catalyst levels, lower onsets of thermal decomposition temperatures are observed. Pt also catalyzes the decomposition of Nafion in PEM fuel cell catalyst layers. The thermal decomposition temperature of Nafion is lowered by about 150 °C to 300 °C in the presence of 46% Pt/Vulcan XC 72. Although Pt lowers the Nafion decomposition temperature, it is still well above PEM fuel cell operation temperatures.

The low-temperature kinetic data for carbon support oxidation may be used to estimate carbon mass loss for a PEM fuel cell at 80 °C, a typical operating temperature for automotive application.[19] For a cell using a 46%Pt/C catalyst

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such as the one employed in this study, about 10% loss of carbon support is predicted after 1 year of continuous operation. This percent mass loss may be a lower limit, as more rapid oxidation occurs at the cathode under electrochemical conditions.[4,5] Clearly, more study is needed to provide a better understanding of carbon support durability.

In summary, our results show that TGA is a valuable analytical tool for determining the relative thermal stability of supported catalysts and catalyst layers. Such studies are important, as good thermal stability of Pt/C catalysts in fuel cell applications is vital to durability.

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