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THE USE OF THERMAL ANALYSIS IN THE CHARACTERIZATION OF A POLYMER SURFACE

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Fuel cells are electrochemical systems that convert hydrogen into electricity without combustion. A proton exchange membrane (PEM) fuel cell power system consists of a polymer membrane, finely disbursed catalyst, and a gas humidifying system. Thermogravimetry (TGA) and differential scanning calorimetry (DSC) are powerful tools that can be used to characterize the physical properties of a polymer membrane. Ion chromatography can monitor the presence of contaminating ions in the aqueous condensate. TGA can easily measure the distribution of metal catalysts on a polymer surface due to the much lower decomposition temperature of the polymer. DSC can be used to measure the concentration of Teflon in a polymer blend by measuring the melting energy.

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INTRODUCTION

Fuel cells are electrochemical devices similar in structure to batteries with two porous electrodes separated by an electrolyte. Electricity is generated through the chemical reaction of a hydrogen-based fuel and an oxidant-containing oxygen inside the fuel cell. Hydrogen flows over the anode, which is a porous electrocatalyst that splits the hydrogen into positively charged hydrogen ions and electrons. Electrons flow through the external circuit, while only hydrogen ions can pass through the anode and into the electrolyte toward the cathode. The returning electrons from the circuit reduce the oxygen at the porous cathode. The hydrogen and oxygen ions then react to form water and thermal energy.

The most critical element of the fuel cell is the membrane assembly. The membrane, typically Nafion, has polytetrafluoroethylene-like segments with sulfonic acid regions in the structure, and the surfaces are coated with a fine dispersion of various metal catalysts. Fuel gases require humidification to moisten the membrane in order to transport the protons from the anode to the cathode. The stability of the membrane and dispersion of the catalyst on the surface are critical elements to the success of a solid polymer fuel cell. Ion chromatography, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) are powerful tools to monitor the exhaust condensate and to characterize the membrane.

EXPERIMENTAL ANALYSIS

Water samples of condensate taken periodically from both the anode and cathode side of a fuel cell during testing were analyzed. After the cell was disassembled, samples of the anode and cathode membrane were also analyzed.

Water samples were taken at periodic intervals during the fuel cell test and analyzed for anions by ion chromatography. We used a Dionex model DX-120 with an AG4 guard column and an AG4 separator column. Then emission spectroscopy for metals was conducted using a Perkin-Elmer model 6500 ICP-ES. The water samples for chromatography were analyzed without dilution or pretreatment. Accordingly, the standards and samples were sealed in 5-ml vials and placed in a model AS40 auto-sampler for analysis. The samples were injected into the system using a 25-microliter sample loop with a system flow rate of 2.8 ml/minute at a pressure of 600 psi. An analysis was run for 10 minutes using an eluent of sodium carbonate/sodium bicarbonate. The data were analyzed using a three-point calibration method for each ion. Samples for emission spectroscopy were also analyzed without pretreatment. These samples and standards were aspirated into an argon plasma, and a calibration curve of emission count versus concentration for the standards was established.

Samples of a new and used membrane were analyzed by DSC to determine the concentration of Teflon-like polymer backbone in the Nafion membrane. Also TGA was used to measure the concentration of catalyst on the membrane surface. Samples for both techniques were prepared by cutting a specimen 2.159-mm in diameter with a brass cork borer.

Samples for DSC analysis were weighed on a microbalance and encapsulated in hermetically-sealed aluminum pans. The samples and reference were placed in a Perkin-Elmer DSC 7 and scanned at 10°C/minute to 375°C. Then they were cooled at the same rate to room temperature to remove any possible thermal history. The samples were reheated at 10°C/minute to 350°C with the heat flow measured versus temperature. The area of the melting peak was measured and the enthalpy of melting determined. Using the measured enthalpy of a pure Teflon material, the percentage of Teflon in the membrane was determined.

Samples for TGA analysis were sectioned and placed in a Perkin-Elmer TGA 7. These samples were weighed, heated at 20°C/minute to 950°C, then held at temperature for 60 minutes. One set of samples was heated at 20°C/minute to 950°C, held at temperature for 30 minutes, then cooled at 20°C/minute to 50°C to measure any oxidation of the catalyst. The samples were analyzed in an air environment to oxidize the polymer membrane and the weight loss versus time and temperature was recorded.

RESULTS

Water samples of the deionized water supply and of the condensate from the fuel cell were taken at periodic intervals during the cell test and were analyzed for fluoride, chloride, and sulfate using ion chromatography. The samples were examined for metals by ICP-ES. From the results in Table 1, there was no detection of any anions or metals in the initial deionized water sample. In fact, there was no detection of metals in any of the samples. The cathode sample taken on 27 December 1997 showed a trace of both chloride and sulfate, but no fluoride in the condensate. Subsequent anode and cathode samples taken from 6 January on, showed detectable levels of all three anions. The cathode results for fluoride exhibited an increase in concentration with time, reaching a maximum on 11 January 1998, then decreasing through the remainder of the test. The anode samples also increased in concentration levels, but due to the limited number of samples, it could not be determined if this trend continued. The chloride results for both the anode and cathode had trace levels, except for the anode sample dated 6 January 1998. There was no explanation for this sudden increase in concentration. The cathode results for sulfate showed levels that were approximately three times higher than the observed levels for chloride. Sulfate concentrations in the anode samples were significantly higher, 1.8 mg/l on 11 January 1998 and 1.1 mg/l on 22 January 1998. Again, there were insufficient data to determine any trend in the anode for sulfate concentration during the cell test.

Table 1. Anion and Metal Concentrations in Fuel Cell Condensate Samples

Samples	F (mg/l)	Cl (mg/l)	SO4 (mg/l)	Cr (mg/l)	Pt (mg/l)	Al (mg/l)	Mn (mg/l)	Cu (mg/l)	Fe (mg/l)
Initial Water Sample	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cathode #3 12/27/97	ND	0.2	0.4	ND	ND	ND	ND	ND	ND
Cathode #3 1/6-1/7	1.1	0.2	0.5	ND	ND	ND	ND	ND	ND
Anode #3 1/6-1/7	0.3	1.9	0.1	ND	ND	ND	ND	ND	ND
Anode #3 1/11/98	1.2	0.2	1.8	ND	ND	ND	ND	ND	ND
Cathode #3 1/11/98	1.6	0.1	0.2	ND	ND	ND	ND	ND	ND
Anode #3 1/22/98	1.7	0.1	1.1	ND	ND	ND	ND	ND	ND
Cathode #3 1/22/98	1.4	0.1	0.2	ND	ND	ND	ND	ND	ND
Cathode #3 1/26/98	0.9	0.1	O.6	ND	ND	ND	ND	ND	ND
Cathode #3 1/31/98	0.4	0.1	0.4	ND	ND	ND	ND	ND	ND

(Note: ND = No Detection)

It was obvious from looking at the ion chromatography data that fluoride, chloride, and sulfate were somehow being introduced into the water during the fuel cell operation. Based on the structure of the Nafion membrane, which contains Teflon and sulfonic acid groups, there must have been some interaction with the membrane. The presence of chloride was interesting because there were no identifiable sources of contamination in the system. To determine if the membrane was the source of the fluoride contamination, three samples of the membrane—new, used anode, and used cathode—were analyzed by DSC for Teflon. Figure 1 shows typical DSC scans for all three samples and the Teflon standard. The samples and reference materials all contain well-defined melting peaks with an onset of melting occurring between 310 and 320°C.

Table 2 shows that the average percentage of Teflon in the used cathode sample was reduced by 31 percent and in the used anode sample, it was decreased by 59 percent. Comparing the used cathode sample, with a 31 percent decrease in Teflon concentration, to the used anode sample, with a 59 percent decrease in the Teflon concentration, showed that the used anode sample had a significantly larger Teflon reduction occurring during the cell test. It should be noted that the membranes used in the fuel cell test came from the same lot of material as the new membrane and that all the samples were sectioned using the same sampling procedure. There was significant scatter observed in the data within each sample set. It is not clear whether this is variation in the samples themselves or in the technique. However, the scatter in the melting enthalpy measurement for the standard was much lower than that observed in the samples, indicating a heterogeneous distribution of the Teflon on the membrane. Based on a sample size of 2.159 mm and a surface area (one side only) of 3.66 mm^2, the new membrane had a distribution of 5.60 mg/mm^2, the used anode had a distribution of 1.35 mg/mm^2, and the used cathode had a distribution of 2.29 mg/mm^2.

Table 2. Teflon Analysis by DSC

Sample	Peak (°C)	Onset Temp (°C)	Enthalpy (Joules/g)	Sample Weight (mg)	Teflon (%)	Average Teflon (%)
New Membrane	317.0	310.8	2.83	5.00	13.43	
New Membrane	316.9	309.5	2.68	5.44	12.72	
New Membrane	317.2	310.2	2.83	5.47	13.43	
New Membrane	325.9	319.2	1.86	5.77	8.82	12.1 ±2.21
Used Anode	317.0	310.1	1.05	3.49	4.98	
Used Anode	318.4	312.7	1.08	2.90	5.13	
Used Anode	318.0	311.7	1.45	3.58	6.88	
Used Anode	326.0	322.0	0.58	3.20	2.75	4.93 ±1.69
Used Cathode	318.5	310.9	2.44	3.82	11.58	
Used Cathode	318.5	311.5	1.96	3.28	9.30	
Used Cathode	318.4	313.1	1.26	4.14	5.98	
Used Cathode	326.2	319.5	1.39	3.82	6.60	8.37 ±2.58
Teflon Standard	321.9	315.3	22.17	7.08		
Teflon Standard	321.2	315.0	22.85	6.14		
Teflon Standard	315.2	307.6	20.00	8.08		PTFE STD
Teflon Standard	317.2	308.5	19.26	11.84		21.07 ±1.71

It is interesting to note from Table 2 that the weight for each sample (all samples were taken using the same diameter cork borer) fell into three distinct groups: new 5.42 ±0.32 mg, used anode 3.29 ±0.31, and used cathode 3.77 ±0.36. This follows the same trend as the average percentage for Teflon.

Another point concerning the membrane was the initial distribution of catalyst on the surface and whether there was any change in this distribution that occurred during the fuel cell operation. Using TGA, samples were oxidized in an oxygen environment, heated at a constant rate, then held at constant temperature to try and reduce the metal oxide that formed during heating. The literature cites the oxidation of finely dispersed particles of metals, such as platinum, as they are heated in an oxygen environment with a subsequent loss of oxide as the temperature is increased, until eventually all the oxide disappears. Figure 2 shows that after oxidation of the membrane, the sample was slow cooled at 10°C/minute back to room temperature. At about 75 minutes, the catalyst began to oxidize as noted by an increase in the sample weight.

Figure 3 shows an overlay of typical plots of weight loss versus temperature for the new membrane, the used membrane, and the 30 percent catalyst sample. As seen in Table 3, the results for 30 percent catalyst and 60 percent catalyst powder showed reasonable agreement, at 27.27 percent for the former and 57.60 percent for the latter. Surprisingly, the sample of used membrane contained 4.65 percent catalyst, while the new membrane contained 2.99 percent. This is most likely because of method used to apply the catalyst. Comparing the sample weights, the used samples had a higher average sample weight at 3.93 mg than the new membrane, which had an average weight of 2.31 mg. The catalyst loading was 1.27 mg/mm^2 for the used membrane and 0.82 mg/mm^2 for the new membrane.

Table 3. New and Used Membrane Analysis by TGA

	30% Pt Powder		60% Pt-Ru Powder		New Membrane		Used Membrane	
	Sample wt.	wt. %	Sample wt.	wt. %	Sample wt.	wt. %	Sample wt.	wt. %
Sample 1	2.160	25.68	3.401	54.97	1.821	3.200	4.026	4.16
Sample 2	4.694	28.29	3.140	59.67	2.330	1.028	4.634	4.06
Sample 3	2.035	27.76	1.987	58.16	3.203	4.810	3.137	5.73
Sample 4					2.321	2.710		
Sample 5					1.849	2.640		
Sample 6					2.330	3.580		
Average		27.27 ±1.38		57.60 ±2.40		2.99 ±1.25		4.65 ±0.94

CONCLUSION

Analysis of condensate samples taken from the fuel cell test showed positive results for fluoride, chloride, and sulfate, while the water supply showed no detectable levels of contamination. Since there was no indication of anions in the water prior to the test, it must be concluded that the anions were the result of some interaction between the water, gases, and membranes. The dissolved fluoride most likely is the result of some chemical interaction with the Teflon. This is supported by the DSC scans that showed a decrease in Teflon in the used samples. It is also curious that the used anode sample had less Teflon than the used cathode sample, possibly indicating some preferential reaction at the anode. The presence of sulfate probably is the result of some oxidation of the sulfonic acid group in the Nafion. At this time, there is no explanation for the presence of chloride.

The TGA results for catalyst concentration show good agreement for the 30 percent catalyst and 60 percent catalyst powder. The new membrane had a significantly lower catalyst concentration than the used membrane, which may indicate some need to refine the method for applying the catalyst. Based on experimental data, TGA and DSC provide useful methods for the characterization of a fuel cell membrane without the need for extensive sample preparation.

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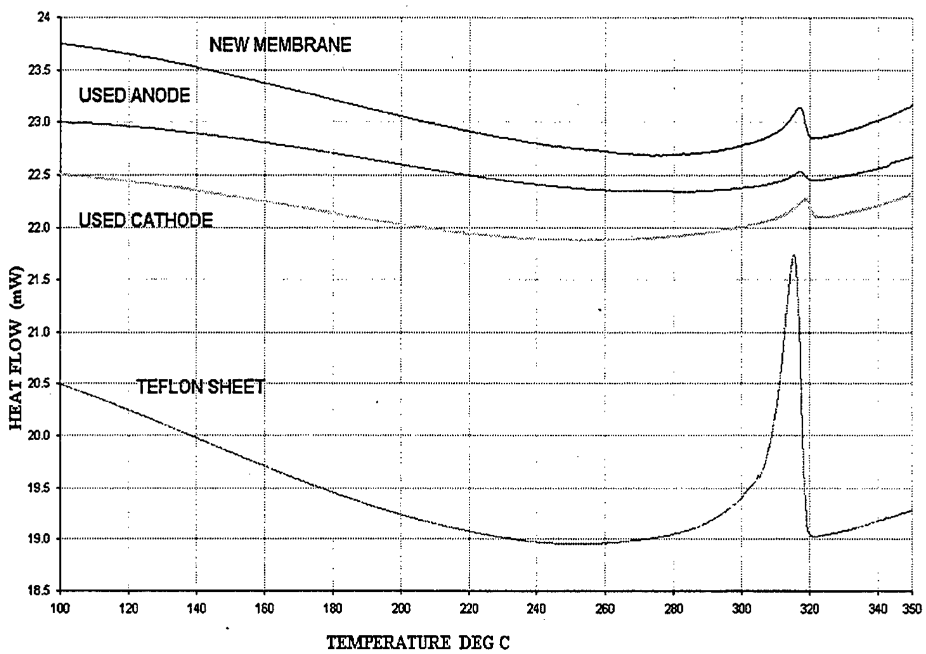

Figure 1. DSC scan of membrane samples and standard.

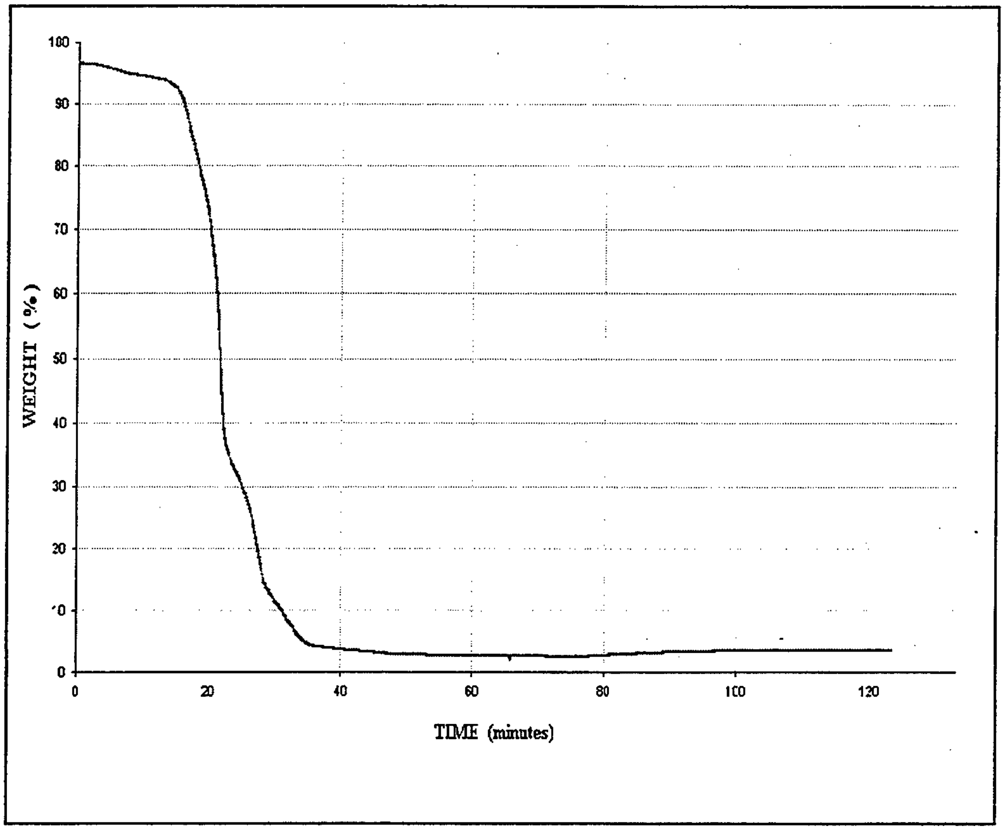

Figure 2. Oxidation of membrane and catalyst.

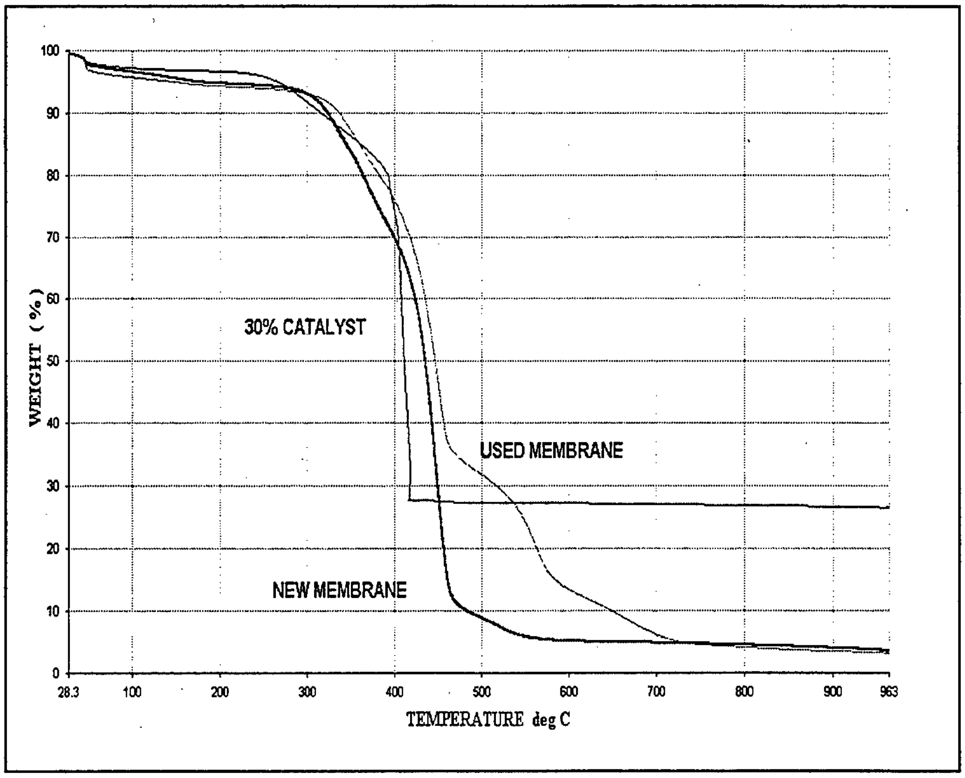

Figure 3. Oxidation of new and used membrane and catalyst powder.

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