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The use of thermal analysis in the characterization of a polymer surface

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Abstract

Fuel cells are electrochemical systems that convert hydrogen into electricity without combustion. Proton exchange membrane (PEM) fuel cell power systems consist of a polymer membrane, finely dispersed catalyst and a gas humidifying system. Thermogravimetry (TGA) and differential scanning calorimetry (DSC) 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 measure decomposition of the polymer material and the residual metal catalyst that remains, which can be correlated to the distribution of metal catalysts on a polymer surface. DSC can be used to measure the concentration of Teflon in a polymer blend by measuring the melting enthalpy. Published by Elsevier Science B.V.

Keywords: Polymer membrane; Thermogravimetry; Teflon

1. Introduction

Fuel cells are electrochemical devices similar in structure to batteries with two porous electrodes separated by an electrolyte. Electricity is generated through a 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 [1].

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. The 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 the dispersion of catalyst on the surface are critical elements to the success of a solid polymer fuel cell. Ion chromatography, differential scanning calorimetry and thermogravimetric analysis can be used to monitor the exhaust condensate and to characterize the membrane.

2. Experimental

Samples of water 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 taken at periodic intervals during the fuel cell test were analyzed for anions by ion

chromatography using a Dionex model DX-120 with an AG4 guard column and an AG4 separator column and emission spectroscopy for metals using a Perkin-Elmer model 6500 ICP-ES. The water samples for chromatography were analyzed without dilution or pretreatment. 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 μ l sample loop with a system flow rate of 2.8 ml/min. The analysis was run for 10 min using an eluent of (0.19 g/l) sodium carbonate! (0.14 g/l) sodium bicarbonate. The data was analyzed using a three point calibration method for each ion. The samples for emission spectroscopy were also analyzed without pretreatment. The 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 and by TGA to measure the concentration of catalyst on the membrane surface. The samples for both techniques were prepared by cutting a specimen 2.16 mm in diameter using a brass cork borer.

The 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/min to 375°C in a nitrogen atmosphere, then cooled at the same rate to room temperature to remove any possible thermal history. The samples were then

reheated at 10°C/min 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 percent of Teflon in the membrane was determined [3]. The Teflon standard was obtained from Garlock Inc. at a reported purity of 99%.

The samples for TGA analysis were sectioned and placed in a Perkin-Elmer TGA 7, weighed, heated at 20°C/min to 950°C, then held at that temperature for 60 min. One set of samples were heated at 20°C/min to 950°C, held at that temperature for 30 min, then cooled at 20°C/min to 50°C to measure any oxidation of the catalyst. The samples were analyzed in an air environment, at a flow rate of 20–35 cm³/min, to oxidize the polymer membrane and the weight loss versus time and temperature was recorded [3].

3. Results

Water samples of the deionized water supply used to humidify the fuel cell gases and of the condensate from the fuel cell, which were taken at periodic intervals during the cell test, were analyzed for fluoride, chloride and sulfate using ion chromatography. The samples were analyzed for metals by ICP-ES. Table 1 shows that there was no detection of any anions or metals in the initial deionized water sample. There was no detection of metals in any of the samples. The cathode sample taken on 12/27/97 showed a trace of both chloride and sulfate, but no

Table 1
Anion and metal concentrations in fuel cell condensate samples

Samples	F ⁻ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ⁼ (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	0.6	ND	ND	ND	ND	ND	ND
Cathode #3 1/31/98	0.4	0.1	0.4	ND	ND	ND	ND	ND	ND

fluoride in the condensate. The subsequent anode and cathode samples taken from 1/6/98, all showed detectable levels of all three anions. The cathode results for fluoride showed an increase in concentration with time, reaching a maximum on 1/11/98, then decreased 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 1/6/98. 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. The sulfate concentration in the anode samples were significantly higher, 1.8 mg/l on 1/11/98 and 1.1 mg/l on 1/22/98. Again there was insufficient data to determine any trend in the anode for sulfate concentration during the cell test.

After looking at the ion chromatography data, it was obvious 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 between the membrane, gases and condensate that oxidized some of the sulfonic acid to sulfate and extracted fluoride from the Teflon in the membrane.

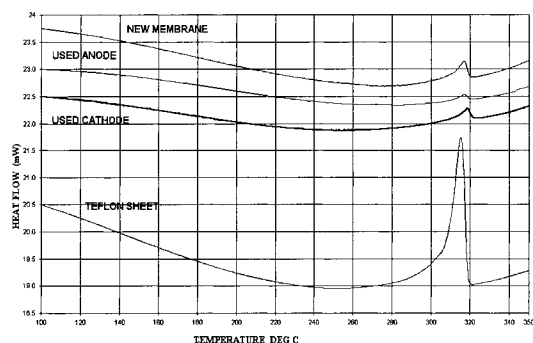


Fig. 1. DSC scan of membrane samples and standard.

The presence of chloride was interesting because there were no identifiable sources of chloride in the system. To determine if the membrane was the source of the fluoride contamination, three samples of the membrane (new membrane, used anode membrane and used cathode membrane) were analyzed by DSC for Teflon.

Fig. 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 % of Teflon in the used cathode sample was reduced by 31% (Average % Teflon = [(% Teflon in the used cathode)/(% Teflon in

Table 2
Teflon analysis by DSC

Sample	Peak (°C)	Onset temperature (°C)	Enthalpy (J/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	9.3	
Used cathode	318.4	313.1	1.26	4.14	5.98	
Used cathode	326.2	319.5	1.39	3.82	6.6	8.37±2.58
Teflon std.	321.9	315.3	22.17	7.08		
Teflon std.	321.2	315.0	22.85	6.14		
Teflon std.	315.2	307.6	20.00	8.08		PTFE std.
Teflon std.	317.2	308.5	19.26	11.84		21.07±1.71

the new membrane)](100%)) and in the used anode sample it was decreased by 59% (Average % Teflon= $[(\% \text{ Teflon used anode})/(\% \text{ Teflon new membrane})](100\%))$). Comparing the average % Teflon for the used cathode sample and used anode sample, it can be seen that the used anode had a larger decrease of Teflon concentration (59%) during the fuel cell test period than the used cathode (31%). 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 due to variation in the samples themselves or in the sampling 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 diameter of 2.16 mm, the surface area (one side only) was 3.66 mm² and thus the new membrane had a Teflon distribution of 5.60 mg/mm², the used anode had a Teflon distribution of 1.35 mg/mm² and the used cathode had a Teflon distribution of 2.29 mg/mm².

In Table 2, it is interesting that the sample weight for each sample (all samples were taken using the same diameter cork borer) fell into three distinct groups, new membrane 5.42±0.32 mg, used anode 3.29±0.31 and used cathode 3.77±0.36, which follows the same trend as the average % Teflon.

Another point of concern with the membrane was the initial distribution of catalyst on the surface and if there was any change in this distribution occurring during the fuel cell operation. Using thermogravimetric analysis, samples were analyzed in an oxidizing environment, heated at a constant rate to oxidize the organic components and measure the remaining Pt catalyst. The sample was then held at constant temperature, to obtain a stable baseline, and then cooled at 10°C/min to room temperature. As seen in Fig. 2, after oxidation of the membrane, only the Pt catalyst remained, however as the sample was cooled, at approximately 75 min, the catalyst began to oxidize as noted by an increase in the sample weight. Bayer and Wiedemann reported the formation and dissociation of Pt, Ir, Ru and Pd oxides were dependent on heating rate, oxygen pressure and surface area of the particles. Thus, finely dispersed particles of platinum

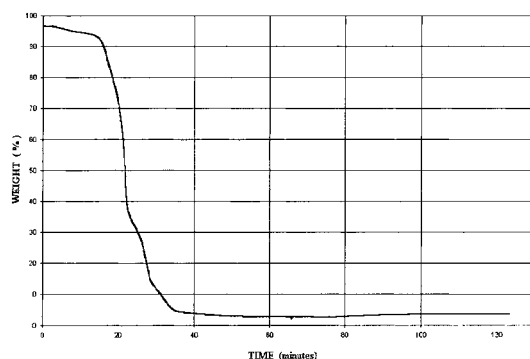


Fig. 2. Oxidation of membrane and catalyst.

on the membrane sample will oxidize as it is heated in an oxidizing environment and will subsequently lose oxygen as the temperature is increased, until eventually the platinum returns to the metallic state [2,4].

Fig. 3 shows an overlay of typical plots of weight loss versus temperature for the new membrane, the used membrane and the 30% catalyst sample. As seen in Table 3, the results for 30% catalyst and 60% catalyst powder showed reasonable agreement, at 27.27% for the former and 57.60% for the latter. Surprisingly the sample of used membrane contained 4.65% catalyst, while the new membrane had 2.99%. This most likely has to do with the method used to apply the catalyst. Comparing the sample weights, the used samples had a higher average sample weight of 3.93 mg than the new membrane, which had an average weight of 2.31 mg. The catalyst loading was 1.27 mg/mm² for the used membrane and 0.82 mg/mm² for the new membrane.

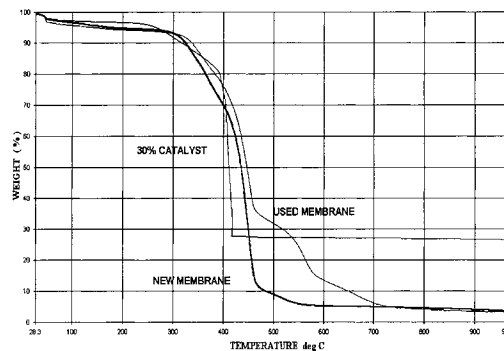


Fig. 3. Oxidation of new and used membrane and catalyst powder.

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	2.16	25.68	3.401	54.97	1.821	3.2	4.026	4.16
Sample 2	4.694	28.29	3.14	59.67	2.33	1.028	4.634	4.06
Sample 3	2.035	27.76	1.987	58.16	3.203	4.81	3.137	5.73
Sample 4					2.321	2.71		
Sample 5					1.849	2.64		
Sample 6					2.33	3.58		
Average		27.27±1.38		57.60±2.40		2.99±1.25		4.65±0.94

4. Conclusion

Analysis of condensate samples taken from the fuel cell test showed positive results for fluoride, chloride and sulfate, while the water supply used showed no detectable levels of these species. 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 reaction of the Teflon occurring during the fuel cell test. This is supported by the DSC scans which showed a decrease in Teflon concentration in the used samples. It is also curious that the used anode sample had lower Teflon concentration than the used cathode sample, possibly indicating some preferential reaction occurring 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 a good agreement for the 30% catalyst and the 60% catalyst powder. Thus, TGA provided a quick and

reasonably accurate method for determining catalyst distribution on the membrane surface. However, there was no way of determining if any catalyst had been lost during the fuel cell test because the new membrane had a significantly lower catalyst concentration than did the used membrane and the used membrane was not tested prior to assembly of the fuel cell. Since the new membrane and used membrane came from the same lot, this may indicate some need to refine the method for applying the catalyst to the membrane surface. Based on the experimental data, TGA and DSC provide a useful method for the characterization of a fuel cell membrane without the need for extensive sample preparation.

References

- [1] Baird, S., Alternate Energy Review Ontario Hydro, 1991.
- [2] W.W. Wendlandt, Thermal Analysis, 3rd ed., Wiley, New York, 1986, pp. 179–181.
- [3] A.A. Turi, Thermal Characterization of Polymeric Materials, Academic Press, Orlando, 1981.
- [4] G. Bayer, H.G. Weidemann, Thermochim. Acta 79 (1975) 11.