

Modification of Vulcan XC-72 for Enhanced Durability of PEMFC Catalyst Layer

A. Uzunoglu^{*,**,*}, F. Dunder^{*, ***,} and A. Ata^{*}

^{*}Nanotechnology Research Center, Gebze Institute of Technology, 41420 Kocaeli, Turkey

^{**}School of Materials Engineering, Purdue University, 701 West Stadium Avenue, West Lafayette, IN 47907, US

^{***} Department of Mechanical Engineering, Meliksah University, 38280, Kayseri, Turkey

[†]Corresponding author: A. Uzunoglu, Tel.: +1 765 775-6528, E-mail address: auzunogl@purdue.edu

Received: 06.11.2014 Accepted: 13.12.2014

Abstract-A series of SiO₂ modified Vulcan XC-72 support materials were prepared to investigate the effect of silica modification on the durability of the catalysts layer of Polymer Exchange Membrane Fuel Cells (PEMFC). XRD, TGA, BET, DLS, EDX and TEM were used to examine structural and microstructural properties. The performance of the catalysts layers were evaluated using a single cell operating at 60°C under fully humidified H₂ and O₂ purge. Electrochemical Impedance Spectroscopy (EIS) experiments were carried out to observe the impedance behavior of the MEAs. The MEAs were cycled between 0.6V to 1.2V for 24 hours at 20 mV/s (1440 cycles) under hydrogen and nitrogen purge to conduct Accelerated Durability Tests (ADTs). The modification of Vulcan XC-72 was found to be an effective way to improve both the performance and the durability of the catalyst. The MEA with 22.9 wt% SiO₂ content showed 13 times less performance loss than that of the MEA prepared with commercial catalyst after ADTs.

1. Introduction

In the last decade, much effort has been devoted to improve the PEM fuel cell durability since it is of utmost importance for commercialization of PEM fuel cells [1-3]. Membrane electrode assembly (MEA) degradation is a key factor affecting the durability of PEMFC; however, it is inevitable to prevent gradual performance loss of MEA under operational conditions [4]. The degradation rate should be minimized to reach the expected life-time target values which are 5000, 20000, 40000 hours for cars, busses and stationary systems, respectively [4, 5].

Catalyst layer is one of the important components of PEMC and its durability influences the long term performance of the cell, profoundly [2, 4, 5]. Pt and Pt based alloys deposited on conductive high surface area support materials are used as electrocatalysts in PEMFCs. Although these materials meet the required performance and cost expectations, they have lack of durability. In long term operations, the gradual performance drop is linked to dissolution, oxidation, poisoning or agglomeration of platinum particles, as well as corrosion of the support in the catalyst layer [6-9].

Life time of a fuel cell can be assessed using a steady-state lifetime test, but it is not feasible because of being very expensive and time consuming for large scale

applications [5]. Accelerated degradation test (ADT) methods have been introduced to assess the durability of the PEMFCs to reduce the required time and cost of the steady-state lifetime experiments [3]. During ADTs, MEAs are exposed to harsh conditions in a short period simulating fuel cell performance for long operating times [3, 10-12].

To the best our knowledge, although much work has been done to improve the durability of the catalyst layer in PEMFCs, the effects of silica on the performance and durability of catalyst layer encompasses Pt alloys as electrocatalyst has not been studied. In this work, we modified Vulcan XC-72 with various amount of aerogel SiO₂ and prepared C-SiO₂ supported Pt-Co catalyst in order to investigate the effect of C-SiO₂ composite material on the performance and durability of Pt-Co catalysts.

2. Experimental

2.1 Electrocatalyst Synthesis

1 g of Vulcan XC-72 was homogeneously dispersed in 60 ml aqueous ethanol solution (60 vol% ethanol) using an

ultrasonic stirrer. The amount of Tetra Methyl Ortho Silicate (TMOS) was adjusted according to the intended SiO₂ content. To modify Vulcan XC-72 with 3wt% SiO₂; 360 µl TMOS was added to the stirred solution. Distilled water was slowly added into the solution which contains TMOS and Vulcan XC-72 to form SiO₂ via decomposition of methyl groups and subsequently the solution was left stirring for 96 hours. The samples were filtered and dried at 80°C under vacuum atmosphere. Fine C-SiO₂ powders with high surface area were obtained by crunching and sieving.

Pt-Co/C and Pt-Co/C-SiO₂ catalysts with 45 wt% Pt loading were prepared using a coprecipitation method conducted at room temperature. 0.1 g of H₂PtCl₆x6H₂O was dissolved in 150 ml distilled water and used as a precursor solution in the synthesis. Before the reduction process, the pH of the solution was adjusted to 5 using a dilute ammonium hydroxide solution. 50 mg of the support material, on which metal particles were deposited, was dispersed ultrasonically in aqueous ethanol solution (60 wt% ethanol) for 15 minutes, followed by the addition of excess amount of NaBH₄. The solution was then quickly added into the aqueous precursor solution. Subsequently, the catalyst solution was filtered, dried at 80°C under vacuum, crunched and sieved to form catalyst powders with a fine particle size distribution. In the preparation of Pt-Co catalysts, the stoichiometric amount of CoCl₂x6H₂O was used as the source of Co.

Commercial catalysts, T1 (Pt/C, 28.7 wt% Pt) and T3 (Pt/C, 36 wt% Pt), obtained from Tanaka, were also used in the study to compare the durability values with our homemade catalysts although they have different amount of Pt than that of our home made catalysts.

2.2 Physical Characterization Techniques

Thermo Gravimetric Analysis (TGA) was conducted to determine the content of SiO₂ in the modified samples under oxygen atmosphere by heating the specimens up to 800°C with a 20°C/min heating rate.

N₂ adsorption-desorption analysis at -196°C was used to measure the surface area of the samples employing Quantachrome Autosorb 1B Instrument. Prior to N₂ physisorption, the samples were degassed at 300°C for 3h and the surface area values were calculated using Branauer-Emmett-Teller (BET) theory.

Dynamic light scattering (DLS) technique was employed to measure the average hydrodynamic diameters of the particles with a Zetasizer Malvern Instrument operated at room temperature. The samples were diluted in

ethanol and homogenized ultrasonically just before the DLS experiments.

X-Ray diffraction measurements were conducted using a Bruker D8 Advance X-Ray diffractometer with Cu Kα (λ=0.154nm) radiation at the scan rate of 1°·min⁻¹ over 2θ values between 20° and 90°. The mean particle size and lattice parameters of the catalysts were calculated using Scherrer's equation.

Transmission Electron Microscopy (TEM) images of the catalysts were recorded with a FEI TECHNAI G2 F-20 200 kW coupled with an Energy Dispersive X-ray (EDX) analyzer. The samples were dispersed ultrasonically in an aqueous ethanol solution. A copper grid was immersed into the solution and dried at 40°C. The atomic ratios of the Pt-Co/C catalysts were obtained from EDX analyzer.

2.3 Fuel Cell Measurements

The membrane electrode assemblies (MEAs) with an active surface area of 5 cm² were prepared using Nafion 212 membrane of Dupont. Catalyst ink slurries were prepared by mixing catalysts material (X g), water (10X g), isopropanol (10X g), propenediol (10X g), and Nafion solution (5 wt% Nafion) (5X g). The mixture was subsequently homogenized using Hielsher 400S ultrasonic homogenizer. Screen printing coupled with the decal transfer method was selected to fabricate the MEAs. The anode and cathode catalyst layers with 0.4 mgPt/cm² loadings were hot pressed on both sides of the Nafion 212 membrane.

The performance of the MEAs were evaluated using a single cell operating at 60°C under fully humidified H₂ and O₂ purge at a fixed flow rate of 0.2 lt/min and 0.5 lt/min, respectively. Electrochemical Impedance Spectroscopy (EIS) experiments were conducted at 200 mA/cm² between 0.1 Hz and 10 kHz. The performance and EIS tests were both carried out using the frequency response analyzer hardware of Scribner 850C fuel cell test station.

The durability of the cathode layer of the custom made MEAs were assessed by accelerated durability tests consisting of potential cycling between 0.6 V and 1.2 V at 80°C for 24 hours at a scan rate of 20 mV/s, which is equal to 1440 cycles [13, 14]. Fully humidified H₂ and N₂ gasses were supplied to the anode and the cathode sides, respectively at 80°C during the accelerated durability tests. The performances of the MEAs after the ADTs were evaluated at 60°C to determine the performance losses of the MEAs.

3. Results and Discussion

The SiO₂ content was analyzed using thermo gravimetric analysis in air by heating the specimens to 800°C. Carbon is removed via the combustion process at elevated temperatures and the remaining which represents SiO₂ content was estimated by calculating the difference [14, 15]. A representative TGA profile of a SiO₂ containing support is shown in Fig. 1. Table 1 shows the TGA results and the amount of TMOS used to modify the support material. The TGA results revealed that the actual SiO₂ contents of the modified support materials were consistent with the intended SiO₂ contents.

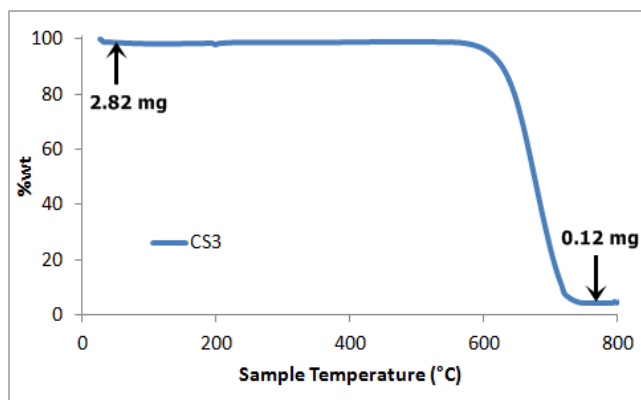


Fig. 1. TGA curve of CS3 in air.

Nitrogen absorption-desorption isotherms of the samples showed that while the addition of silica at a portion less than 5 wt% resulted in a decrease in the BET surface area of the modified samples, the sample with more than 5 wt% SiO₂ content had relatively higher BET surface area. This was also confirmed by having the smallest particle size distribution among all. The DLS

Table 1. Contents of SiO₂, particles size and surface area values of the support materials.

Sample	Amount of TMOS (µl)	Expected Contents of SiO ₂ (wt%)	Contents of SiO ₂ (wt%)	BET Surface Area (m ² /gr)	Particles Size (nm)
CS1	0	0	0	339.1	318
CS2	360	3	2.9	228.9	301
CS3	720	5	4.4	336.2	353
CS4	2400	20	22.9	435.2	257
Pure Silica	-	100	100	-	45

results indicated that the agglomeration of Vulcan XC-72 was decreased by the introduction of silica on the surface. Our previous study showed that the average particle size of pure SiO₂ is 45 nm [13]. No peak was observed at around 45 nm for the composite support materials, which indicated that aerogel silica was not discrete in the structure (Fig. 2).

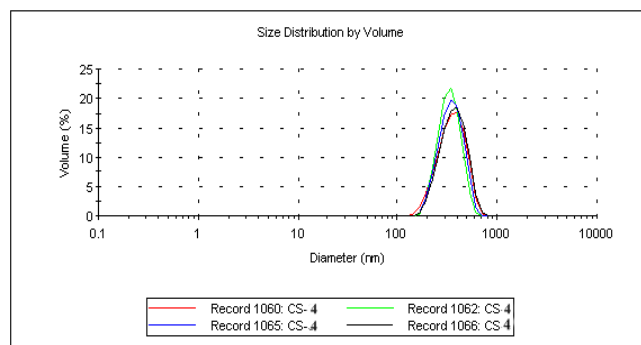


Fig 2. Particle size distribution of CS4 (22.9 wt% SiO₂).

Fig. 3 shows the XRD patterns of Pt/C, Pt-Co/C and Pt-Co/C-SiO₂ catalysts. The first broad peak located at about 24.8° corresponds to Vulcan XC-72 [16]. The other four peaks at ca. 2θ = 39°, 47°, 67°, 83° belong to the (111), (200), (220) and (311) planes of face centered cubic crystalline structured platinum, respectively [16-18]. The XRD peaks of Pt shifted towards higher 2θ values for alloy catalysts. This effect is due to the fact that smaller Co atoms substituted Pt atoms, which confirmed the formation of a solid solution. The XRD results of the sample revealed that silica used to modify carbon has amorphous structure since any peak associated with the silica was not observed.

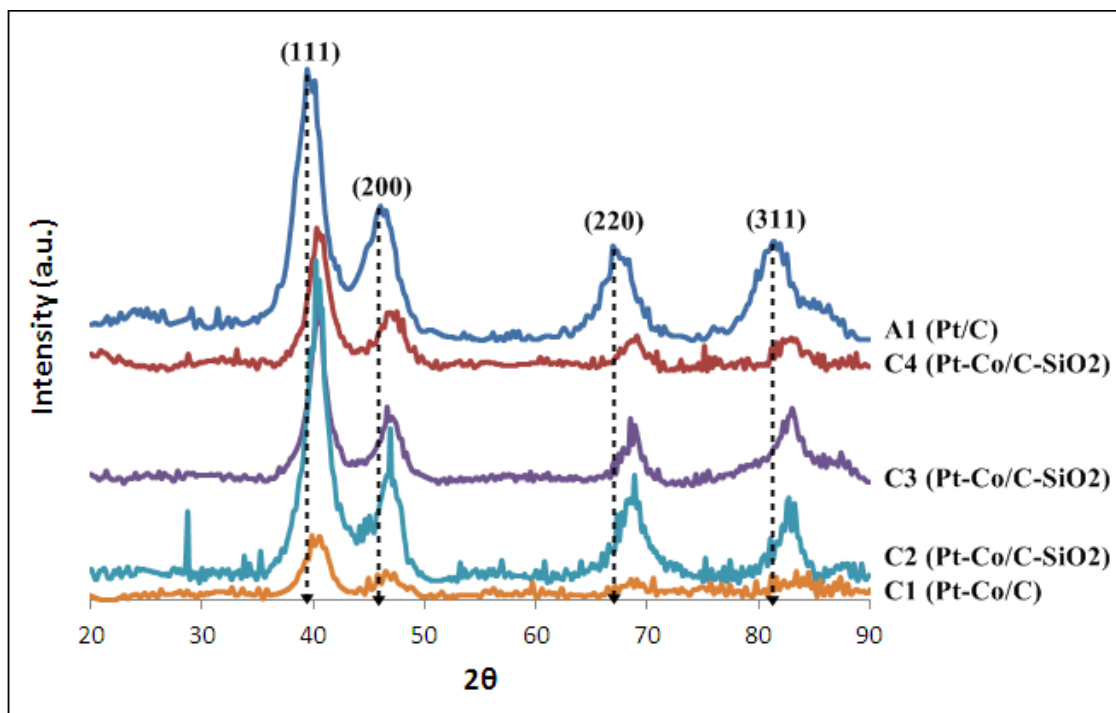


Fig 3. XRD diffraction spectra of the catalysts.

The average crystalline size and lattice parameter of platinum were calculated using Scherrer formula from Pt (111) peak and the values are listed in Table 2 [19]. It was observed that the formation of the solid solution resulted in a decrease in the lattice parameter. The lattice parameter values of the Pt-Co catalysts with various SiO₂ contents were found to be reasonably close to each other. Although the modification process led to an increase in the average crystalline sizes of the catalysts, any linear relationship was not observed between the increasing silica contents

and the average crystalline sizes. With respect to the effect of particle size on the performance of the Pt catalyst, there seems to be no agreement in the literature. Some authors reported that the maximum Pt-normalized mass activity (current/g Pt) was obtained at the particle sizes ranging from 3nm to 5nm [20, 21]. Although the modification of Vulcan XC-72 with silica brought about an increase in the particle size of the Pt metals, the obtained particle size values are still in the optimum performance range.

Table 2. Characterization of catalysts by EDX and XRD techniques.

Catalyst Code	Catalyst	Composition Pt:Co	Lattice Parameter (Å)	α_{fcc}	Particle Size (nm)
A1	Pt/C	-	3.946		3.45
C1	Pt-Co/C	79:21	3.848		4.41
C2	Pt-Co/C-SiO ₂	84:16	3.877		4.53
C3	Pt-Co/C-SiO ₂	83:17	3.848		4.49
C4	Pt-Co/C-SiO ₂	83:17	3.868		5.28

TEM images of the samples shown in Fig. 4 proved that the catalyst particles were homogeneously dispersed on the surface of Vulcan XC-72 and the increasing silica content did not show any sensible effect on the dispersion of the particles. In addition to the dispersion of the catalyst particles, the particles' shape remained practically

unchanged with the addition of SiO₂. It was also confirmed that slightly coarser catalyst particles were obtained for high silica content (22.9 wt%) which is compatible with the XRD results. The EDX results listed in Table 2 showed that the desired Pt:Co ratios were obtained with slight

deviations which might be attributed to either low EDX

signals or heterogeneous nature of the Pt:Co particles.

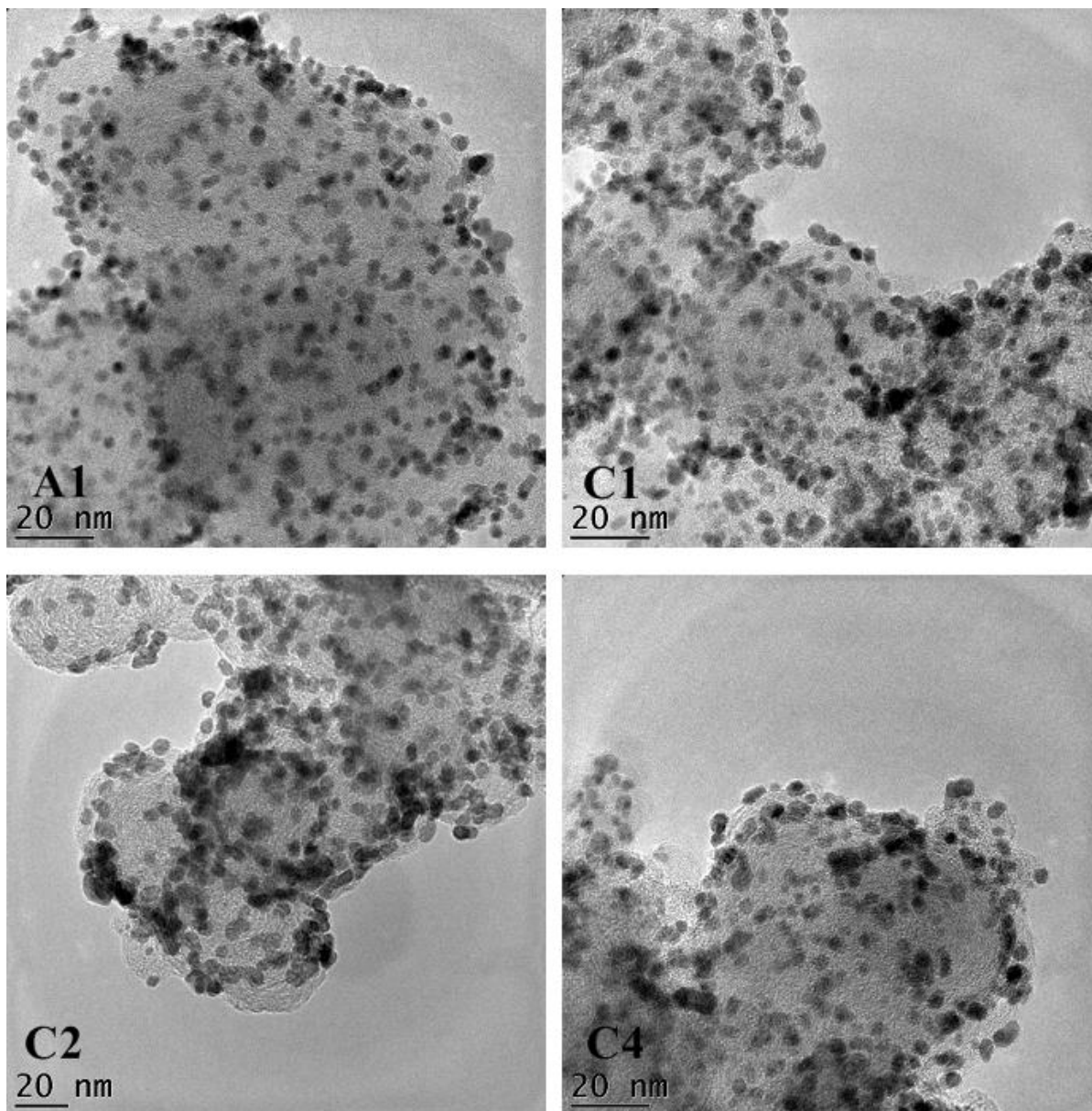


Fig 4. TEM images of synthesized catalysts (A1: Pt/C, 0 wt% SiO₂, C1: Pt-Co/C, 0 wt% SiO₂, C2: Pt-Co/C-SiO₂, 2.9 wt% SiO₂, C4: Pt-Co/C-SiO₂, 22.9 wt% SiO₂).

The single cell activities of the homemade catalysts were assessed using the MEAs with 0.4 mgPtcm⁻² anode and cathode loadings. The performance curves of the MEAs with various SiO₂ loadings obtained at 60 °C under fully humidified H₂/O₂ are shown in Figure 5. The single cell experiments revealed that the addition of the silica into the catalyst layer enhanced the performance of the MEAs remarkably. The increase in the performance might be attributed to the wetting property of SiO₂ [22]. Although silica has a detrimental effect on the electronic

conductivity [23], it enhances the wetting property of the catalysts layer; thereby it enhances the ionic conductivity of the MEAs. It may be hypothesized that the decrease in the conductivity of the catalyst layer was compensated by the enhancement of the ionic conductivity thus; an increase in the overall performance of the MEA was obtained. It is apparent that further increase in the silica content resulted in a better wetting property which resulted in a mass transfer problem, especially at high current densities. The relatively low performances of the prepared MEAs with

either homemade or commercial catalysts are due to other experimental factors, such as the quality of the gasket, and the contacts. The single cell experiments showed that the high silica content (22.9 wt%) resulted in water management problem in the cell, which led to dramatic performance drop at high current density values. Although the commercial catalysts do not contain the same amount

of Pt and Co with the homemade ones, their single cell performances were used for durability comparison. Fig. 6 shows the polarization curves of the MEAs prepared using commercial catalysts. The reason to use the commercial catalysts was to show that the low performance of the MEAs are not directly related to the prepared catalysts, but associated with the experimental setup.

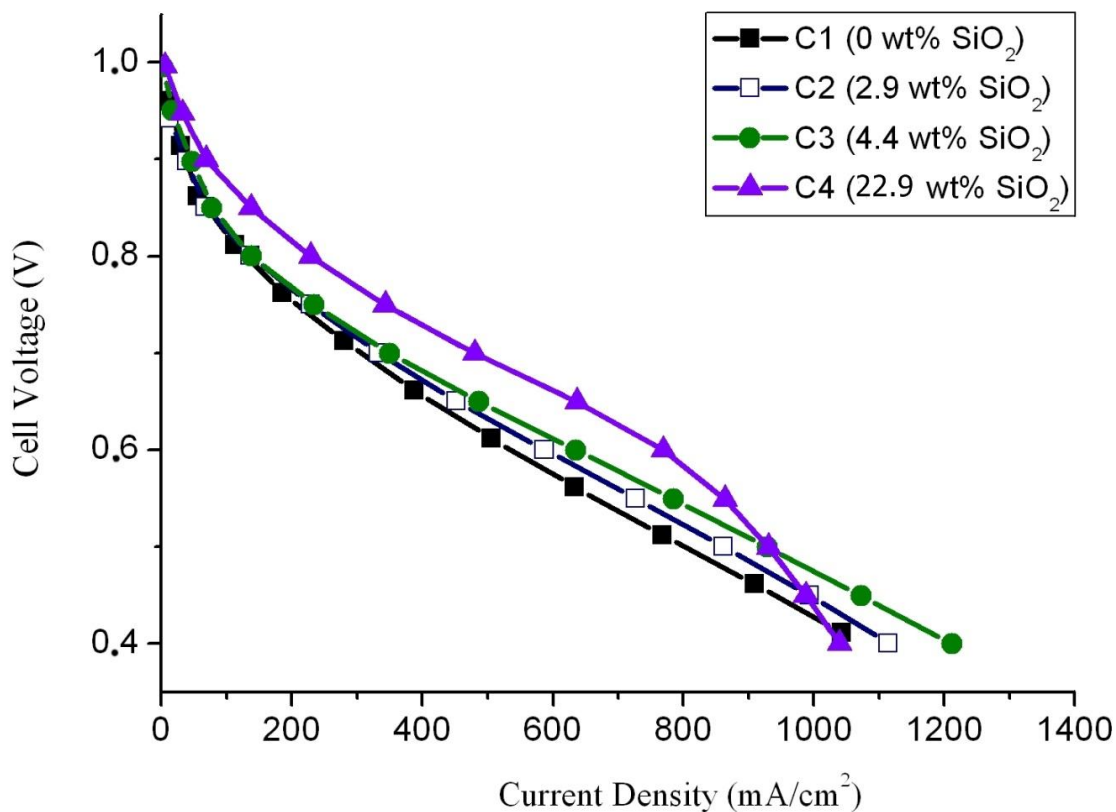


Fig. 5. Polarization curves of Pt-Co/C and Pt-Co/C-SiO₂ catalysts at 60 °C with 2 atm back pressure (Fully humidified H₂/O₂ gasses).

In situ impedance curves and their corresponding resistance values are shown in Figure 7 and Table 3, respectively. The results showed that the modification of the catalyst layer with silica resulted in a drop in ohmic and charge transfer resistances. This suggests that the presence of silica in the catalysts layer improved the ionic and electronic conductivity of the catalyst layer. Although the ionic conductivity showed a good correlation to the amount of silica added to the catalyst layer, the same linear trend was not observed in the charge transfer resistance. In the literature, it is reported that high silica contents deteriorates the performance of the MEAs because of its poor electronic conductivity [14, 23, 24]. However, our results indicated that the addition of silica improved the performance of the MEAs. It may be speculated that the

decrease in the electronic conductivity of the catalyst layer was compensated by the promoted wetting property of the catalyst layer, which resulted in an improvement in the conductivity of the cell. The Nyquist plots of the commercial catalysts are also shown in Figure 7 and the corresponding resistance values are listed in Table 3. It is noteworthy to mention that T1 showed the lowest resistance values among all. This might be explained with a well dispersion of the catalyst at low Pt contents. On the other hand, T3 (36.0 wt% Pt/C), which has higher platinum content than T1 (28.7 wt% Pt/C), had one of the highest resistance values. It should also be noted that our silica free homemade catalyst showed the similar resistance values with the commercially available T3 catalyst.

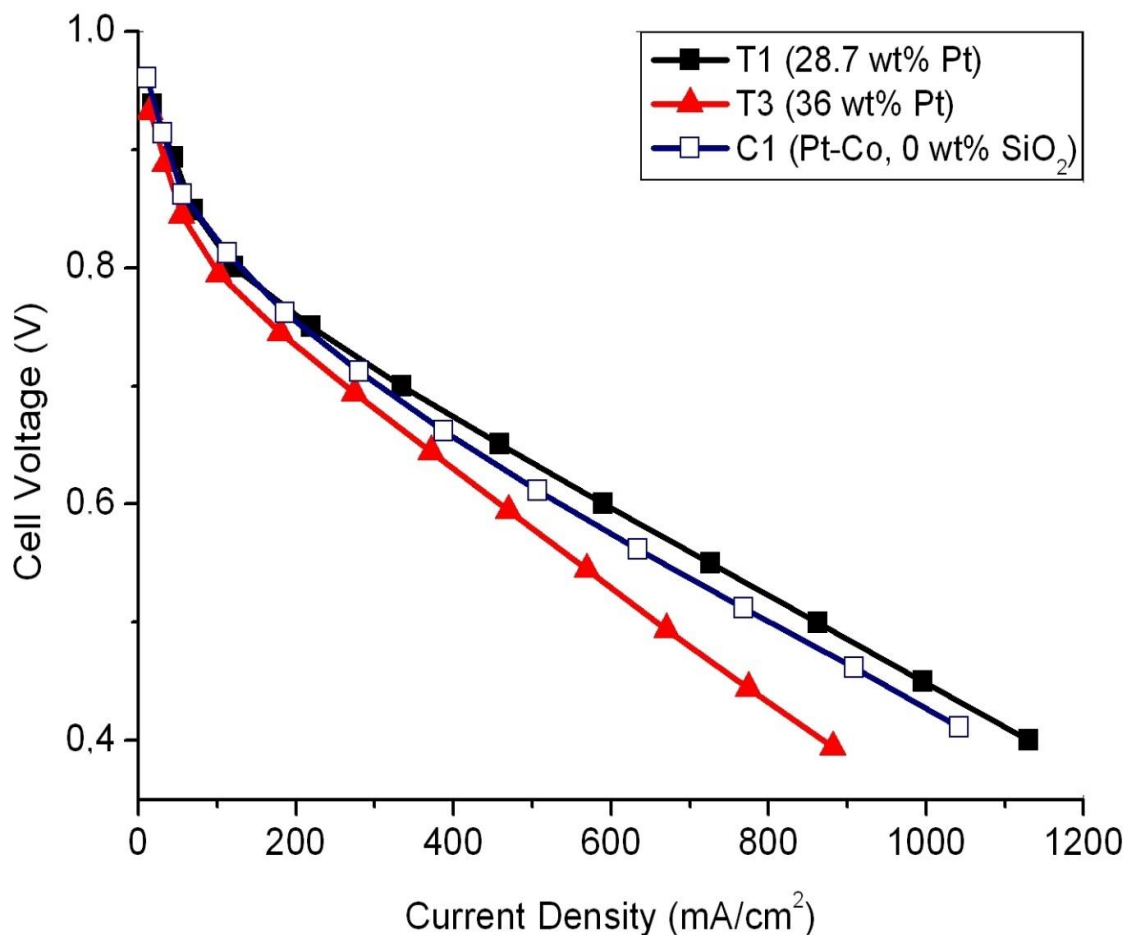


Fig. 6. Polarization curves of commercial Pt/C and homemade Pt-Co/C catalysts at 60 °C with 2 atm back pressure (Fully humidified H₂/O₂ gasses).

Table 3. Resistance values obtained from in situ impedance curves of the MEAs at 200 mA/cm².

Catalysts	R _Ω (mΩ*cm ²)	R _{ct} (mΩ*cm ²)
C1 (0 wt% SiO ₂)	72.2	109.8
C2 (2.9 wt% SiO ₂)	65.2	60.8
C3 (4.4 wt% SiO ₂)	58.5	94.5
C4 (22.9 wt% SiO ₂)	54.4	91.0
T1 (commercial)	54.7	44.0
T3 (commercial)	64.8	103.5

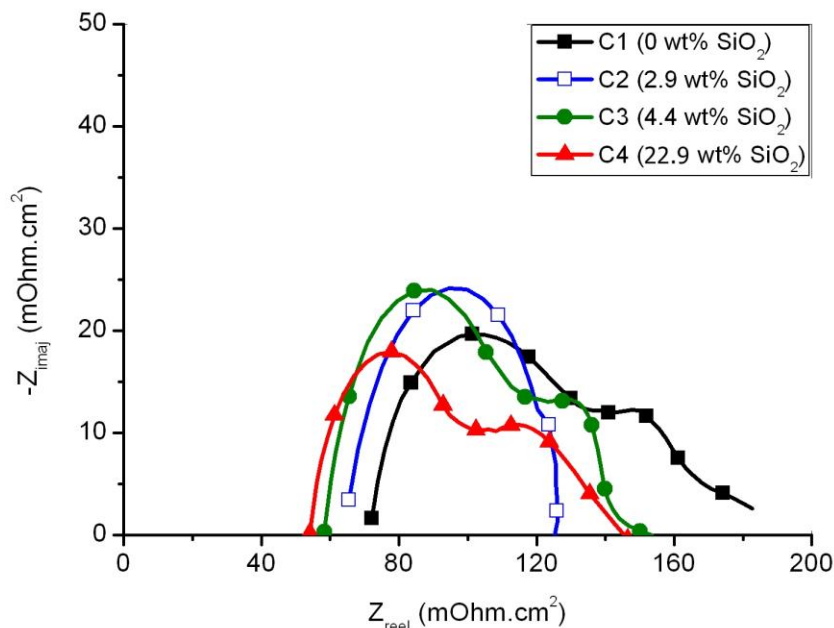


Fig. 7. Impedance curves of the MEAs consisting of Pt-Co/C, Pt-Co/C- SiO_2 at the current density value of 200mA/cm².

Subsequently, the homemade the MEAs prepared with the Pt-Co/C, Pt-Co/C- SiO_2 catalysts were subjected to accelerated durability test (ADT) in order to examine the effect of the silica modification on the catalysts layer durability. The MEAs were cycled continuously for one

day from 0.6 to 1.2 V (vs SHE) with a 20 mV/s scan rate at 80 °C. The performance losses of the MEAs were determined at 0.5 V after ADTs. Figure 8 shows the polarization curves of the homemade MEAs obtained after ADT tests.

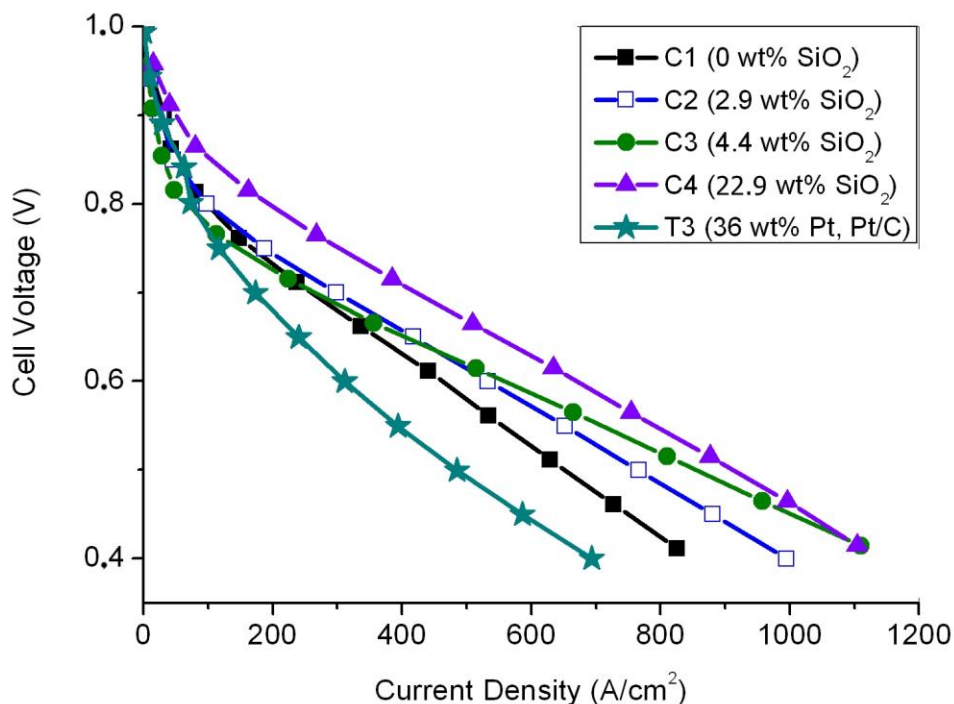


Fig. 8. Polarization curves obtained from Pt-Co/C and Pt-Co/C- SiO_2 catalysts at 60 °C with 2 atm back pressure after ADT tests (Fully humidified H_2/O_2 gasses).

The MEA degradation is affected by various factors, such as membrane degradation, electrocatalyst and catalyst layer degradation, gas diffusion layer degradation. During the ADTs, other key components also experience the severe working conditions, which results in additional performance loss. On the other hand, in the study, it was assumed that the difference in the performance losses of the MEAs mainly resulted from the silica content present in the catalyst layer since all the components and the methods implemented to prepare and test the single cells were the same and had the similar effect on the performance losses of the MEAs containing various silica contents. The ADT results showed that the modification of Vulcan XC-72 with silica improved the durability of the

catalysts layer, remarkably. The durability of the commercial catalyst was surpassed by all SiO₂ modified catalysts. A good correlation was established between the amount of silica introduced to the catalyst layer and the durability of the MEAs. The current density drop at 0.5V was selected to quantify the performance loss (Table 4). The lowest performance loss is obtained for C4, which has the highest silica content. The MEA prepared with the commercial T3 catalyst was also subjected to the accelerated durability test. It was observed that the MEA prepared using our homemade catalyst with 22.9 wt% SiO₂ showed the best durability. It had 13 times less performance loss than that of the MEA prepared with T3 after ACTs.

Table 4. Performance loss at 0.5 V before and after the ADTs.

Catalysts	Current Density Before ADT (mA/cm ²)	Current Density After ADT (mA/cm ²)	Performance Loss (%)
C1 (0 wt% SiO ₂)	794	655	18
C2 (2.9 wt% SiO ₂)	857	767	11
C3 (4.4 wt% SiO ₂)	927	848	9
C4 (22.9 wt% SiO ₂)	930	911	2
T3 (commercial)	657	486	26

4. Conclusion

Vulcan XC-72 was successfully modified with various SiO₂ contents by decomposition of TMOS. The modified Vulcan XC-72 was then used to prepare catalyst layers consisting of Pt-Co as electrocatalyst with a 45 wt% Pt loading. The effects of silica content on the performance and the durability of the catalyst layers were examined. It was found that the addition of silica in the catalyst layer had a positive effect on both the performance and durability of the catalyst layer. However, the increasing silica content led to significant mass transfer losses due to the hydrophilic nature of silica.

Acknowledgements

This work has been supported by Gebze Institute of Technology in house project (BAP 2010 – A27). The authors would like to acknowledge the helps of technicians, Omer Faruk Deniz and Adem Sen performing the analytical measurements.

References

- [1] Bezerra, C. W. B., Zhang, L., Liu, H. S., Lee, K. C., Marques, A. L. B., Marques, E. P., Wang, H. J., and Zhang, J. J., 2007, "A review of heat-treatment effects on activity and stability of PEM fuel cell catalysts for oxygen reduction reaction," *Journal of Power Sources*, 173(2), pp. 891-908.
- [2] Sayin, E. S., Bayrakceken, A., and Eroglu, I., 2012, "Durability of PEM fuel cell electrocatalysts prepared by microwave irradiation technique," *International Journal of Hydrogen Energy*, 37(21), pp. 16663-16672.
- [3] Liu, D., and Case, S., 2006, "Durability study of proton exchange membrane fuel cells under dynamic testing conditions with cyclic current profile," *Journal of Power Sources*, 162(1), pp. 521-531.
- [4] Zhang, S. S., Yuan, X. Z., Hin, J. N. C., Wang, H. J., Friedrich, K. A., and Schulze, M., 2009, "A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells," *Journal of Power Sources*, 194(2), pp. 588-600.
- [5] Zhang, S. S., Yuan, X. Z., Wang, H. J., Merida, W., Zhu, H., Shen, J., Wu, S. H., and Zhang, J. J., 2009,

- "A review of accelerated stress tests of MEA durability in PEM fuel cells," *International Journal of Hydrogen Energy*, 34(1), pp. 388-404.
- [6] Cheng, X., Shi, Z., Glass, N., Zhang, L., Zhang, J. J., Song, D. T., Liu, Z. S., Wang, H. J., and Shen, J., 2007, "A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation," *Journal of Power Sources*, 165(2), pp. 739-756.
- [7] Cheng, X., Zhang, J. L., Tang, Y. H., Song, C. J., Shen, J., Song, D. T., and Zhang, J. J., 2007, "Hydrogen crossover in high temperature PEM fuel cells," *Journal of Power Sources*, 167(1), pp. 25-31.
- [8] Watanabe, M., Tsurumi, K., Mizukami, T., Nakamura, T., and Stonehart, P., 1994, "Activity and Stability of Ordered and Disordered Co-Pt Alloys for Phosphoric-Acid Fuel-Cells," *Journal of The Electrochemical Society*, 141(10), pp. 2659-2668.
- [9] Akita, T., Taniguchi, A., Maekawa, J., Siroma, Z., Tanaka, K., Kohyama, M., and Yasuda, K., 2006, "Analytical TEM study of Pt particle deposition in the proton-exchange membrane of a membrane electrode-assembly," *Journal of Power Sources*, 159, pp. 461-467.
- [10] Wu, J. F., Yuan, X. Z., Martin, J. J., Wang, H. J., Zhang, J. J., Shen, J., Wu, S. H., and Merida, W., 2008, "A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies," *Journal of Power Sources*, 184(1), pp. 104-119.
- [11] Mitsushima, S., Kawahara, S., Ota, K. I., and Kamiya, N., 2007, "Consumption rate of Pt under potential cycling," *Journal of The Electrochemical Society*, 154(2), pp. B153-B158.
- [12] Knights, S. D., Colbow, K. M., St-Pierre, J., and Wilkinson, D. P., 2004, "Aging mechanisms and lifetime of PEFC and DMFC," *Journal of Power Sources*, 127(1-2), pp. 127-134.
- [13] Chen, Y. G., Wang, J. J., Liu, H., Li, R. Y., Sun, X. L., Ye, S. Y., and Knights, S., 2009, "Enhanced stability of Pt electrocatalysts by nitrogen doping in CNTs for PEM fuel cells," *Electrochemistry Communications*, 11, pp. 2071-2076.
- [14] Dunder, F., Uzunoglu, A., Ata, A., and Wynne, K. J., 2012, "Durability of carbon-silica supported catalysts for proton exchange membrane fuel cells," *Journal of Power Sources*, 202, pp. 184-189.
- [15] Pinchuk, O. A., Dunder, F., Ata, A., and Wynne, K. J., 2012, "Improved thermal stability, properties, and electrocatalytic activity of sol-gel silica modified carbon supported Pt catalysts," *International Journal of Hydrogen Energy*, 37(3), pp. 2111-2120.
- [16] Huang, Q., Yang, H., Tang, Y., Lu, T., and Akins, L. D., 2006, "Carbon-supported Pt-Co alloy nanoparticles for oxygen reduction reaction," *electrochemistry Communications*, 8, pp. 1220-1224.
- [17] Xu, Y., Ruban, V. A., and Mavrikakis, M., 2004, "Adsorption and dissociation of O₂ and Pt-Co and Pt-Fe alloys," *J Am Chem Soc*, 126, pp. 4717-4725.
- [18] Antolini, E., Salgado, J. R. C., and Gonzalez, E. R., 2006, "The stability of Pt-M (M=first row transition metal) alloy catalysts and its effect on the activity in low temperature fuel cells A literature review and tests on a Pt-Co catalyst," *Journal of Power Sources*, 160, pp. 957-968.
- [19] Santiago, E. I., Varanda, L. C., and Villullas, H. M., 2007, "Carbon-supported Pt-Co catalysts prepared by a modified polyol process as cathodes for PEM fuel cells," *Journal of Physical Chemistry C*, 111(7), pp. 3146-3151.
- [20] Sattler, M., and Ross, P. N., 1986, "THE SURFACE-STRUCTURE OF PT-CRYSTALLITES SUPPORTED ON CARBON-BLACK AND THE RELATION TO ACTIVITY FOR OXYGEN REDUCTION," *Journal of the Electrochemical Society*, 133(8), pp. C300-C300.
- [21] Peuckert, M., Yoneda, T., Betta, R. A. D., and Boudart, M., 1986, "OXYGEN REDUCTION ON SMALL SUPPORTED PLATINUM PARTICLES," *Journal of the Electrochemical Society*, 133(5), pp. 944-947.
- [22] Travitsky, N., Rippenbein, T., Golodnitsky, D., Rosenberg, Y., Burshtein, L., and Peled, E., 2006, "Pt-, PtNi- and PtCo-supported catalysts for oxygen reduction in PEM fuel cells," *Journal of Power Sources*, 161(2), pp. 782-789.
- [23] Takenaka, S., Hirata, A., Tanabe, E., Matsune, H., and Kishida, M., 2010, "Preparation of supported Pt-Co alloy nanoparticle catalysts for the oxygen reduction reaction by coverage with silica," *Journal of Catalysis*, 274(2), pp. 228-238.
- [24] Uzunoglu, A., Dunder, F., and Ata, A., 2011, "C-SiO₂ supported catalysts for durability and performance improvement in PEM fuel cells," *Journal of electrochemical Society Transactions*, 41(1), p. 1257.