



## Performance Evaluation of PtAgFe/C as a Cathode Catalyst in PEM Fuel Cell

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### Article Info

Received: 12/10/2016

Accepted: 25/12/2017

### Keywords

PEM

Cathode

Oxygen reduction  
reaction

Ternary catalyst

### Abstract

PtAgFe/C catalysts with different atomic ratios were synthesized by wet impregnation reduction method in order to be used in the catalysis of the oxygen reduction reaction (ORR) in the polymer electrolyte membrane (PEM) fuel cell. Physical characterization studies showed that the surface areas of the catalysts varied between 162 and 181 m<sup>2</sup>/g and the pore textures were mainly macroporous. The mean particle sizes were as small as 3.01 nm, which is for Pt<sub>6</sub>AgFe/C, but increased as the Pt atomic ratio decreased. The highest electrochemically active area was obtained as 557 cm<sup>2</sup>/mg from the Pt<sub>6</sub>AgFe/C which has the highest Pt atomic ratio. However, mass activities were higher in the catalysts with lesser Pt content. Finally, catalysts were tested in a home-made PEM single cell by preparing membrane electrode assemblies (MEA). Pt<sub>6</sub>AgFe/C had comparable performance to the commercial Pt/C catalyst when Pt content was taken into consideration. Results show that PtAgFe/C ternary catalysts can be used as a cost effective alternative in PEM fuel cells.

## 1. INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells are very promising energy conversion systems which can be used in transportation, stationary power generation and portable devices. However, commercial use of the PEM fuel cells is hindered by high costs arising from the use of platinum catalysts at the electrodes. Particularly, larger amounts of Pt is needed at the cathode side because of the much slower rate of oxygen reduction reaction (ORR) with respect to the anode side half reaction. Therefore, reducing the Pt loading at the cathode has been one of the main objectives in the development of PEM cells for a long time. Recent studies showed that some platinum based multi-metallic catalysts such as Pt-Fe, Pt-Co, Pt-Ni, etc., may exhibit higher mass activities towards the ORR than pure platinum in typical PEM conditions [1-7]. The activity enhancement is attributed to the tuning of the electronic structure of Pt on the surface after alloying with transition metals [8]. Heat treatment of the catalyst has also been found to enhance the activity by changing the surface morphology and particle size [9].

Platinum-based ternary catalysts have attracted considerable attention recently. They are typically prepared by the impregnation-reduction method where the metal precursors (nitrates, sulfates, chlorides etc.) are impregnated on carbon black and then reduced to metallic form by addition of a reducing agent. This is generally followed by a heat treatment which aims to modify the surface properties of the metallic phase. Low temperature heat treatments are reported to give higher activities without the formation of an alloy phase [10]. Xiong reported that a heat treatment temperature of 200 °C led to higher activities in Pt binary catalysts [11]. Heat treatments at low temperatures are often beneficial due to the removal of surface oxide groups, while elevated temperatures cause adverse effects such as metal agglomeration.

Structural characteristics and electrochemical properties of Pt ternary catalysts were extensively reviewed by Antolini [12,13]. Neyerlin et al. reported that Pt<sub>20</sub>Cu<sub>20</sub>Co<sub>60</sub> catalyst can retain a kinetic enhancement

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relative to Pt/C in the membrane electrode assembly (MEA) [14]. Fang et al. studied the performance of PtNiFe catalysts in PEM fuel cell. They found that the ternary catalysts exhibit excellent performance, even better than the commercial Pt catalyst. However, in this study higher temperatures of heat treatment was found to be more effective [15]. Li et al. found that PtFeNi alloy has improved electrocatalytic ORR activity as compared to pure Pt [16]. Zhao et al. also studied PdPtNi catalysts and found that all ternary catalysts show much improved mass activity compared to the state-of-the-art Pt catalyst [17]. Nguyen et al. studied Pt-based transition metal catalysts, including Pt<sub>2</sub>FeCo, Pt<sub>2</sub>FeNi and Pt<sub>2</sub>CoNi. These ternary catalysts showed significant oxygen reduction reaction activities [18]. Mohanraju et al. prepared PtMCo/C (M=Cr, Mn, Fe, Ni, Cu) catalysts in the atomic ratios of 6:3:1. Of these catalysts, PtFeCo/C had the highest surface area and showed the best ORR performance [19].

PtAgFe/C catalysts with different atomic ratios were studied with the aim of providing an alternative to commercial Pt/C in PEM fuel cells. Many studies can be found in the literature where the performance of the catalysts are measured in testing stations with built-in cell equipment. However, the works using home-made cells are few, and most of them studied cell parameters rather than the catalyst [20]. In this study, the prepared catalysts were tested in an original home-made single cell. PtAgFe/C catalysts were synthesized by wet impregnation reduction method followed by heat treatment at low temperature. Physical and electrochemical characteristics were investigated through various methods including nitrogen adsorption, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and cyclic voltammetry (CV).

## 2. EXPERIMENTAL

### 2.1. Preparation of the Catalysts

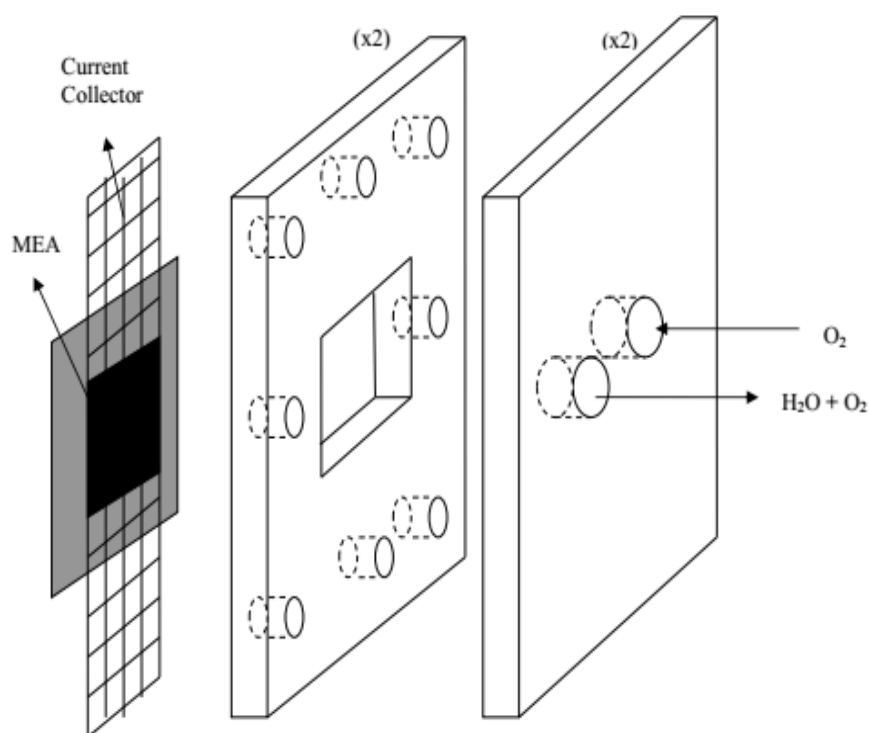
PtAgFe/C catalysts were prepared in three different atomic ratios (Pt<sub>6</sub>AgFe/C, PtAgFe/C and PtAg<sub>6</sub>Fe<sub>6</sub>/C) using the wet impregnation - reduction technique. Carbon black (Vulcan XC-72R) was used as the support material. Metal precursors; chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), silver nitrate (AgNO<sub>3</sub>) and iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>) were added to a carbon black suspension in required amounts to adjust the desired atomic ratios. The total metal contents of the catalysts were set to 20% by weight. After 30 min of stirring and an additional 30 min ultrasonical blending, the reduction step was carried out by dropwise addition of sodium borohydride (NaBH<sub>4</sub>, 1% w/w). The solution was also rendered slightly alkaline by addition of NaOH prior to the reduction of metals. After the reduction step, the suspension was filtered to separate the catalyst particles and washed with distilled water several times. Catalysts were dried in an oven for 24h at 90 °C and finally heat treated at 200 °C in a controlled atmosphere of 95% N<sub>2</sub> and 5% H<sub>2</sub> for 1 h in a tube furnace.

### 2.2. Characterization and Single Cell Tests

Surface characteristics of the catalysts were investigated by nitrogen adsorption using an Autosorb model Quantachrome sorptometer. Samples were preheated at 150 °C before the measurements. Crystalline phases, mean particle sizes and lattice parameters were determined by XRD. Measurements were carried out by a Rigaku D/MAX-IIIC diffractometer using Cu-K $\alpha$  radiation and 50 kV excitation potential. EDS analysis was also employed for the analysis of surface composition.

Electrochemically active surface areas (EAS) and activities of the catalysts (i.e. mass activity and specific activity) were determined by cyclic voltammetry. Measurements were performed in an AFCBP1 model Pine bipotentiostat with a three electrode set-up where a saturated calomel electrode was used as reference electrode, platinum wire as counter electrode and a 5.00 mm diameter glassy carbon disk as the working electrode. A catalyst slurry was prepared by mixing 0.13 mg of catalyst, 250  $\mu$ l deionized water and 200  $\mu$ l nafion solution (5% w/w) and then 10  $\mu$ l of this mixture was applied onto the working electrode. The mixture on the electrode surface was allowed to dry in ambient air for 10 min until a thin catalyst layer was formed. Measurements were performed in a 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution by scanning the potential between -0.2 V and 1.0 V at a 50 mV/s scan rate.

For the single cell tests, membrane electrode assemblies (MEA) were prepared for each catalyst. To prepare the MEAs, nafion 117 membrane was pretreated by boiling in 3%  $\text{H}_2\text{O}_2$  and then activated by boiling in 0.1 M  $\text{H}_2\text{SO}_4$ . Catalysts were mixed with nafion solution and applied onto 2.5 cm x 2.5 cm sized carbon cloth by brushing technique. Several uniform layers of catalyst were brushed until a catalyst loading of  $1 \text{ mg/cm}^2$  was obtained. The layers painted with PtAgFe/C catalysts served as the cathode, while commercial Pt/C (E-TEK) catalyst painted sides served as the anode. The electrodes were hot-pressed onto the opposite sides of the nafion membrane under 1 bar pressure and  $85^\circ\text{C}$  temperature for 5 minutes. A home-made PEM single cell was constructed using the prepared MEAs, along with methyl methacrylate (plexiglas) backing layers and nickel mesh as current collector. The single cell was connected to the same bipotentiostat used in CV measurements to control the potential. Polarization curves (i-V curves) were obtained in a pure hydrogen and oxygen flow, each with a flow rate of 50 ml/min and at room temperature. The potential was swept at a scan rate of 10 mV/s starting with 0 V up to the potential where cathodic current was no longer observed. The scheme of the cell is shown in Fig. 1.



**Figure 1.** Scheme of the cathode side of the PEM single cell.

### 3. RESULTS and DISCUSSION

#### 3.1. Physical Characterization

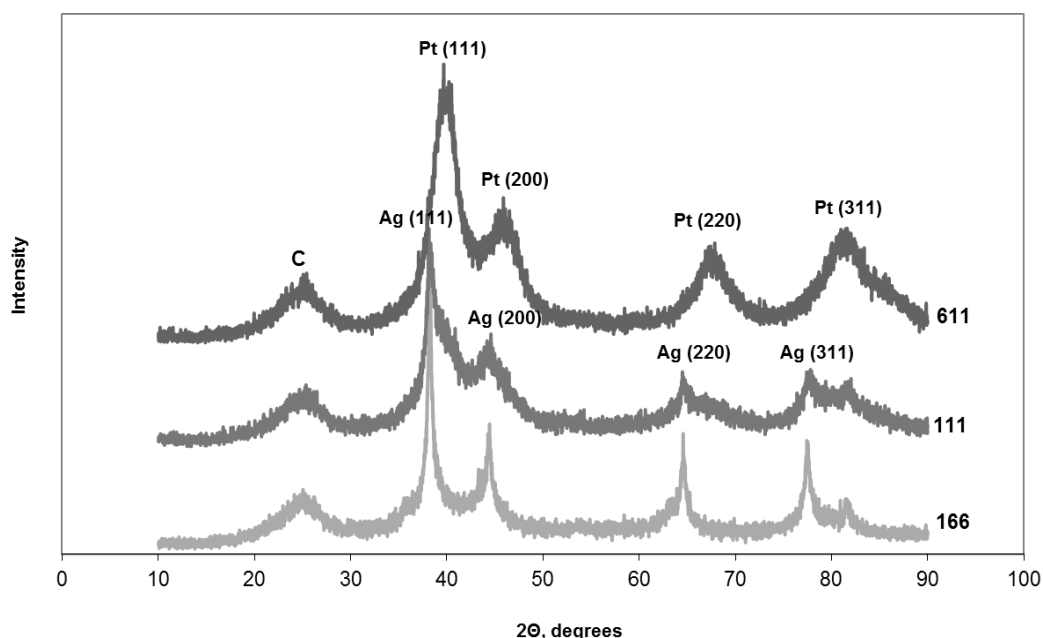
Textural properties of the catalysts were studied by the nitrogen adsorption technique. The adsorption-desorption isotherms of the catalysts were almost identical in nature and displayed type II behavior, typical of pure carbon black. Evaluation of the surface areas were based on the Brunauer-Emmett-Teller (BET) adsorption model. The surface areas were measured as  $168 \text{ m}^2/\text{g}$ ,  $162 \text{ m}^2/\text{g}$  and  $181 \text{ m}^2/\text{g}$  for PtAgFe/C, Pt<sub>6</sub>AgFe/C and PtAg<sub>6</sub>Fe<sub>6</sub>/C respectively (Table 1). The surface area of pure carbon black was also measured separately as  $226 \text{ m}^2/\text{g}$ , showing that the surface areas were reduced by 20-30% after metal loading. This was expected and consistent with earlier literature reports. For instance, Yu reported the surface area of blank Vulcan XC 72R as  $232 \text{ m}^2/\text{g}$ , which dropped to  $107 \text{ m}^2/\text{g}$  after loading with Pt-Ru catalysts [21].

**Table 1.** Surface areas, pore volumes and pore diameters of the PtAgFe/C catalysts prepared in different atomic ratios

Catalyst type	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	% Decrease	$V_{\text{pore}}$ ( $\text{cm}^3/\text{g}$ )	$d_{\text{pore}}$ (nm)
PtAgFe/C	168	26	1.34	1.8
Pt <sub>6</sub> AgFe/C	162	28	1.35	1.2
PtAg <sub>6</sub> Fe <sub>6</sub> /C	181	20	1.32	1.9

The reduction in surface area is possibly caused by the clogging of micropores by the metal particles. There may also be residues remaining after the reduction of precursors with borohydride, causing the slight difference in surface areas of the catalysts with different atomic ratios. The mean pore sizes are close to the mesopore (2-50 nm) range. However, the adsorption-desorption isotherms indicate wide pore size distributions in which both micropores and macropores exist. Nitrogen adsorption studies showed that the reduction in surface areas is tolerable and the pore sizes are adequate for mass transport.

The X-ray diffraction (XRD) patterns of the catalysts are shown in Fig 2. The broad peaks at  $25^\circ$  are due to the carbon support. The diffraction pattern of Pt<sub>6</sub>AgFe/C suggests a face centered cubic (fcc) crystal formation for the Pt atoms as the peaks observed at  $41^\circ$ ,  $46^\circ$ ,  $69^\circ$  and  $83^\circ$  correspond to the (111), (200), (220) and (311) planes of Pt, respectively. Since the Ag and Fe peaks are not significant, the Pt<sub>6</sub>AgFe/C catalyst can be considered as a disordered solution of Ag and Fe within the fcc lattice of Pt. Diffraction patterns of PtAgFe/C and PtAg<sub>6</sub>Fe<sub>6</sub>/C do not show significant Pt peaks except a weak (311) peak at  $83^\circ$ . In these catalysts, patterns are dominated by the characteristic fcc peaks of Ag with peaks at  $38^\circ$ ,  $44^\circ$ ,  $65^\circ$  and  $78^\circ$ , corresponding to the (111), (200), (220) and (311) planes of Ag, respectively. This shows that the crystal structure is formed either by Pt or Ag depending on the atomic ratio. In case of the PtAgFe/C in which the atomic ratio of Pt and Ag is even, the (111) peaks of Pt and Ag coincide at around  $46^\circ$  although the Ag atoms are dominant in the crystal structure.

**Figure 2.** XRD spectra of the PtAgFe/C catalysts prepared in different atomic ratios

The mean platinum particle sizes were calculated by Scherrer equation which gave 3.01 nm, 4.22 nm and 13.6 nm for Pt<sub>6</sub>AgFe/C, PtAgFe/C and PtAg<sub>6</sub>Fe<sub>6</sub>/C respectively. The only diffraction peak which is common in all three catalysts was the (311) peak so it was taken as the basis in calculations. The mean particle size is smaller in the catalysts with higher Pt atomic ratio. It is desirable for the catalyst particles

to be as small as possible since it affects the surface area of the catalyst. Also, a smaller particle size makes the catalyst loading easier without any clogging of the micropores. For Pt<sub>6</sub>AgFe/C and PtAgFe/C the average Pt particle sizes may be deemed adequate since they are comparable to the particle size of pure Pt/C catalyst which is generally slightly over 3 nm. For example, Xu et al measured the average particle sizes of in-situ prepared Pt/C catalyst to be between 3 and 6.5 nm [22].

**Table 2.** The mean platinum particle sizes and lattice parameters

Atomic ratio, nominal (Pt/Ag/Fe)	Atomic ratio, actual (Pt/Ag/Fe)	Mean Pt size, nm	a, Å
1:1:1	30/36/34	4.22	3.806
6:1:1	69/16/15	3.01	3.861
1:6:6	7/48/45	13.60	-

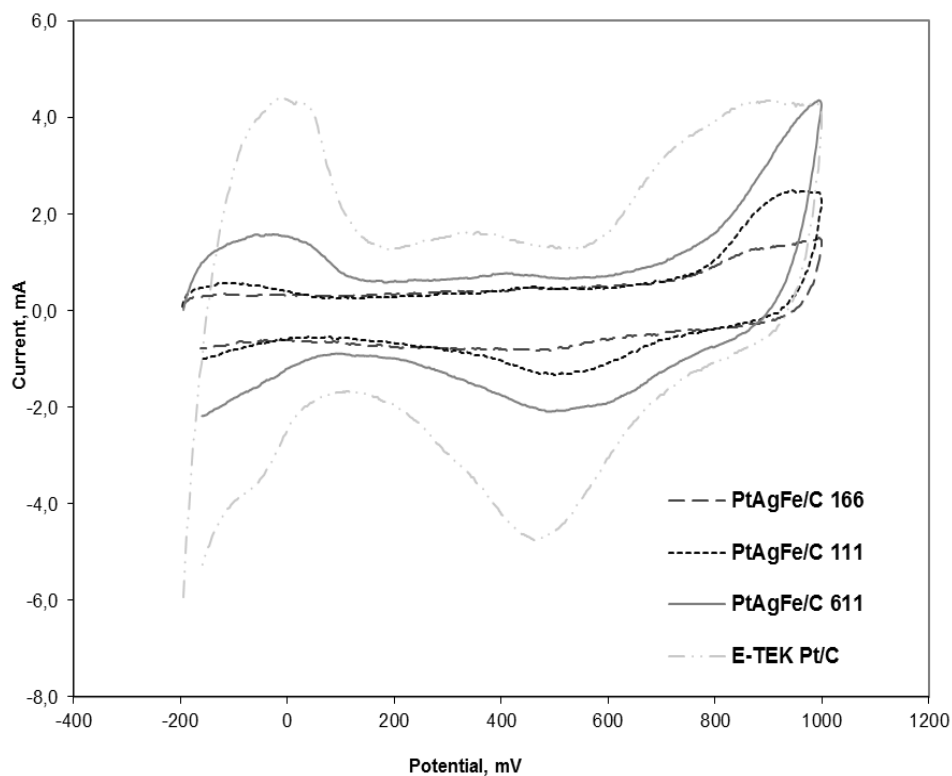
The lattice parameters of PtAgFe/C and Pt<sub>6</sub>AgFe/C were found to be slightly smaller compared to that of the pure Pt crystal which is 3.914 Å. The contraction of unit cell size may be indicative of a small degree of alloying between the different metals. A lattice parameter for Pt in PtAg<sub>6</sub>Fe<sub>6</sub>/C could not be determined due to the absence of an ordered Pt crystal lattice.

Energy dispersive X-ray spectroscopy (EDS) was used to find the actual atomic ratios of the catalysts, which are given in Table 2 and compared with the nominal ratios. The Pt atomic ratios were found to be slightly smaller than the nominal values in each case. On the other side, the Ag ratios were slightly greater than the expected values which shows a relatively better deposition on the carbon black. This may be attributed to a larger particle size of Ag, which is also evident from the narrow peaks in XRD.

### 3.2. Cyclic Voltammetry and Single Cell Tests

Cyclic voltammetry (CV) measurements were carried out to measure the electrochemically active surface areas (EAS) and the mass and specific activities of the catalysts. The current-potential curves for the catalysts are shown in Fig 3. In the low potential region (below 200 mV), the anodic scan produces a positive current which is due to the desorption of hydrogen atoms from the Pt surface and this current manifests itself as a broad peak. The area under this peak gives the total amount of charge which is transferred during the process and it can be used to calculate the EAS of a catalyst. The peak baselines were determined by extrapolating the double layer regions. It was assumed that a total of 210 μC/cm<sup>2</sup> charge is transferred for the desorption of a single layer of hydrogen from a unit surface area of Pt [23,24]. Pt<sub>6</sub>AgFe/C was found to have the highest EAS with 557 cm<sup>2</sup>/mg and the EAS values increased with the Pt atomic ratio as shown in Table 3.

Although the EAS value of Pt<sub>6</sub>AgFe/C is lower than the commercial Pt/C, it is comparable to many of the binary and ternary catalysts reported in the literature. Li et al. measured the EAS of Pt/C and PtFe/C as 683 cm<sup>2</sup>/mg and 636 cm<sup>2</sup>/mg respectively [25]. Similarly, Mani et al. reported the electroactive surface areas of Pt/C, Pt/Co and Pt/Cu as 630 cm<sup>2</sup>/mg, 700 cm<sup>2</sup>/mg and 720 cm<sup>2</sup>/mg, respectively [26].



**Figure 3.** Cyclic voltammograms of the PtAgFe/C catalysts prepared in different atomic ratios

**Table 3.** Electrocatalytical properties of the catalysts

Catalyst	$Q_h$ , mC	EAS, $\text{cm}^2/\text{mg}_{\text{Pt}}$	MA, $\text{mA}/\text{mg}_{\text{Pt}}$	SA, $\text{mA}/\text{cm}^2$
Pt/C, E-TEK	11.2	903	30.2	0.033
PtAgFe-166	0.04	41	102.2	2.47
PtAgFe-111	1.37	338	31.3	0.092
PtAgFe-611	5.06	557	29.1	0.052

$Q_h$ : Total amount of charge transferred, EAS: Electrochemically active surface area, MA: Mass activity, SA: Specific activity

It is known that the surface crystal structure of Pt has an important role in the adsorption and desorption processes. The shapes of desorption peaks can give information about the surface structure of Pt [27]. The broadly shaped desorption peaks show that the surface is non-uniform and the electroactivity results from the mixed contribution of various different surface formations like steps and terraces.

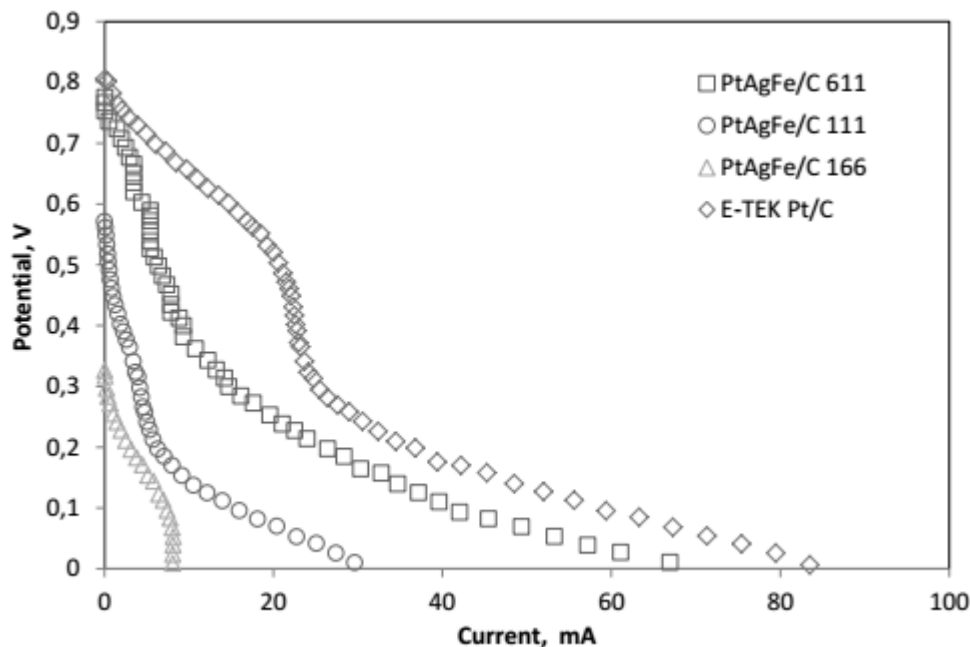
The mass activities of catalysts can be calculated from the cathodic current at 0.7 V where the reduction of PtO to Pt occurs. Since this type of activity is defined on the basis of Pt mass, it provides a more meaningful comparison. As seen in Table 3, the mass activities of Pt<sub>6</sub>AgFe/C, PtAgFe/C and commercial Pt/C are very close. The highest mass activity is obtained from PtAg<sub>6</sub>Fe<sub>6</sub>/C with 102.2 mA/mgPt which shows that Pt utilization is more efficient in catalysts with lesser amounts of Pt. The activities of the catalysts can be also evaluated in terms of specific activity which is defined as the ratio of the mass activity to the EAS. In this regard, PtAg<sub>6</sub>Fe<sub>6</sub>/C again has the highest specific activity showing that the Pt mass and the active surface area is utilized to a greater extent than the other catalysts. According to these results, even though PtAgFe catalysts have smaller active areas their activities are comparable to Pt/C when based on unit active area.

Single cell tests were performed to measure the performances of catalysts in a home-made PEM single cell. Since the oxygen reduction reaction at the cathode is the much slower and rate limiting reaction, the

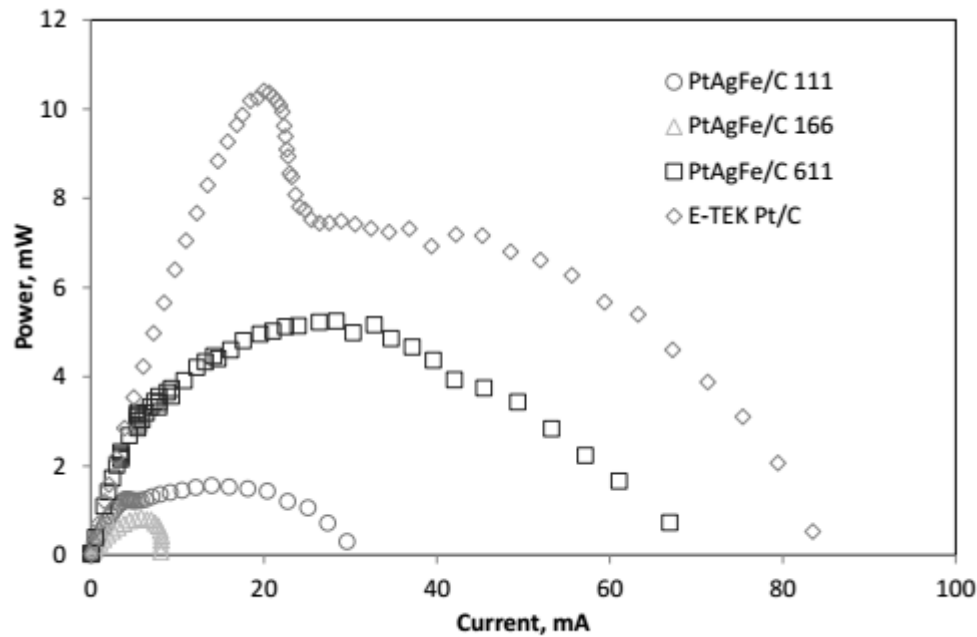
PtAgFe catalysts were employed on the cathode side while commercial Pt/C catalyst was employed on the anode side of the MEAs. Polarization curves of the catalysts are shown in Fig. 4. It should be noted that the current values obtained from the cathode were actually negative, thus the absolute current values were taken into consideration. The open circuit voltage (OCV) increased with the Pt content, as expected. However, the OCV of the Pt<sub>6</sub>AgFe/C catalyst (0.78 V) is comparable to that of the commercial Pt/C catalyst with 0.8 V. Although the measured OCV values are still significantly below the theoretical cell potential (1.23 V at 298 K), the results show that the Pt<sub>6</sub>AgFe/C and Pt/C have close performances at low current values in the studied single cell.

The cell voltage drops with increasing current because of the kinetic, ohmic and concentration losses, which are observed at low, middle and high currents, respectively. The maximum current obtained by Pt<sub>6</sub>AgFe/C catalyst is 68 mA while the Pt/C catalyst yielded a maximum of 85 mA. The variation of the power with the current is given in Fig. 5. Pt<sub>6</sub>AgFe/C gave a maximum power of 5 mW at around 20-35 mA. On the other hand, the P-I curve for the Pt/C catalyst features an unusual peak below 25 mA which gives a maximum power of 10.5 mW and then follows a more typical P-I behaviour with a maximum power of 7.5 mW. This is because the kinetic losses in Pt/C are very low, but once the ohmic losses and concentration losses takes effect, the catalytic activity is sharply reduced due to high cell resistances and mass transport limitations of the home-made single cell.

Considering the Pt mass difference in PtAgFe/C and the Pt/C catalysts, the difference in maximum power values is reasonable. It can be concluded that, the PtAgFe/C catalysts can be safely used instead of the commercial Pt catalyst in low to middle current regions (20-40 mA). However, for purposes that need higher current densities the PtAgFe/C catalyst will yield inferior results than the commercial Pt/C catalyst.



**Figure 4.** Single cell polarization curves of the catalysts



**Figure 5.** Variation of the power output in the single cell

#### 4. CONCLUSIONS

PtAgFe/C catalysts with varying atomic ratios were synthesized by wet impregnation reduction method. Physical characterization of the catalysts revealed macroporous structures with surface areas between 162 and 181 m<sup>2</sup>/g. The smallest particle size was obtained from Pt<sub>6</sub>AgFe/C with 3.01 nm. Voltammetric measurements showed that PtAgFe/C ternary catalysts have high mass activities even though their electroactive areas are smaller than the commercial catalyst. This means that their activities can be improved by use of better support materials and developed catalyst loading techniques enabling a better catalyst distribution to increase the active area. Single cell tests showed that the PtAgFe/C catalyst can yield significant currents compared with pure Pt and may offer a cost effective option for the catalysis of the oxygen reduction reaction in low current applications. The high mass activity of Pt<sub>6</sub>AgFe/C catalyst shows that Ag and Fe incorporation into the catalyst can increase the platinum utilization ratio.

#### ACKNOWLEDGEMENTS

The financial supports of the TÜBİTAK through the scientific research project no. 107M072 is greatly acknowledged.

#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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