Enhancing the CO tolerance of Pt/C as PEM fuel cell anode catalyst by modifying the catalyst synthesis method

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Abstract

The most important challenge in Proton Exchange Membrane (PEM) fuel cells is poisoning of the anode catalyst in the presence of impurities, especially carbon monoxide (CO) in the hydrogen feed. So, synthesis of catalysts with high CO tolerance is important for the commercialization of PEM fuel cells. In this study, a common borohydride reduction method was modified to synthesize a carbon supported Platinum Nanocatalyst (Pt/C) with a higher stability in the presences of CO impurity compared to a commercial Pt/C catalyst. The catalysts were characterized by X-ray diffraction and Scanning Electron Microscopy (SEM). The electrochemical cyclic voltammetry (CV) test procedure was used to evaluate the catalyst's resistance to long-term CO exposure. The results showed that the synthesized catalyst's electrochemical activity for CO electro-oxidation was comparable to commercial Pt/C under the same conditions. Moreover, the endurance of our catalyst for CO electro-oxidation after 100 CV with continuous CO gas bubbling is remarkable compared to the commercial catalyst performance, which dropped about 88 percent from its initial amounts.

1. Introduction

Proton Exchange Membrane (PEM) fuel cells are promising environmentally-friendly energy sources with a high power density and low pollution, which makes them a suitable choice for stationary, automotive industry and portable applications [1]. Platinum (Pt), the best-known catalyst for PEM fuel

cells, shows high catalytic activity in conventional PEM fuel cells operation conditions [2], but suffers catalyst poisoning by carbon monoxide (CO), particularly when reformed hydrogen (consisting of 50–100 ppm of CO) is used as the anode reactant. CO strong adsorption occurs on the anode Pt catalyst active sites, which prevents the adsorption and oxidation of hydrogen [1, 3]. Several studies have synthesized and developed catalysts with enhanced CO tolerance to make a more efficient anode for PEM fuel cells [4, 5]. According to these studies, more resistance against CO poisoning is achievable by decreasing the adsorption of CO molecules or facilitating the oxidation of CO on the catalyst surface. In addition to the catalyst composition, catalyst stability against CO content in the hydrogen feed depends on the catalyst's structure properties, such as particle size, particle morphology, and crystalline structure, which are related to the catalyst preparation method [5, 6]. When the particle size of Pt clusters is less than 5 nm, reduction in crystallite size influences the CO oxidation potential as strong adsorption of CO on the Pt particles is reported [6], while the greater crystallite size shows better stability against the CO poisoning effect [6-8]. Since catalyst structure and morphology can affect catalyst function and stability [9, 10], the preparation method has a significant impact on its performance and adequate deposition of Pt particles on the carbon surface remains a challenging issue [11]. The main synthesis methods for preparation of fuel cells catalysts are Chemical reduction [12-15], the Watanabe method [16], the polyol process [17, 18], and the micro-emulsion process [19, 20].

The half-cell cyclic voltammetry (CV) test is a less expensive technique to evaluate catalysts, and CO stripping current voltammetry in a half-cell is a common procedure for surveying the CO electro-oxidation capability of catalysts [21]. The effectiveness of this method depends on the absorption of a monolayer of CO molecules on the working electrode catalyst, which is stripped in the first anodic cycle. Formation of a single monolayer on the active sites is very far from real conditions,

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Previous studies have tried to overcome CO poisoning by adding promoters, replacing part of the commonly used platinum catalyst, which performs better in H_2 oxidation than other compounds, with other elements. This not only complicates the catalyst preparation process but also results in reducing anode performance. The present work attempts to improve CO tolerance of the commercial catalyst (Pt/C) by modifying the common catalyst preparation method (borohydride reduction). Thereby, improving its CO tolerance while maintaining anode performance.

2.Materials and Methods

2.1.Materials

NaH_4B and tetrahydrofuran (THF) were purchased from from RANKEM Chemicals (India) and $H_2PtCl_6.6H_2O$, sulphuric acid (98%), ethanol and iso-propyl alcohol were obtained from Merck. Commercial Pt/C and carbon paper (TorayTM Carbon paper) were purchased from the Fuel Cell Store. Carbon Vulcan X-72 was purchased from Cabbot. Nafion Solution

LQ-1115, 1100 EW 15%wt was purchased from Ion Power.

2.2.Catalyst synthesis

A Nano-structural Pt/C catalyst containing 20 wt% metal on a carbon support was synthesized via direct chemical reduction of metal salts with sodium borohydride [12]. Chemical reduction with borohydride in an aqueous media results in a solid metal, metal borate or metal oxide [13]. Tetra hydro furan (THF) was used as an organic media to insure metal solid particles were obtained [14]. While sodium borohydride is not soluble and active in THF, Prabhuram et al. [15] were able to use methanol in a complicated and time-consuming procedure to accomplish the reaction. Since methanol is toxic solvent, we propose a simple and fast method of using ethanol to activate the sodium borohydride before its addition to the reaction pot. In brief, 265.6 mg of $H_2PtCl_6.6H_2O$ were dissolved in 25 mL THF. Then, 400 mg of carbon Vulcan was added to the solution under a nitrogen atmosphere and the precursor was aged for 30 minute. Sodium borohydride with a molar ratio of 10:1 to Pt salt was added to the ethanol pot with the same volume of THF, and the contents of the pot were then poured into a reaction flask. The solution was rigorously stirred under N_2 atmosphere for 3-5 hours, centrifuged, and then continually washed with distillate water and ethanol until the filtrate TDS (total dissolved solid) and pH will be the same as distilled water ones. Finally, the catalyst was dried in a 60°C oven overnight. The obtained catalyst was analysed by X-ray diffraction (XRD) and its morphology studied by scanning electron microscopy (SEM, MIRA II TESCAN). A powder X-ray diffraction (XRD) scan was conducted on a PANalytical powder diffractometer (Philips PW3710) using Ni-filtered Cu Kα radiation (λ= 1.541874 A°) and generator setting (30 mA, 40 kV). The measured angle range started from 10° went up to 80° with a step size of 0.02° and an accumulating time of 0.5s per step.

2.3.Electrode Preparation

20 mg of synthesized catalyst, 1 mL distilled water, 1.5 mL iso-propyl alcohol and 67 µl 15 %wt Nafion solution were mixed and sonicated (BANDELIN UW3200, Germany) for 30 min to get a uniform catalyst ink. 150 µL of prepared mixture was spread on Teflonized carbon paper by a micro-sampler in two or three steps and dried in a 60 °C oven between each step. The electrode was carefully weighed to prepare 0.4 mg.cm^{-2} of net metal catalyst on the catalyst layer. The final catalyst spot had a 9 mm diameter.

2.4.Electrochemical test set-up

An in-house half-cell was made with a 100 mL total volume. An exposed catalyst surface with a 0.5 cm^2 area and 8 mm diameter was foreseen via a hole in the bottom of the cell, and gas flow was led to the working electrode surface by a PTFE tube. Adequate bores were made in the cell cap to hold the reference electrode, counter electrode, and gas leading tube. The Ag/AgCl reference electrode and platinum rod counter electrode were purchased from AZAR Electrode (Urmia, IRAN), and EMSTATE 3$^+$ Potansioastate from Palm Sense Co. (Netherland) was used for the electrochemical tests. Generated data was collected by PC and recorded by PSTRACE4 version 4.6.1 (Palm Sense Co.) interface software. Half-cell and electrochemical test devices are presented in Fig. 1.

2.5. Electrochemical measurements

Cyclic voltammetry was employed to evaluate the electrochemical activity of the catalysts. CV tests were carried out in a conventional three-electrode half-cell containing 0.5 M H_2SO_4 electrolyte at room temperature. Before each experiment the half-cell was washed with distillate water and 0.5 molar Sulphuric acids to assure elimination of possible impurities, thereafter a working electrode was fixed and the cell filled with approximately 60-70 ml electrolyte. The
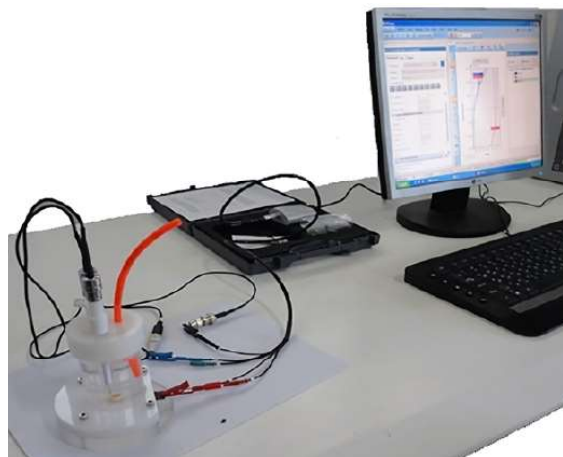
Fig. 1. Half-cell and electrochemical test setup

cell was purged with nitrogen gas for 15 min to deaerate the catalyst and electrolyte media. CV tests were executed from 0.0 to 1.0 V with a 20 mV.s⁻¹ step. First, blank CVs were done for each test to remove any possible impurities from the catalyst. Second, CVs were carried out under continuous bubbling hydrogen gas in the electrolyte as a H_2 CV to simultaneously check the H_2 electro-oxidation capability and activate the catalyst. After insuring complete catalyst activation, five blank cycles, as explained above, are first completed to test the blank CVs and record the background electrochemical activity of the catalyst. Then, 110 CVs are set, 100 cycles are applied to the working electrode surface under continuous bubbling CO gas to produce the CO CVs, and then the gas stream is stopped for 10 CVs to produce the after test blank CVs. The blank CVs were continued until the CV curve repeated on itself. The last CV produced was considered as the last blank CV after the CO CV test.

3. Results and discussions

3.1. Catalyst characterization

The X-ray diffraction patterns of the commercial Pt/C (Pt/Ccom) and the synthesized Pt/C (Pt/Csyn) electro-catalysts are displayed in Fig. 2.

The first broad peak at 20–25∘ is associated with the Vulcan XC-72 supporting material. Deposition of amorphous particles in the catalysts reduces the intensity of carbon peak at this position. The formation of metallic platinum was confirmed by XRD results, and are presented in Fig. 2. In addition, the XRD peaks show the particle crystalline intensity of the synthesized catalyst is higher than the commercial sample; and as mentioned before, the crystallinity of the particles increases the stability of the catalyst structure.

Scherrer formula was applied to calculate the average crystalline size and the results are presented in Table 1. The average crystalline size of the synthesized catalyst particles is 44.3 Nanometres, which is greater than the commercial catalyst (32.5 Nanometers). This phenomenon proves the higher It is important to note that the crystalline size, based on XRD data calculation, is related to the area of coherent diffraction; furthermore, the actual particle size is normally larger than the calculated size [24]. SEM images were taken to investigate the morphology and particle size of the synthesized and commercial catalystsand are depicted in Fig. 3. As the images show, the particles are spherical and nanosize. Average particle size and particle size distribution were calculated by analysing the SEM images with Digimizer software and the results are summarised in Table 1 and Figs. 4 and 5.

As presented in Figs. 4 and 5, about 80% of the synthesized catalyst particles range in size from 35-50 nm, while 73% of commercial catalyst particle are in the 25-40 nm range. This means that the
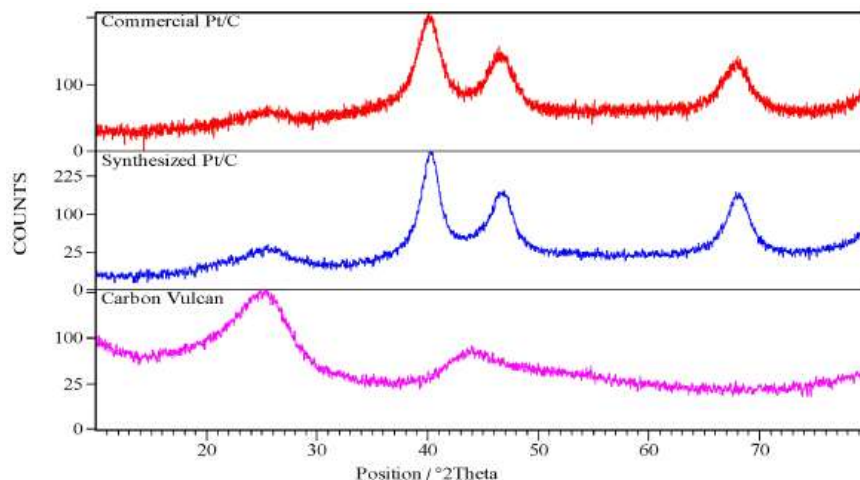
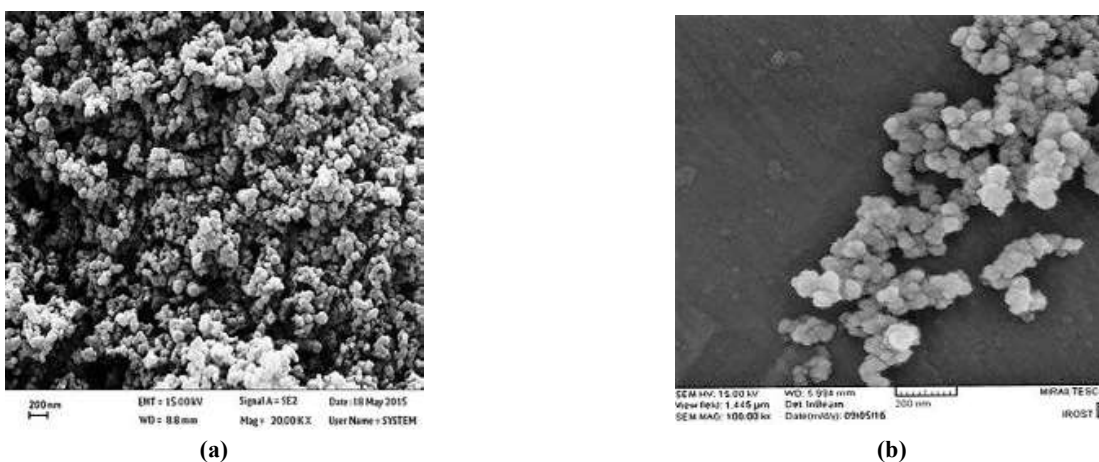**Fig. 2. XRD patterns for the a) Commercial Pt/C, b) synthesized Pt/C, and c) Carbon Vulcan.**

(a)

(b)

Fig. 3. SEM images for the a) commercial Pt/C and b) synthesized Pt/C.

Table1. Comparing results for the synthesized catalyst and commercial Pt/C.

Catalyst name	Commercial Pt/C	Synthesized Pt/C
Average Catalyst crystalline Size (nm)	4.15	5.73
Average Particle Size (nm)	32.5	44.3
Onset potential for CO CV [Beg-End] (volt)	0.06-0.04	0.04-0.08
Onset potential for Last blank CV	0.61	0.69
Max current charge for CO electro-oxidation [Beg-End] (µA)	4870-2993	4172-3651

modified synthesizing method resulted in a much more uniform particle size.

2.2.Electrochemical evaluations

CVs with bubbling H_2 gas activated the inactive catalyst sites on the working electrode. The H_2 bubbling CVs for Pt/Ccom and Pt/Csyn are depicted in Fig. 6. anAs can be seen, the charge amounts are low at the beginning of the test and continuous H_2, bubbling resulted in complete activation of the catalyst sites.

Fig. 6 shows H_2 electro-oxidation charges on the synthesized catalyst start at 6000 µA in 0.0 volt up to 35200 µA in 1.0 volt, and for the commercial catalyst begins from 5050 µA in 0.0 volt and ends in 28600 µA
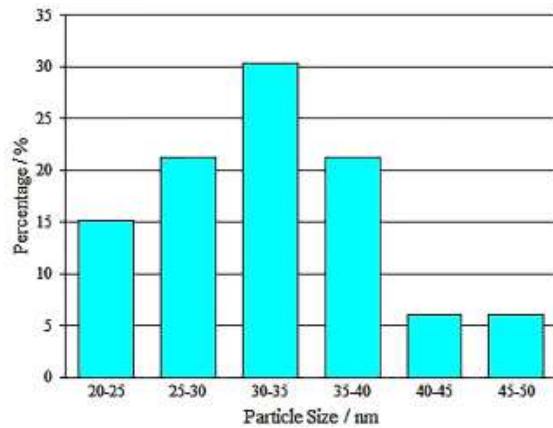
Fig. 4. Particle size distribution for the commercial Pt/C.
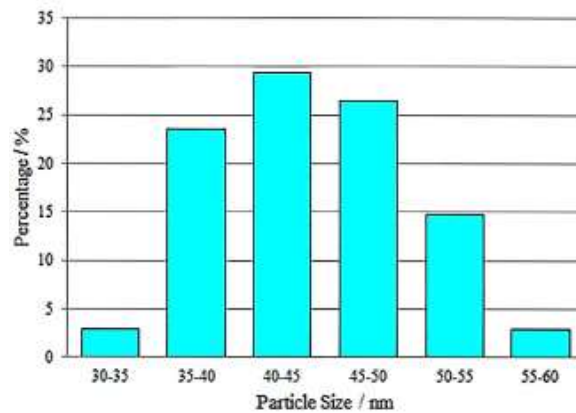

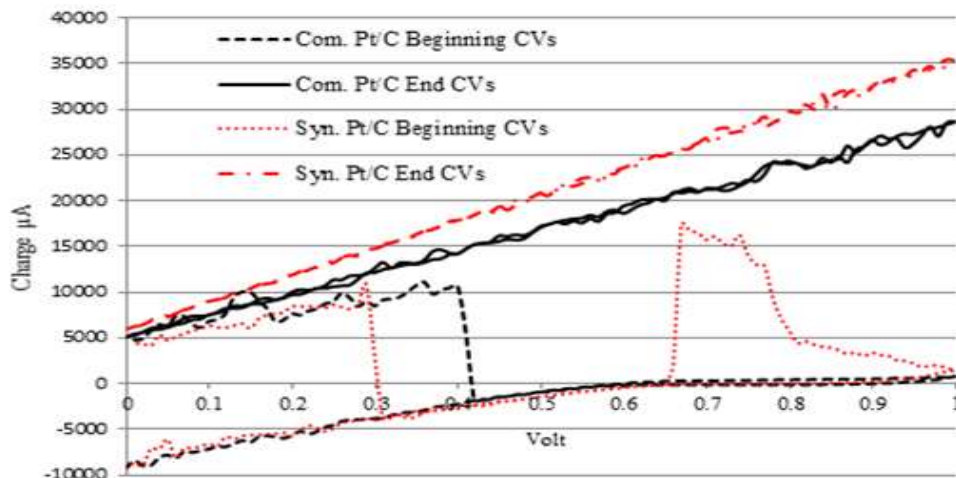**Fig. 5. Particle size distribution for the synthesized Pt/C.**

Fig. 6. H$_2$ Bubbling CVs for the Commercial and Synthesized Pt/C

in 1.0 volt. The results show better activity for the synthesized catalyst.

After first constructing the CVs with hydrogen bubbling and then ensuring complete activation of catalyst sites, 100 CVs performed along with continuous CO bubbling as described in section 2.5. Fig. 7 shows the CO CVs results for the commercial

lyst and Fig. 8 shows the CO CV curves for the synthesized catalyst., Additionally, the blank CVs before and after the test are showed for each catalyst.

The blank CVs charge amounts before and after the Pt/Ccom CO CV test are almost the same, which proves the complete activation of the catalyst and that all changes in charge amounts between these two
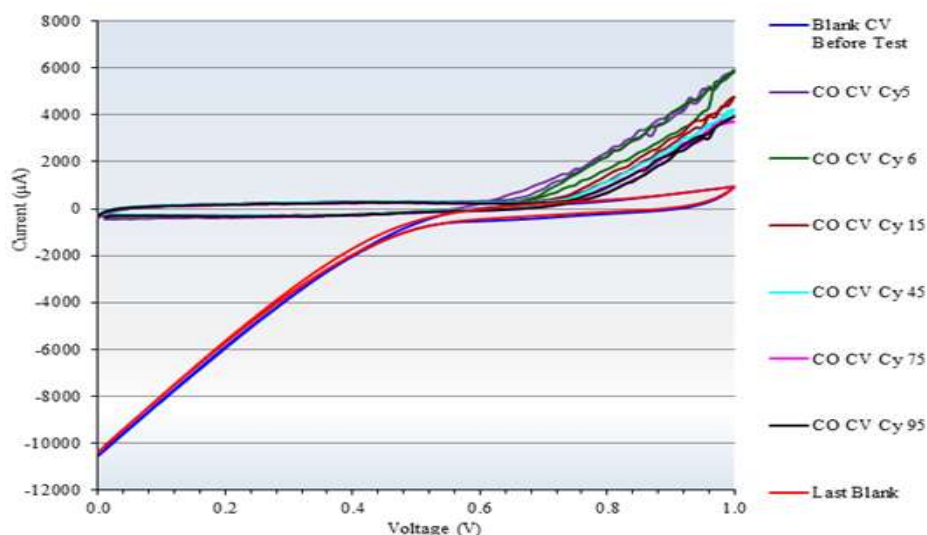
Fig. 7. CO CVs with before and after blank CVs for Commercial catalyst
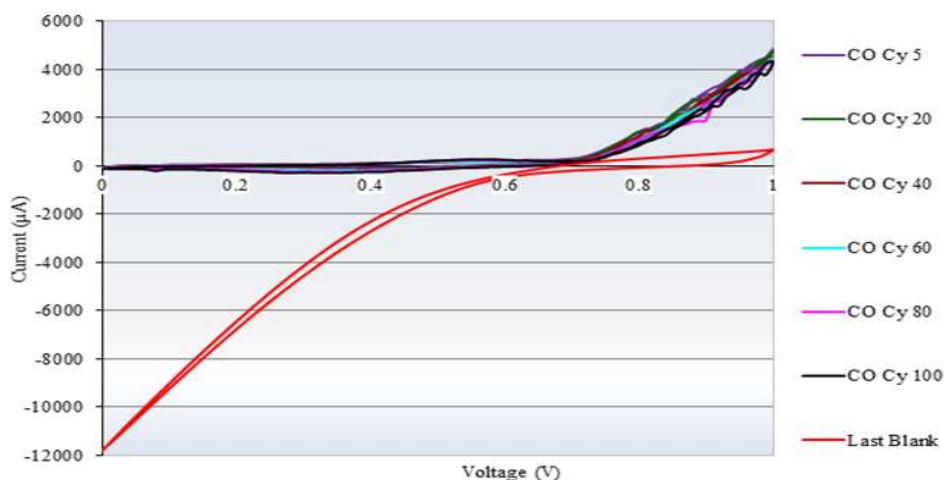

Fig. 8. CO CVs with before and after blank CVs for Synthesized catalyst

blank test are related to catalyst electrochemical activity in the presence of CO molecules.

To get the net current charges attributed to CO electro-oxidation, the positive amounts of the background activity charge should first be subtracted from the CO CVs current charge. Fig. 9 and Fig. 10 shows the curves obtained from subtracting the last blank CV charge from the CO CV charges in the same potentials for the commercial and synthesized catalysts, respectively.

As shown in Fig. 9 and Fig. 10, CO oxidation starts at low potentials near 0.0 V for both catalysts, whereas, the CO electro oxidation onset potential was reported to be about 0.7 V in previous studies [25]. This difference results from our CV test procedure. In pre-

vious works, a CO monolayer stripping method was used to evaluate the CO oxidation. This method only shows the electrochemically absorbed molecules stripping charge and potentials, while other possible desorption mechanisms are missed. Doing the CV test along with CO gas bubbling makes it possible to record any possible oxidation charge. So, charges obtained in the 0.0-0.7 V potential range, could be result of CO molecules desorption by any mechanisms other than chemical adsorption-desorption. Also the charge amounts in this potential range, does not affected by CO poisoning after 100 CVs. At potentials above 0.7 V, the electro oxidation rate rose up to about 5000 µA in 1.0 V. In addition, charge amounts
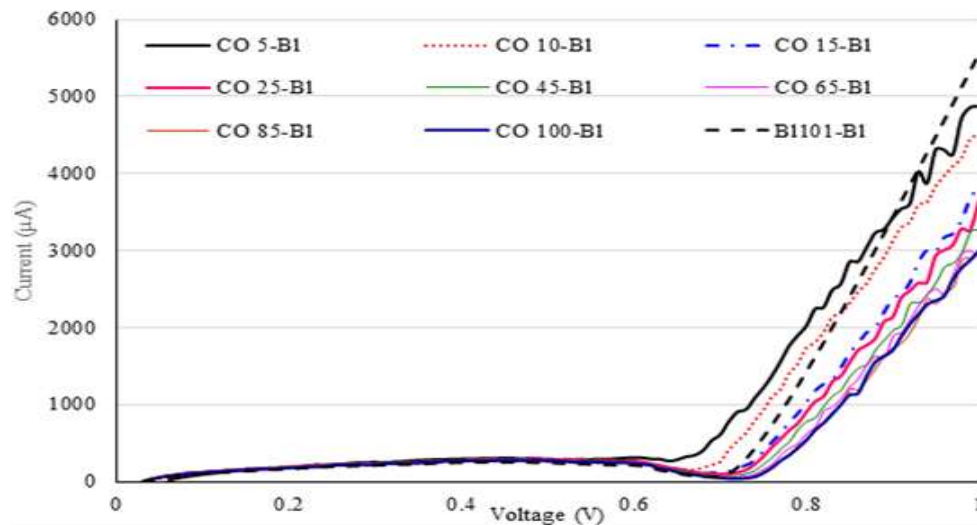
Fig. 9. net CO electro-oxidation charge amounts vs. voltage for the Pt/C$_{com}$
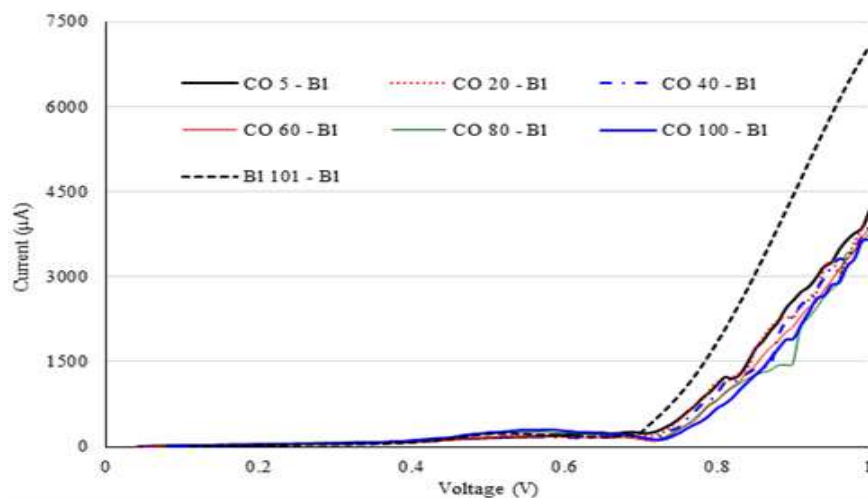

Fig, 10. The net CO electro-oxidation charge amounts vs. voltage for the Pt/C$_{syn}$

decreased by repeating the CVs in high potentials. Dramatic reduction in charge amounts occurred up to cycle 15, specially in (Pt/C) com., and then the reduction continued at a slower rate until the end of the test. The reduction in charge amounts results from CO poisoning at the catalyst active sites. In the first cycles, quick contamination of easy accessible sites takes place, the contamination continued when CO molecules penetrated deeply into the catalyst crystals structure, which appears as a slow decrease of electro-oxidation charges after cycle 15. Whereas, in the case of (Pt/C) syn., the catalyst shows good resistance against CO penetration and poisoning, its catalyst activity was more stable than the commercial one. Fig. 11 shows a comparison of net CO oxidation charge curves at the beginning and end of the test for the commercial and synthesized catalyst. Comparing the results in Fig, 11 proves that although the charge amounts for (Pt/C) com. are greater than the amounts for (Pt/C)syn., the synthesized catalyst has remarkable enhanced resistant against CO contamination. The poisoning effect of CO on the commercial catalyst is obvious, especially at the fuel cell operation potential range of 0.5-0.8 V.In Fig. 12, a close view of the comparison in the 0.5-0.8 V potential range is presented.

Another important point shown in Fig. 9 and Fig. 10 is the charge amounts for the first blank CV after the CO CV test, it is greater than cycle 100 CO CV charges for both catalysts. After ceasing the CO gas bubbling at the end of the CO CV test the working electrode media is saturated with CO molecules.
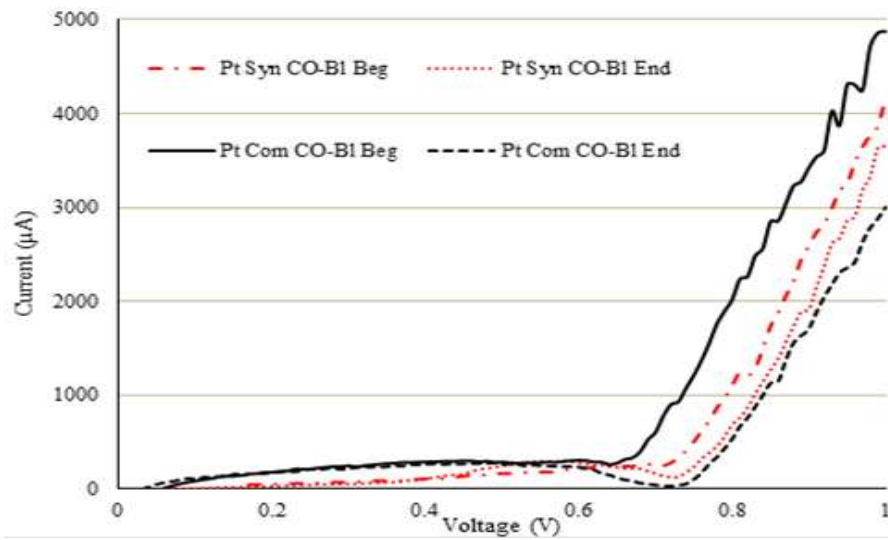
Fig. 11. The net CO electro-oxidation charge amounts vs. voltage for the commercial and synthesized Pt/C under continouos CO
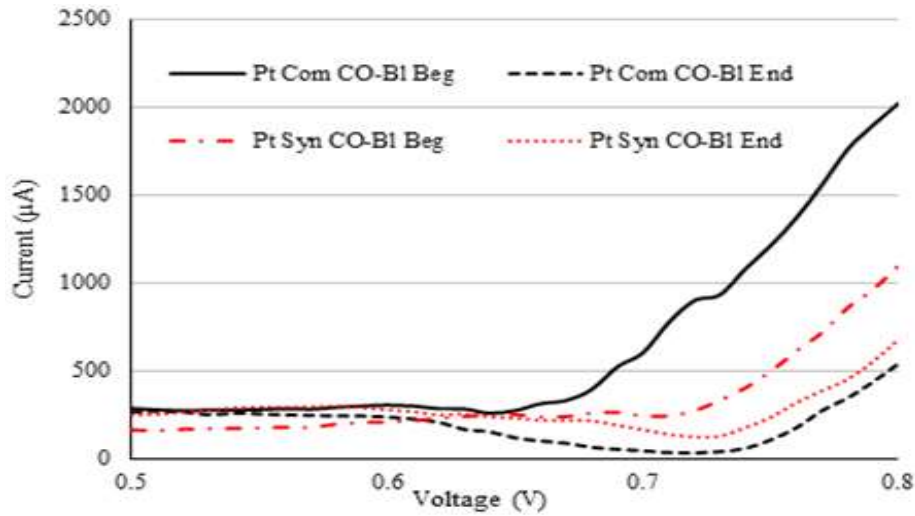

Fig. 12. Close view of net charge of two catalyst for the commercial and synthesized Pt/C under continouos CO bubbling at the
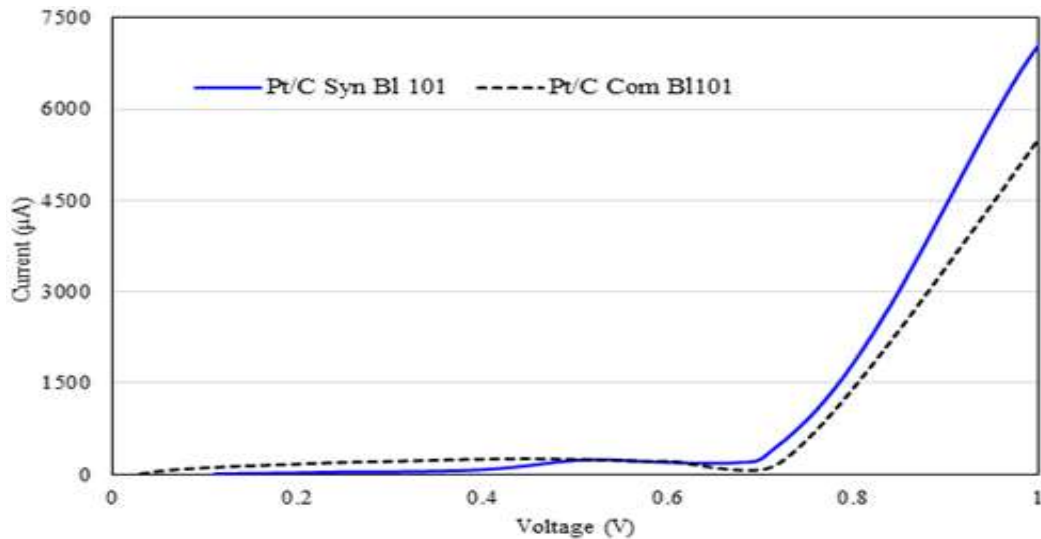

Fig. 13. Comparing the cycle 101 blnak CV net charges

Therefore, by releasing the CO gas stream driving force and turbulence, effective contacts between catalyst active sites and free CO molecules at the boundary layer of catalyst increased. This resulted in greater charge amounts at the first blank cycle. The first blank CV net charges for the commercial and synthesized catalyst are compared in Fig 13. This figure shows, with unblenched boundary layer conditions, the synthesized catalyst is more active to electro oxidation of CO. On the other hand, gas stream turbulence has more effect on synthesized catalyst activity and if the laminar gas stream is provided, the (Pt/C) syn. could be more active than (Pt/C) com. . The physical properties and activity potentials and charges for CO and blank CVs are summarized in Table 1.

3.Conclusions

A modified borohydride reduction synthesise method was used to form metallic platinum Nano particles. The synthesized and commercial Pt/C were characterized by XRD analysis and SEM images. The results showed that the synthesized catalyst has greater crystal and particle size and more uniform particle size distribution than the commercial one. Electrochemical CV test along with a continuous gas bubbling procedure, a method originally developed to study the catalyst stability against long-term CO exposure, was used to survey the catalyst activity for H_2 and CO electro-oxidation. The results showed better activity of the synthesized catalyst for H2 oxidation. The commercial catalyst had higher activity for CO electro-oxidation but less tolerance after 100 CVs under steady CO gas bubbling condition. The synthesized catalyst electrochemical activity for CO electro-oxidation in the same conditions was comparable to the commercial Pt/C. Moreover, our catalyst endurance for CO electro-oxidation after 100 CV with continuous CO gas bubbling was remarkable, whereas the commercial catalyst performance dropped about 88 percent from its initial amounts. Our electrochemical test technique showed that in

the 0.0-0.7 V potential range, the Pt/C catalyst had CO oxidation activity with mechanisms other than electrochemical adsorption-desorption..

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