Layered Pt.ZSM-5-C by greener chemical reduction for catalysing fuel cell reactions

Basu M. Daas[1],* and Susanta Ghosh[2]

[1]Department of Chemistry, Netaji Subhash Mahavidyalaya, Udaipur 799 120, India
[2]Integrated Science Education and Research Centre, Visva-Bharati, Santiniketan 731 235, India

Metal ion exchanged catalysts are known now and are successfully used for many catalytic processes. But supported metal nanoparticles on the zeolite bed, and their use as catalysts is still under experimental probe. ZSM-5 supported platinum nanoparticles are synthesized from *in-situ* chemical reduction of platinum chloride solution in the presence of zeolite, by zinc dust chemical reduction method which is comparatively 'greener'. This platinum nanoparticle loaded ZSM-5 is studied in the role of catalyst in electro-oxidation of methanol and ethanol using Nafion-117 to bind the catalyst on carbon felt. The platinum nanoparticle loaded ZSM-5 is found to be a better catalyst compared to pure ZSM-5 and pure platinum. This greener chemical reduction method can be used as the results show that zeolite modified catalysts are as good as those prepared by other less environment friendly methods, if not better.

Keywords: Chemical reduction, electro-oxidation, platinum nanoparticles, zeolite modified electrode, ZSM-5.

METAL nanoparticles are potential catalysts due to their physicochemical properties. Zeolites are the micro- and mesoporous acid catalysts studied and are used extensively as catalysts in the petroleum industry and for water purification as well. Here the metal under study is platinum nanoparticles (PNPs) and the zeolite is ZSM-5. Metal ion exchanged catalysts are now known and successfully used for many catalytic processes. However, supported metal nanoparticles on the zeolite bed, and their use as catalysts is still under experimental probe[1–4]. Pt electro-catalyst is poisoned by intermediates produced during the oxidation of ethanol oxidation[5–7]. Adding a second catalyst is an effective way to promote the cleavage of C–C bond and accelerate alcohol oxidation[4,8]. Pt-based alloy like Pt-Ru, Pt-Sn, Pt-Rh and Pt-Sn-Ni can be used as a second catalyst. Oxides like Pt-MgO, Pt-CeO$_2$, Au-Fe$_2$O$_3$, Pd-Al$_2$O$_3$ and Pt-SiO$_2$ can be used as a second catalyst[5,6,9–16]. Carbon nanotubes as catalyst support have promising electro-catalytic properties for anodic oxidation of ethanol[4]. ZSM-5 was chosen as a supporting catalyst because of its protonic entities on the surface which makes it more hydrophilic than carbon. ZSM-5 is a highly ordered microporous aluminosilicate species consisting of tetrahedra of four numbers of oxygen at the corners, surrounding a cation[17–20]. So use of ZSM-5 in electrochemical reactions lowers the resistance ohmic power loss compared to carbon-based electrodes[21]. Moreover, the structure of ZSM-5 has sieves with high surface area that allow reactants to permeate through sieves ensuring close contact of reactants with catalytic sites[17,22–25]. Carbon in some form or the other is necessary to provide good electronic conductivity in the catalyst medium[21,26–31]. Pang *et al.*[21] used NaBH$_4$ for chemical reduction. However, this is hazardous and not user-friendly. In case of reduction by NaBH$_4$ at room temperature, the initial rapid reduction gets subdued by the formation of basic metaborate ions and increase in pH[21,32,33]. In this study layered ZMEs were prepared by chemical reduction with zinc dust (Zn dust) to investigate the catalytic ability of the resultant layered ZMEs in fuel cell electro-oxidation reactions.

Experimental details

Materials and methods

All chemicals, ZSM-5, Zn dust, chloroplatinic acid hexahydrate and carbon black used were of analytical grade. ZSM-5 used was bought from Greenstone (Switzerland). Zn dust was from Merck, India. Chloroplatinic acid hexahydrate was purchased from Sigma-Aldrich while carbon black and 99% pure and 6.4 mm thin carbon felt (C-felt) were from Alfa Aesar (USA). Fresh triple distilled water was used for all purposes to avoid contamination.

Preparation of electrodes

Metal ions can be incorporated in zeolite framework by reducing them. One gram of ZSM-5 was pre-heated at 120°C for 3 h. It was then soaked in 30 ml of 1×10^{-3} M chloroplatinic acid hexahydrate solution and stirred for more than 15 min. The reducing agent, Zn dust, was then added slowly with constant stirring. The solution changed to whitish yellow suggesting the formation of ZSM-5 supported PNPs. The solution was stirred for 15 min and subject to ultrasonic irradiation for 30 min to ensure

---

complete reduction of Pt into PNPs. Then 1 g of carbon black was added to the Pt/ZSM-5 formed by constant stirring. The black blend was then subjected to ultrasonic irradiation for 3 h to ensure a homogeneous mix which was filtered by Whatman 41 filter paper and washed with distilled water and then dried in vacuum for 1 week to obtain Pt/(ZSM-5-C). The composite was layered on C-felt and used as electro-catalyst for electro-oxidation of alcohols. These PNP incorporated catalysts were sprayed on C-felts of 1×1 cm^2 size to obtain Pt/(ZSM-5-C)/C electrodes. Similarly, Pt/C electrode was made by the same chemical reduction method, the only exception being the absence of ZSM-5 addition step in the process. The initial and final weights were noted for estimation of mass activity in terms of mA/mg which is a criterion to identify and quantify better catalysis[21].

Characterization results

BET analysis

Brunauer-Emmett-Teller (BET) analysis of ZSM-5 at 77 K shows that the specific surface area is 361.7 m^2/g and average pore size of 14 Å (Figure 1 i). BET analysis of Pt/ZSM-5-C at 77 K shows that the specific surface area is 43.4 m^2/g and average pore sizes of 18 Å (Figure 1 ii). The smaller peaks are ignored as their intensity or amplitude is negligible compared to the primary peak.

Powder XRD analysis

Powder X-ray diffraction (XRD) was analysed with CuKα radiation over a scanning range of 2θ from 5° to 70° with 30 kV voltage and 0.015 A current (Figure 2).
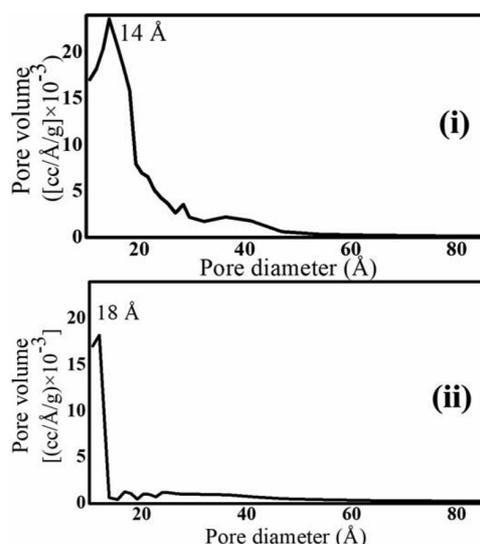
Figure 1. BET analysis of (i) ZSM-5 and (ii) Pt/ZSM-5-C.

XRD analysis of before and after treatment for PNPs incorporation indicates that the ZSM-5 framework is maintained. In the case of ZSM-5, the diffractogram pattern contains (301), (011), (101), (020), (503), (051) and (501) *hkl* peaks at 7.92°, 8.82°, 14.76°, 22.99° and 23.89° respectively, establishing pure ZSM-5 (ref. 17). The (002) *hkl* peak of carbon is due to carbon content from the C-felt[34,35]. The *hkl* peaks of (100), (002), (101), (102), (110), (103), (200), (112) and (201) at 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 61.75°, 66.3°, 67.9° and 69.05° respectively, establish zinc content (JCPDS 5-0664)[36–38]. The diffraction peaks at 40°, 41.3° and 41.4° correspond to the (111) *fcc* lattice of platinum; the peaks at 41.3° and 41.4° were caused by smaller size of PNPs. The peaks at 43.8°, 44.7° and 44.8° represent the (200) structure of platinum; the latter two peaks being for smaller PNPs formed. Again, the peaks at 68.1°, 68.5° and 68.6° demonstrated (220) *fcc* lattice of platinum; the latter two peaks being for smaller PNPs[39–42].

SEM-EDS and TEM analysis

The scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis also proves the incorporation of PNPs in the ZSM-5 framework stuck on C-felt (Figure 3). EDS analysis of ZSM-5 reveals that the weight percentage of Si, Al and O are 50, 23 and 26 respectively. The ratio of Si : Al : O is 2 : 1 : 1 approximately (Table 1).

In the EDS analysis of Pt/ZSM-5-C, the weight percentage of C, Si, Al, O, Zn and Pt was 42, 26.3, 13, 12.3, 6 and 0.4 respectively. EDS established the presence of deposited PNPs on the ZSM-5 loaded C-felt. The ratio of Si : Al : O was 2 : 1 : 1 approximately which is roughly constant.

Transmission electron microscopy (TEM) analysis of Pt/ZSM-5-C shows PNPs incorporated in the composite
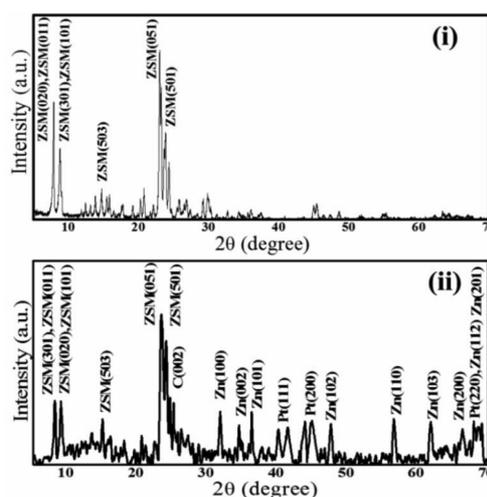
Figure 2. XRD analysis of (i) ZSM-5 and (ii) Pt/ZSM-5-C.
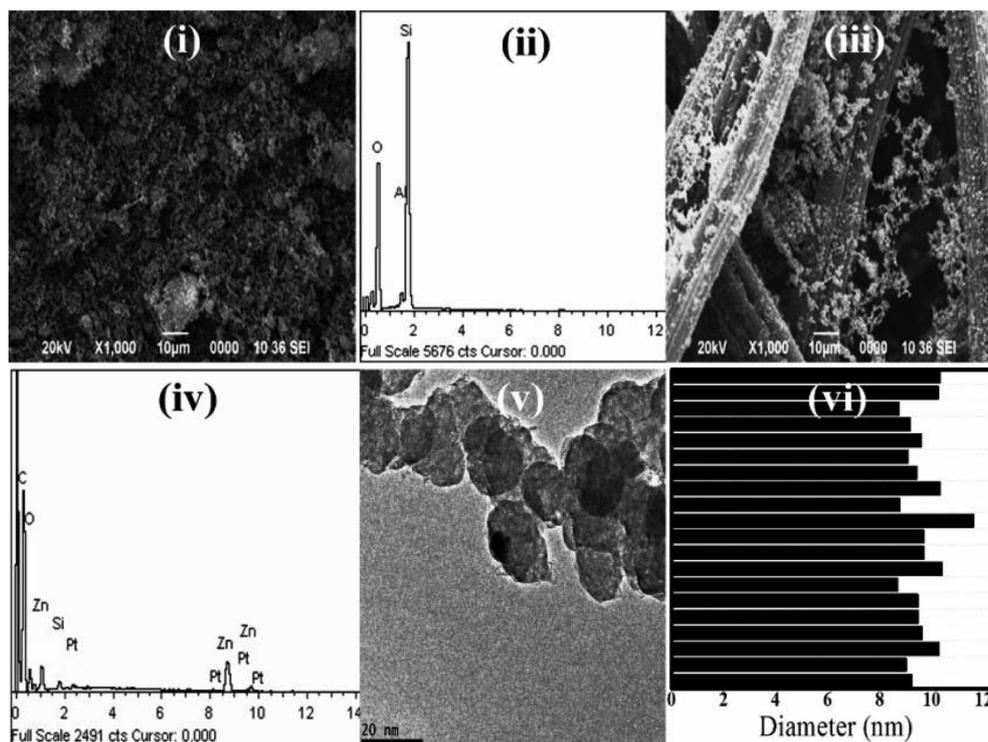
Figure 3. (i) SEM micrograph, (ii) EDS analysis, (iii) TEM micrograph of ZSM-5, (iv) SEM micrograph, (v) EDS analysis and (vi) TEM micrograph of Pt/ZSM-5-C.

Table 1. Elemental analyses of ZSM-5 and Pt/(ZSM-5-C)

Element	ZSM-5	Pt/(ZSM-5-C)
C	×	42
Si	50	26.3
Al	23	13
O	26	12.3
Zn	×	6
Pt	×	0.4

Table 2. Size, number and percentage distribution of PNPs on Pt/ZSM-5-C

Size (nm)	Number	Percentage (%)
<9	3	15
9–10	12	60
10–11	4	20
11–12	1	5

framework. PNPs incorporated are of smaller sizes having diameters within 9 to 12 nm (Table 2).

Electrochemical analysis

Electrochemically active surface area (EAS), cyclic voltammetric, chronoamperometric, tafel plot and multiple scan analyses were done to investigate the catalytic ability and durability of the layered catalysts.

EAS analysis

EAS was used in analysing the electrochemically active sites per unit mass of the catalysts. It is a vital criterion of electrocatalytic supports distinguishing the surface activity between different electro-catalytic materials[43,44]. The current versus potential curves of the two electrodes show the presence of Pt on the electrodes, evident from downward lumps in the potential range of 0.5–0.6 V in both cases which is due to reduction of oxidized PNPs deposited (Figure 4). The peak towards the left of the voltammogram is due to adsorption–desorption of hydrogen[43,45–48]. The higher electrochemically active surface area is due to formation of smaller PNPs because higher is the surface area exposed and available for catalysing the electrochemical reactions[21].

Cyclic voltammetric analysis

CV is an important analytical method in electrochemistry employed widely due to its versatility, inexpensiveness and ease-of-use[49,50]. The base voltammograms for the blank C-felt window, a potential window of 0.0–1.0 V, showed no recognizable peak in either forward or backward scans. But when (ZSM-5-C)/C was used, there was appearance of appreciable forward and backward peaks. These peaks were pronounced appreciably for Pt/C, as Pt is a much better catalyst for electro-oxidation of both MeOH (Figure 5) and EtOH (Figure 6).

Nevertheless, when Pt/(ZSM-5-C)/C electrode was used, the peaks became more prominent both in forward and backward scans. The mass activities of the electrodes are calculated based on the weight percentage of PNPs in the electrodes. The percentage of Pt is 0.69 in the chemically reduced zeolite modified electrodes (ZMEs) (Table 3).

The increase in mass activity of ZME when compared to that of chemically prepared Pt/C and (ZSM-5-C)/C
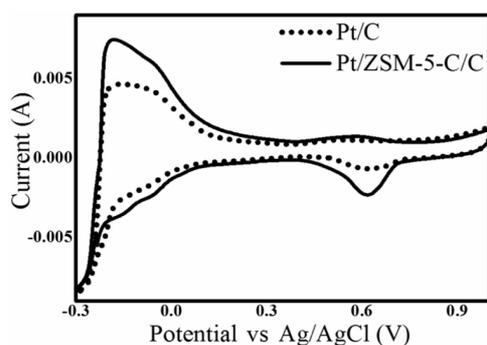
Figure 4. EAS analysis of Pt/C and Pt/(ZSM-5-C)/C electrodes.
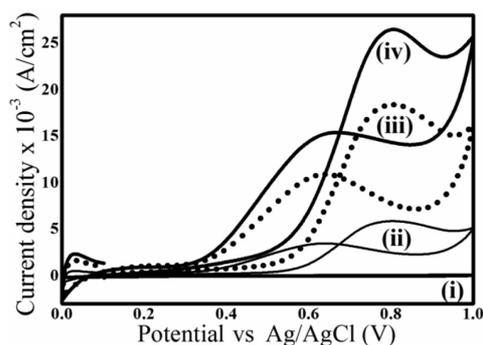
Figure 5. Base voltammograms of Nafion 117 binder on C-felt in 1.0 M MeOH + 0.5 M H$_2$SO$_4$; electro-oxidation of 1.0 M MeOH in 0.5 M H$_2$SO$_4$ catalysed by (ZSM-5-C)/C, Pt/C and Pt/(ZSM-5-C)/C at 0.05 versus scan rate.
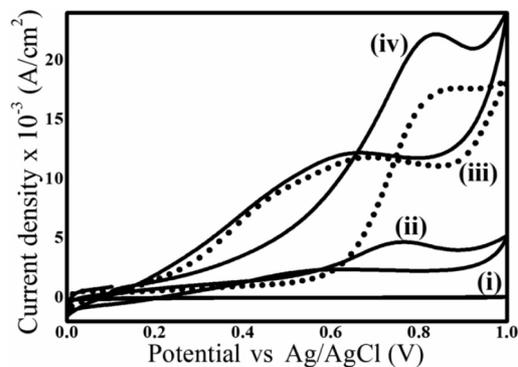
Figure 6. Base voltammograms of Nafion 117 binder on C-felt in 1.0 M EtOH + 0.5 M H$_2$SO$_4$; electro-oxidation of 1.0 M EtOH in 0.5 M H$_2$SO$_4$ catalysed by (ZSM-5-C)/C, Pt/C and Pt/(ZSM-5-C)/C at 0.05 versus scan rate.

shows that in the presence of zeolite the catalytic ability of PNPs increased considerably. The combination of ZSM-5-C and Pt function was much better when used separately.

Chronoamperometric analysis

This is a commonly used electroanalytical technique for determining D and for investigating kinetics and mechanisms by a single experiment, unlike cyclic voltammetry. When a potential step, large enough to cause an electrochemical reaction, is applied to an electrode the current changes with time[51]. The chronoamperograms of electrodes show higher current density in the order of Pt/(ZSM-5-C)/C < Pt/C < Pt/(ZSM-5-C)/C (Figure 7).

Moreover, in the case of MeOH, current density was more compared to EtOH. This shows that ZMEs are better catalysts than others because ZMEs generate more current which symbolizes more electrochemical reaction. After 30 min, the current density was found to be steady for all electrodes. Turn-over number (TON) was calculated based on the current density at 30 min (i), the number of electrons involved in electro-oxidation (n) and the density of the topmost atoms of Pt(100) surface

Table 3. Peak current densities and mass activities of electrodes

Electrode	Alcohol (1 M)	Forward peak	
		Current density (A/cm^2)	Pt mass activity (mA/mg)
(ZSM-5-C)/C	CH$_3$OH	0.0120	×
(ZSM-5-C)/C	C$_2$H$_5$OH	0.0047	×
Pt/C	CH$_3$OH	0.02091	303.0435
Pt/C	C$_2$H$_5$OH	0.01765	255.7971
Pt/(ZSM-5-C)/C	CH$_3$OH	0.02648	383.7681
Pt/(ZSM-5-C)/C	C$_2$H$_5$OH	0.0222	321.7391
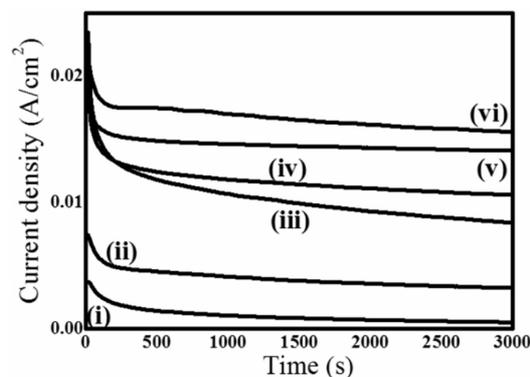
Figure 7. Chronoamperograms of (i) (ZSM-5-C)/C, (ii) Pt/C and (iii) Pt/(ZSM-5-C)/C in 1.0 M EtOH + 0.5 M H$_2$SO$_4$; and (iv) (ZSM-5-C)/C, (v) Pt/C and (vi) Pt/(ZSM-5-C)/C in 1.0 M MeOH + 0.5 M H$_2$SO$_4$.

$(1.3 \times 10^{15} \text{ cm}^{-2})$; while Faraday and Avogadro numbers are constants[43,48].

$$\text{TON} = (6.023 \times 10^{23} \times i)/(1.3 \times 10^{15} \times n \times F),$$

increases in the order of [(ZSM-5-C)/C in EtOH] < [(ZSM-5-C)/C in MeOH] < [Pt/C in EtOH] < [Pt/C in MeOH] < [Pt/(ZSM-5-C)/C in EtOH] < [Pt/(ZSM-5-C)/C in MeOH]. This shows that PNPs in ZME have the best catalytic ability and electro-oxidation of MeOH is more prominent than that of EtOH.

Tafel plot analysis

Tafel plot (TP) analysis is an electrochemical kinetics relation of the rate of an electrochemical reaction with the over-potential[52]. Linear sweep voltammetry is recorded from current (i) versus potential (V) within a potential gradient of 0.0–1.0 V. From this electrochemical data, TPs are constructed. Intersection point of extrapolated cathodic and anodic Tafel slopes at the corrosion potential (E_{corr}) gives the corrosion current density (i_{corr}) (Figure 8).

From the Tafel plots it is clear that Pt/(ZSM-5-C)/C electrode is a better catalyst than Pt/C because in case of both the alcohols i_{corr} values are higher for the former than for the latter. Furthermore, E_{corr} values are lower for Pt/(ZSM-5-C)/C electrode than those of Pt/C electrode, confirming that the ZME facilitates electro-oxidation of both the alcohols at a lower potential which again confirms that the presence of ZSM-5 accelerates the electro-chemical reactions[21].

Multiple scan analysis

For practical purposes the long-term stability (LTS) of electrode is vital. LTS of electrodes can be tested by two hundred or more current versus potential scans, within the potential gradient window of 0.0–1.0 V. The retained current density can be considered equivalent to LTS and repeatability of electrodes[21].

The long-term stability of the Pt/C and Pt/(ZSM-5-C)/C, in 1.0 M MeOH or EtOH and 0.5 M H_2SO_4 was tested as the catalytic power of (ZSM-5-C)/C is insignificant. The cyclic voltammogram within 0.0–1.0 V was cycled continuously for 200 cycles to investigate LTS in terms of retained current density (Figure 9).

The multiple scan analysis showed that the current density was retained more by Pt/(ZSM-5-C)/C electrode catalyst than Pt/C electrode in case of both alcohols. The current density retained after 200 scans was found to be about 84% and 83% for Pt/C in case of EtOH and MeOH respectively. Compared to this the retained current density for Pt/C was found to be 79% for both the alcohols. This confirms that ZME is more stable along with more repeatability than the electrode without ZSM-5 (ref. 21).

Discussion and conclusion

The chemical reduction by means of Zn dust is comparatively a greener approach compared to reduction by $NaBH_4$. Thus, this method of reduction is environment friendly. Moreover, chemical reduction by Zn dust is more effective because in case of reduction by $NaBH_4$ there occurs an internal resistance to the reduction process by the formation of basic metaborate ions and resultant increase in pH. Thus, chemical reduction by Zn dust is a more green and effective option.

Moreover, ZSM-5 acts as a stabilizer for the metal inside sieves, eliminating the use of any stabilizing agent like cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS), ascorbic acid (vitamin C), sodium citrate dehydrate, etc.[21]. Zeolites have a hydroxyl group that can facilitate oxidation of CO_{ads} to make the electrode surface free for further reaction just as 15% and 45% surface concentration of Ru-OH drives out CO_{ads} and reactivates the electrode surface. ZSM-5 on account of possessing SiO_2 and Al_2O_3 can also facilitate cleansing of the catalytic electrode surface. In case of ZME, the oxygen containing species was provided by the framework O-sites or surface-OHs of the zeolite, which
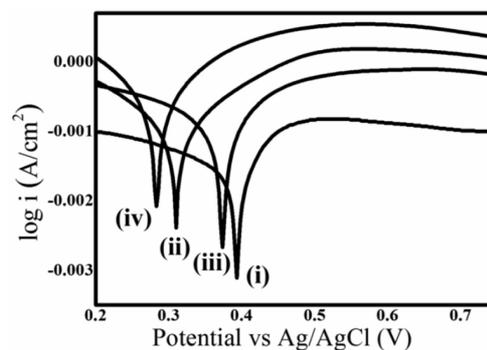
Figure 8. Tafel plots of (i) Pt/C and (ii) Pt/(ZSM-5-C)/C in 1.0 M EtOH + 0.5 M H_2SO_4; and (iii) Pt/C and (iv) Pt/(ZSM-5-C)/C in 1.0 M MeOH + 0.5 M H_2SO_4.
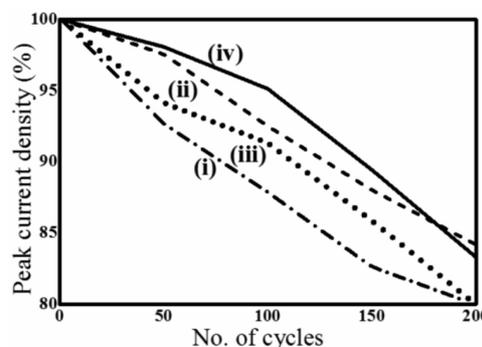
Figure 9. Retained current density for (i) Pt/C and (ii) Pt/(ZSM-5-C)/C in 1.0 M EtOH + 0.5 M H_2SO_4; and (iii) Pt/C and (iv) Pt/(ZSM-5-C)/C in 1.0 M MeOH + 0.5 M H_2SO_4.

strongly react with CO_{ads} on Pt surface to release active sites for further electro-oxidation of alcohols. SiO_2 in zeolite framework and modification of Pt electronic configuration increases the electrocatalytic efficiency of such zeolite supported metal nano-particles. The lower density of valence electron in ZME than that of pure Pt resulted in lesser CO_{ads} concentration and higher electrocatalytic efficiency[21]. ZSM-5 can also conduct electricity and hence facilitate fuel cell energy generation[18,53,54]. It is advantageous to utilize highly stable ZSM-5 as a support and second catalyst[21,54].

The ZME, Pt/(ZSM-5-C)/C prepared by greener chemical reduction, seems to be a much better catalyst than Pt/C which validates recent studies showing that ZMEs are better catalysts than those electrodes without ZSM-5. The presence of ZSM-5 also improves the stability and reliability of the ZME along with greater catalytic ability. The current density generated by ZME prepared by Zn dust reduction is greater and the mass activity is also found to be 26–27% more for ZME by greener reduction. The turnover number is also found to be on the higher side for the ZME by greener reduction; also the repeatability is found to be 5–6% higher. Consequently, compared to ZME prepared by chemical reduction with $NaBH_4$, ZME prepared by reduction with Zn dust has higher catalytic ability, mass activity, long-term stability and repeatability.

The platinum nanoparticles loaded ZSM-5 were found to be a better catalyst compared to pure ZSM-5 and pure platinum. The catalyst produced can be used as an electro-catalyst for the electro-oxidation of alcohols. Further research in this field is of prime importance as the search for alternative energy resources is in full swing all over the globe. The recent discovery of converting atmospheric CO_2 into EtOH with yield of 63% by using inexpensive copper nanoparticle doped graphene[55] has paved a new way to solve the global energy crunch by a concerted process of conversion of CO_2 into EtOH and EtOH into CO_2.

Declaration regarding ethical issue: No such issue as all data, tables and figures are from our own study.

1. Tang, H., Chen, J., Nie, L., Liu, D., Deng, W., Kuang, Y. and Yao, S., High dispersion and electrocatalytic properties of platinum nanoparticles on graphitic carbon nanofibers (GCNFs). *J. Colloid. Interface. Sci.*, 2004, **269**(1), 26–31.
2. He, Z., Chen, J., Liu, D., Tang, H., Deng, W. and Kuang, Y., Deposition and electrocatalytic properties of platinum nanoparticals on carbon nanotubes for methanol electrooxidation. *Mater. Chem. Phys.*, 2004, **85**(2), 396–401.
3. Rajesh, B., Karthik, V., Karthikeyan, S., Thampi, K. R., Bonard, J. M. and Viswanathan, B., Pt–WO 3 supported on carbon nanotubes as possible anodes for direct methanol fuel cells. *Fuel*, 2002, **81**(17), 2177–2190.
4. Wang, M. Y., Chen, J. H., Fan, Z., Tang, H., Deng, G. H., He, D. L. and Kuang, Y. F., Ethanol electro-oxidation with Pt and Pt–Ru catalysts supported on carbon nanotubes. *Carbon*, 2004, **42**(15), 3257–3260.
5. Neto, A. O., Giz, M. J., Perez, J., Ticianelli, E. A. and Gonzalez, E. R., The electro-oxidation of ethanol on Pt–Ru and Pt–Mo particles supported on high-surface-area carbon. *J. Electrochem. Soc.*, 2002, **149**(3), A272–A279.
6. Léger, J. M., Rousseau, S., Coutanceau, C., Hahn, F. and Lamy, C., How bimetallic electrocatalysts does work for reactions involved in fuel cells? Example of ethanol oxidation and comparison to methanol. *Electrochim. Acta*, 2005, **50**(25), 5118–5125.
7. Daas, B. M. and Ghosh, S., Fuel cell applications of chemically synthesized zeolite modified electrode (ZME) as catalyst for alcohol electro-oxidation – a review. *J. Electroanal. Chem.*, 2016, **783**, 308–315.
8. Gonçalves, F., Medeiros, P. R., Eon, J. G. and Appel, L. G., Active sites for ethanol oxidation over SnO 2-supported molybdenum oxides. *Appl. Catal. A Gen.*, 2000, **193**(1), 195–202.
9. de Souza, J. P., Queiroz, S. L., Bergamaski, K., Gonzalez, E. R. and Nart, F. C., Electro-oxidation of ethanol on Pt, Rh, and PtRh electrodes. A study using DEMS and *in-situ* FTIR techniques. *J. Phys. Chem. B.*, 2002, **106**(38), 9825–9830.
10. Spinacé, E. V., Linardi, M. and Neto, A. O., Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt–Sn electrocatalysts. *Electrochem. Commun.*, 2005, **7**(4), 365–369.
11. Xu, C. and Shen, P. K., Enhanced activity for ethanol electrooxidation on Pt-MgO/C catalysts. *Electrochem. Commun.*, 2005, **7**(12), 1305–1308.
12. Xu, C. and Shen, P. K., Novel Pt/CeO$_2$/C catalysts for electrooxidation of alcohols in alkaline media. *Chem. Commun.*, 2004, **19**, 2238–2239.
13. Xu, C. and Shen, P. K., Electrochemical oxidation of ethanol on Pt-CeO$_2$/C catalysts. *J. Power Sources*, 2005, **142**(1), 27–29.
14. Minicò, S., Scirè, S., Crisafulli, C., Maggiore, R. and Galvagno, S., Catalytic combustion of volatile organic compounds on gold/iron oxide catalysts. *Appl. Catal. B*, 2000, **28**(3), 245–251.
15. Bürgi. T., Combined *in situ* attenuated total reflection infrared and UV–Vis spectroscopic study of alcohol oxidation over Pd/Al$_2$O$_3$. *J. Catal.*, 2005, **229**(1), 55–63.
16. Liu, B., Chen, J. H., Zhong, X. X., Cui, K. Z., Zhou, H. H. and Kuang, Y. F., Preparation and electrocatalytic properties of Pt–SiO$_2$ nanocatalysts for ethanol electrooxidation. *J. Colloid. Interface. Sci.*, 2007, **307**(1), 139–144.
17. Beck, J. S. *et al.*, A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Sci.*, 1992, **114**(27), 10834–10843.
18. Rolison, D. R., Zeolite-modified electrodes and electrode-modified zeolites. *Chem. Rev.*, 1990, **90**(5), 867–878.
19. Coombs, D. S., Recommended nomenclature for zeolite minerals, report of the subcommittee on zeolites of the international mineralogical association, Commission on new minerals and mineral names. *Can. Mineral.*, 1997, **35**, 1571–1606.
20. Sun, T. and Seff, K., Silver clusters and chemistry in zeolites. *Chem. Rev.*, 1994, **94**(4), 857–870.
21. Pang, H., Chen, J., Yang, L., Liu, B., Zhong, X. and Wei, X., Ethanol electrooxidation on Pt/ZSM-5 zeolite-C catalyst. *J. Solid. State. Electrochem.*, 2008, **12**(3), 237–243.
22. Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*, 1992, **359**(6397), 710–712.
23. Belaya, L. A., Doronin, V. P., Sorokina, T. P. and Gulyaeva, T. I., Thermal stability of zeolites Y and ZSM-5 in matrices of various compositions. *Russ. J. Appl. Chem.*, 2009, **82**(2), 236–242.
24. Zhdanov, S. P., Feoktistova, N. N., Kozlova, N. I. and Polyakova, I. G., Thermal stability of high-silica zeolites of the ZSM-5 family. *Bull. Acad. Sci. USSR, Divn. Chem. Sci.*, 1985, **34**(12), 2463–2466.

25. Parker, L. M., Bibby, D. M. and Patterson, J., Thermal decomposition of ZSM-5 and silicalite precursors. *Zeolites*, 1984, **4**(2), 168–174.

26. Mentus, S., Mojović, Z. and Radmilović, V., The use of NaX zeolite as a template to obtain a mono-atomic Pt dispersion by impregnation with Pt(II) acetylacetonate/acetone solution. *J. Serb. Chem. Soc.*, 2009, **74**(10), 1113–1123.

27. Mojović, Z., Banković, P., Jović-Jovičić, N., Milutinović-Nikolić, A., Rabi-Stanković, A. A. and Jovanović, D., Electrocatalytic behavior of nickel impregnated zeolite electrode. *Int. J. Hydrogen Energy*, 2011, **36**(21), 13343–13351.

28. Mojović, Z., Mudrinić, T., Rabi-Stanković, A. A., Ivanović-Šašić, A., Marinović, S., Žunić, M. and Jovanović, D., Methanol electrooxidation on PtRu modified zeolite X. *Sci. Sinter.*, 2013, **45**(1), 89–96.

29. Yao, J., Yao, Y. and Mirzaii, H., Proton modified Pt zeolite fuel cell electrocatalysts. In *Renewable Energy in the Service of Mankind*, Springer, London, 2014, vol. 1.

30. Zhang, Q., Li, Z., Wang, S., Xing, W., Yu, R. and Yu, X., The electro-oxidation of dimethyl ether on platinum-based catalyst. *Electrochim. Acta*, 2008, **53**(28), 8298–8304.

31. Samant, P. V. and Fernandes, J. B., Enhanced activity of Pt(HY) and Pt-Ru(HY) zeolite catalysts for electrooxidation of methanol in fuel cells. *J. Power Sourc.*, 2004, **125**, 172–177.

32. Stoeppler, M., *Hazardous Metals in the Environment*, Elsevier, 1992, vol. 12.

33. Schlesinger, H. I., Brown, H. C., Finholt, A. E., Gilbreath, J. R., Hoekstra, H. R. and Hyde, E. K., Sodium borohydride, its hydrolysis and its use as a reducing agent and in the generation of hydrogen. *JACS*, 1953, **75**(1), 215–219.

34. Iwasita, T., Methanol and CO electrooxidation. In *Handbook of Fuel Cells – Fundamentals, Technology and Applications. Electrocatalysis* (eds Vielstich, W., Gasteiger, H. A. and Lamm, A.), Wiley, New Jersey, 2003, vol. 2, pp. 603–624.

35. Li, H., Kang, D., Wang, H. and Wang, R., Carbon-supported Pt-RuCo nanoparticles with low-noble-metal content and superior catalysis for ethanol oxidization. *Int. J. Electrochem. Sci.*, 2011, **6**(4), 1058–1065.

36. Wei, X. and Chen, D., Synthesis and characterization of nanosized zinc aluminate spinel by sol–gel technique. *Mater. Lett.*, 2006, **60**, 823–827.

37. Hu, J. Q., Ma, X. L., Xie, Z. Y., Wong, N. B., Lee, C. S. and Lee, S. T., Characterization of zinc oxide crystal whiskers grown by thermal evaporation. *Chem. Phys. Lett.*, 2001, **344**(1), 97–100.

38. Luo, T., Liu, J., Chen, L., Zeng, S. and Qian, Y., Synthesis of helically coiled carbon nanotubes by reducing ethyl ether with metallic zinc. *Carbon*, 2005, **43**(4), 755–759.

39. Shen, Y., Xiao, K., Xi, J. and Qiu, X. X., Comparison study of few-layered graphene supported platinum and platinum alloys for methanol and ethanol electro-oxidation. *J. Power Sourc.*, 2015, **278**, 235–244.

40. Klug, H. P. and Alexander, L. E., *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York, 1974, 2nd edn.

41. Burton, A. W., Ong, K., Rea, T. and Chan, I. Y., On the estimation of average crystallite size of zeolites from the Scherrer equation, a critical evaluation of its application to zeolites with one-dimensional pore systems. *Microporous. Mesoporous. Mater.*, 2009, **117**(1), 75–90.

42. Monshi, A., Foroughi, M. R. and Monshi, M. R., Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD. *World J. Nano. Sci. Eng.*, 2012, **2**(3), 154–160.

43. Ye, W., Zhang, X., Chen, Y., Du, Y., Zhou, F. and Wang, C., Pulsed electrodeposition of reduced graphene oxide on glass carbon electrode as an effective support of electrodeposited Pt microspherical particles, nucleation studies and the application for methanol electro-oxidation. *Int. J. Electrochem. Sci.*, 2013, **8**, 2122–2139.

44. Sun, S. H., Yang, D. Q., Villers, D., Zhang, G. X., Sacher, E. and Dodelet, J. P., Template- and surfactant-free room temperature synthesis of self-assembled 3D Pt nanoflowers from single-crystal nanowires. *Adv. Mater.*, 2008, **20**(3), 571–574.

45. Rodriguez, J. M. D., Melián, J. A. H. and Peña, J. P., Determination of the real surface area of Pt electrodes by hydrogen adsorption using cyclic voltammetry. *J. Chem. Educ.*, 2000, **77**(9), 1195–1197.

46. Lukaszewski, M., Soszko, M. and Czerwinski, A., Electrochemical methods of real surface area determination of noble metal electrodes – an overview. *Int. J. Electrochem. Sci.*, 2016, **11**, 4442–4469.

47. Watt-Smith, M. J., Friedrich, J. M., Rigby, S. P., Ralph, T. R. and Walsh, F. C., Determination of the electrochemically active surface area of Pt/C PEM fuel cell electrodes using different adsorbates. *J. Phys. D Appl. Phys.*, 2008, **41**(17), 174004.

48. Singh, B., Murad, L., Laffir, F., Dickinson, C. and Dempsey, E., Pt based nanocomposites (mono/bi/tri-metallic) decorated using different carbon supports for methanol electro-oxidation in acidic and basic media. *Nanoscale*, 2011, **3**(8), 3334–3349.

49. Abdelkader, A. M., Kilby, K. T., Cox, A. and Fray, D. J., DC voltammetry of electro-deoxidation of solid oxides. *Chem. Rev.*, 2013, **113**(5), 2863–2886.

50. Heinze, J., Cyclic voltammetry – 'electrochemical spectroscopy', new analytical methods. *Angew Chem. Int. Ed. Engl.*, 1984, **23**, 831–847.

51. Bard, A. J. and Faulkner, L. R., *Electrochemical Methods, Fundamentals and Applications*, Wiley, New Jersey, 2000, 2nd edn.

52. Burstein, G. T., A century of tafel's equation, 1905–2005 – a commemorative issue of corrosion science. *Corros. Sci.*, 2005, **47**(12), 2858–2870.

53. Soghomoniana, V. and Heremans, J. J., Characterization of electrical conductivity in a zeolitelike material. *Appl. Phys. Lett.*, 2009, **95**, 152112, 1–3.

54. Daas, B. M. and Ghosh, S., Electro-oxidation of methanol and ethanol catalyzed by Pt/ZSM-5/C. *Electroanalysis*, 2017, **29**(11), 2516–2525.

55. Song, Y. *et al.*, High-selectivity electrochemical conversion of CO_2 to ethanol using a copper nanoparticle/N-doped graphene electrode. *Chemistry Select*, 2016, **1**(19), 6055–6061.