

# Carbon xerogel supported Pt and Pt–Ni catalysts for electro-oxidation of methanol in basic medium

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## Abstract

Highly mesoporous carbon was obtained by carbonization of a polymer xerogel previously synthesized via sol–gel condensation of resorcinol and formaldehyde. The investigation describes electro-oxidation of methanol in alkaline electrolyte using Pt and Pt–Ni catalysts supported on this high surface area mesoporous carbon. The electrocatalytic tests showed better performance of the catalysts when impregnated with this carbon support.

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## 1. Introduction

Use of noble metal based catalysts seems to be inevitable in direct methanol fuel cells. So far only platinum is chosen as the main anode and cathode material in polymer membrane fuel cells (PMFC) [1]. However transition metals (Cr, Ni) alloyed with platinum [2] as well as manganese oxides [3,4] are also found to be efficient catalysts to decrease the CO poisoning effect. Further these catalysts are effective to reduce the cost compared to pure platinum based electrodes. It is thus imperative to promote optimum utilization of the active catalyst component from within the electrode structure. This is often done by modulating the particle size of the catalyst and the pore structure of the carbon support. Thus Pt supported on microporous supports such as zeolite Y have been recently shown to exhibit enhanced activity for electro-oxidation of methanol [5].

It is known that mesoporosity and oxygenated surface of carbon support is believed to cause higher catalytic activities

in heterogeneous catalysis [6]. In the present investigation a new mesoporous carbon [7] is explored as a support material for Pt and Pt–Ni electrocatalysts with low metal loading  $\sim 1 \text{ mg cm}^{-2}$  in alkaline medium. Presence of nickel in Pt–Ni bimetallics is reported to alter the d-band vacancy in platinum thereby causing influence on geometric effects following chemisorption [8–10]. Nickel is also known to promote breaking of the C–H bond of methanol at the anode and the O=O bond rupture during the cathodic reduction of O<sub>2</sub>.

## 2. Experimental

### 2.1. Synthesis of carbon xerogel (CX) using a polymeric precursor

The polymer precursor was synthesized by condensation of resorcinol and formaldehyde using sodium carbonate as catalyst. The resulting hard brown coloured gel when pyrolysed at 800 °C under inert atmosphere produced mesoporous carbon as described elsewhere [7].

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## 2.2. Synthesis of 10% Pt/CX and 10% Pt–Ni/CX (7:3)

Ten weight percent Pt was loaded on CX by incipient wetness method; wherein calculated amount of chloroplatinic acid dissolved in a minimum amount of water (1.5 ml/g, which is just sufficient to fill the pores of the carbon material) was added dropwise under vacuum and ultrasonic mixing. The thick catalyst slurry was then dried under vacuum and kept overnight in an oven for further drying. Reduction of the metal precursor to its metallic state was achieved by slow addition of 0.1 M sodium formate at 60 °C. The catalyst was washed plentifully in hot water and then dried in an oven. The catalyst is referred to as Pt/CX. Similarly Pt–Ni catalyst on CX was prepared by sequential impregnation technique. Thus 3 wt.% Ni was initially impregnated on the carbon by using NiCl<sub>2</sub> dissolved in a minimal quantity of solvent and mixed thoroughly in an ultrasound bath under vacuum, for 90 min. The catalyst was then dried under vacuum and kept overnight in an oven. Subsequently 7 wt.% Pt was added from a calculated amount of chloroplatinic acid precursor. Pt–Ni/CX catalyst was then obtained in the same way as the Pt/CX catalyst.

## 2.3. Characterisation of the samples

The porous structure of the carbon xerogel was characterised by N<sub>2</sub> adsorption–desorption at 77 K using a Coulter 100CX Omnisorp sorptometer. The t-method was used to evaluate the mesopore surface area ( $S_{\text{meso}}$ ). X-ray powder diffractograms of the samples was obtained using a Rigaku diffractometer using Cu K $\alpha$  radiation of wavelength 0.1540 nm. The platinum load of the carbon was determined by atomic absorption spectrometry (AAS) using arc acetylene flame.

The total amounts of the oxygen-containing surface groups present on CX were determined by temperature programmed desorption (TPD-MS) using Dataquad quadrupole mass spectrometer.

## 2.4. Fabrication of the catalyst layer

The catalyst paste with nafion was made as follows: about 50 mg of the catalyst powder, 0.3 ml of 5 wt.% nafion solution and 3 ml of isopropyl alcohol were mixed in an ultrasonic bath for about 15 min. The thick slurry thus obtained was evenly spread over Toray carbon paper and dried in an oven at 110 °C for 1 h. Thus 2–3 coatings of the

catalyst slurry were applied one over the other and dried in an oven at 110 °C. The geometric surface area of the electrode was about 1 cm<sup>2</sup> having 10 mg of the catalyst powder which contained ~1 mg of metal.

## 2.5. Electrochemical measurements

The cyclic voltammograms (CV's) of the catalyst were recorded between –0.3 and 1.5 V at a sweep rate of 10 mV s<sup>–1</sup> using an EG&G PAR Potentiostat/Galvanostat model 273 A. Before recording the CV, the potential was repeatedly scanned in the same range at the sweep rate of 75 mV s<sup>–1</sup> until a reproducible voltammogram was obtained. The standard calomel electrode (SCE) and a platinum foil served as reference and counter electrodes, respectively. The catalytic activity was evaluated by potentiodynamic polarisation curves also with a sweep rate of 10 mV s<sup>–1</sup> in 0.5 M CH<sub>3</sub>OH and 0.5 M KOH at room temperature. The potential was then referred to that of the normal hydrogen electrode (NHE).

## 2.6. AC impedance studies

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Solartron Frequency Analyser coupled to an electrochemical interface also from Solartron. Z plot software was used for data acquisition using frequencies spanning from 65,000 to 0.001 Hz. The amplitude of the ac voltage was 10 mV. The electrochemical parameters were derived from the ac impedance spectra using non-linear square fitting procedure.

## 3. Results and discussion

Porosity is an important part of any nanostructure system for providing effective molecular transport path. A good electrocatalyst should exhibit multifunctionalities, which is a combination of several factors such as surface reactivity, electronic conductivity and facile surface transport of molecules. It is proposed that a typical electrocatalytic architecture need minimal microporous surface area while maximising surfaces accessible through mesopores [11]. From Table 1 it can be seen that the carbon material CX prepared in this work have a high BET surface area (724 m<sup>2</sup>/g), and nearly 75% of it is mesoporous. Such materials with micropores and mesopores within carbon network are

Table 1  
Electrocatalytic activity of the Pt/CX and Pt–Ni/CX catalysts in relation to their physicochemical characteristics

Sample	BET (m <sup>2</sup> /g)	$S_{\text{meso}}$ (m <sup>2</sup> /g)	CO + CO <sub>2</sub> ( $\mu\text{mol/g}$ )	%Metal content AAS	Tafel slopes (mV dec <sup>–1</sup> )	Current density (A g <sup>–1</sup> (Pt))		
						0.5 V	0.6 V	0.7 V
CX	724	524	926	–	–			
Pt/CX	630	396	–	8	113	13	15.4	19
Pt–Ni/CX	561	362	–	7.9	95	25	26	29

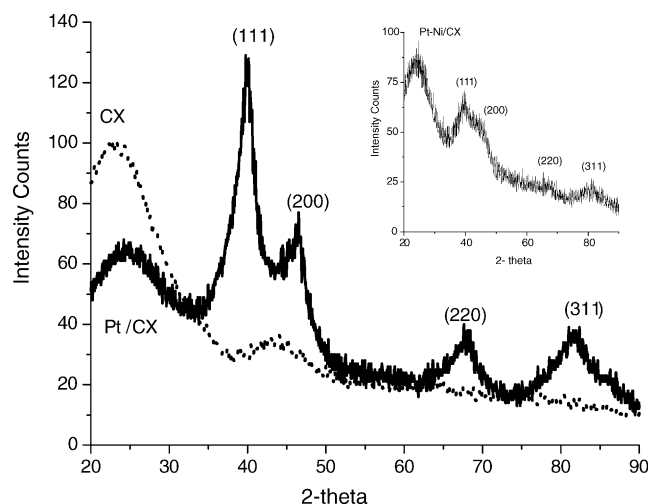


Fig. 1. X-ray diffraction patterns of Pt/CX, Pt–Ni/CX catalysts in relation to the unloaded mesoporous carbon CX.

known to possess excellent characteristics suitable for supercapacitors etc. [12]. When CX was impregnated with either Pt and/or Pt–Ni bimetal, the overall BET surface area as well as mesoporous surface area decreased. The BET surface area decreased by  $\sim 13$  and  $23\%$ , respectively for the two samples. The corresponding decrease in mesopore surface area was  $25$  and  $31\%$ . This decrease was expected as part of the mesopores could be covered by the metals Pt and the Pt–Ni bimetallics.

The TPD–MS investigation revealed presence of large number of surface oxygenated groups as evident from the release of  $\text{CO} + \text{CO}_2$  (Table 1). These surface groups anchor the metal precursors during the catalyst synthesis. This results in better dispersion of the active component with consequent lowering of the particle size. Thus the average particle size as calculated from the XRD pattern using Debye–Scherrer formula was  $\sim 10$  nm (Fig. 1). The metal load of platinum as well as Pt–Ni as determined from AAS (Table 1) agreed well with the calculated metal load of  $10\%$ . Further the electrochemical impedance spectra of CX represented through Nyquist plot (Fig. 2). The nature of the profile is in agreement with that observed for a multiwalled carbon nanotube material having supercapacitor properties [13]. The mesoporous carbon synthesized here thus showed it to be an excellent electronic conductor and an almost ideal capacitor.

The electrocatalytic activity can be conveniently expressed by measuring the current delivered at some fixed over potential. For convenience the currents obtained from the  $I$ – $V$  plots (Fig. 3) at potentials of  $0.5$ ,  $0.6$  and  $0.7$  V are presented in Table 1. It can be seen from the values of current (Table 1), that Pt–Ni showed higher catalytic activity compared to Pt by factor of  $\sim 1.6$  at room temperature at the usually expected values of Tafel slopes of  $\sim 113$  and  $95$   $\text{mV dec}^{-1}$  for the two catalysts. Markovic et al. [14] have

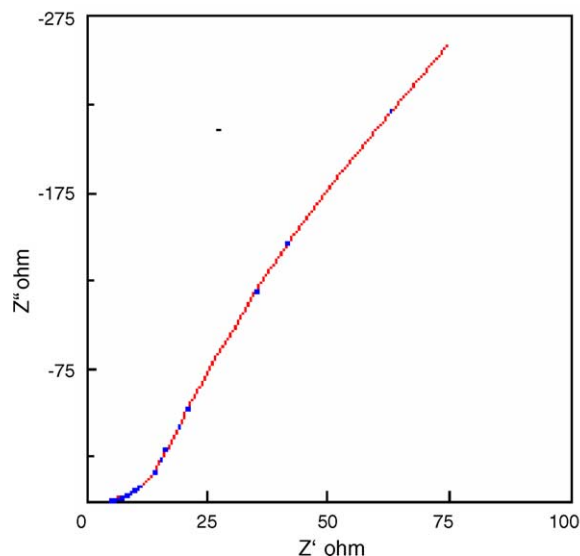


Fig. 2. Electrochemical impedance spectra of CX represented by Nyquist plot.

reported higher activity for Pt catalysts in alkaline medium as compared to that in acid medium. The higher activity of Pt–Ni/CX catalyst is attributed to synergistic interaction between Pt and Ni. Although such promotional effects of the second component are well known for methanol electro-oxidation [9], what is noteworthy here is the large values of current when the active components are supported on the mesoporous carbon CX of the present work. This good performance is attributed to the good ionic as well as electronic conductivity and low fluid diffusional limitations offered by the mesoporous support.

Cyclic voltammetry profiles are shown in Fig. 4. The nature and shape of the voltammetric curve for Pt/CX in alkaline medium (Fig. 4a) is analogous to that reported in literature [14]. Such profiles are typically those observed on the bulk electrode wherein the onset of methanol oxidation is observed around  $0.95$  V. However, different voltammetric behavior is observed in the case of Pt–Ni/CX bimetallic (Fig. 4b) wherein two broad peaks in the potential range of

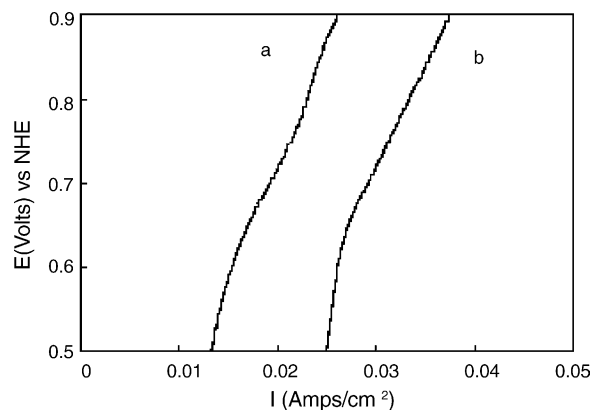


Fig. 3.  $I$ – $V$  plots of (a) Pt/CX and (b) Pt–Ni/CX in  $0.5$  M  $\text{CH}_3\text{OH}$  and  $0.5$  M  $\text{KOH}$  at a scan rate of  $10$   $\text{mV s}^{-1}$  in potential range  $0.5$  to  $-0.9$  V NHE.

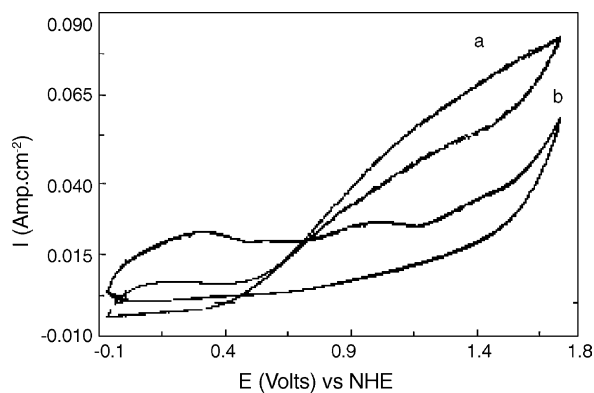


Fig. 4. CV profiles of (a) Pt/CX and (b) Pt-Ni/CX recorded in 0.5 M CH<sub>3</sub>OH and 0.5 M KOH at scan rate of 10 mV s<sup>-1</sup> at room temperature.

0.1–0.4 V and 0.8–1.1 V are observed. Previous investigations on either supported or unsupported Pt–Ni catalysts in acidic medium [8,9] did not report any such peak in the potential range of 0.1–0.4 V. This unique peak observed in alkaline medium could be due to adsorption of OH species from KOH solution while the second broad peak is the normally assigned peak for the oxidation of methanol. It is believed that OH<sup>-</sup> of the alkaline medium facilitates abstraction of protons from adsorbed methanol by preferential C–H bond cleavage resulting in formation of loosely bonded (CO)<sub>x</sub> clusters on Pt–Ni nucleation centers as envisaged earlier [5]. The mesoporosity of the surface could assist in more facile decomposition of (CO)<sub>x</sub> clusters into CO<sub>2</sub>, in addition to providing facile diffusion paths to the reactants/products during the electro-oxidation of methanol. Thus CV profiles signify that different mechanism operates on Pt–Ni and Pt catalysts supported on the high surface area mesoporous carbon and requires further studies. The behavior of CV is similar to that was observed on Pt–Mo electrocatalysts for CO and methanol oxidation as reported by Baltruschat et al. [12].

#### 4. Conclusions

- (1) Mesoporous carbon xerogel acts as a good support material due to presence of surface groups, high porosity and excellent capacitor properties.

- (2) The carbon using high surface area can provide better ionic conductivity and fluidity for the reactants and/or products during electrocatalytic oxidation of methanol.
- (3) Pt–Ni/CX showed better performance than Pt/CX in alkaline medium for the electrocatalytic oxidation of methanol. Different shapes of CV on Pt/CX and Pt–Ni/CX indicates that different mechanism operates on Pt–Ni/CX than on conventional Pt surfaces.

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