



## Platinum nanophase electro catalysts and composite electrodes for hydrogen production

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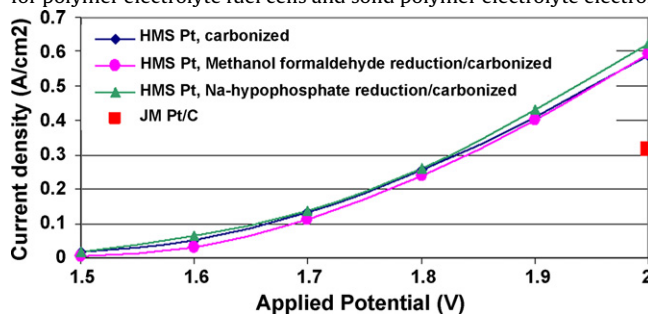
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### ABSTRACT

Nanophase Pt electro catalysts were prepared by impregnating a Pt salt containing solution upon a high surface area hexagonal mesoporous silica (HMS) matrix, which was then carbonized to varying degree by chemical vapour deposition of liquid petroleum gas (LPG). Thereafter the HMS Si matrix could be removed by chemical etching with NaOH to immediately form a Pt containing carbon analogue or ordered mesoporous carbon (OMC) with a porous structure similar to the parent HMS. Nanoparticles of Pt electro catalysts were thus successfully stabilized without agglomeration on both HMS and upon the porous HMS carbon analogue or OMC, which was graphitic in nature. The catalysts were electro active for the hydrogen evolution reaction and their activity compared favourable with an industry standard. Such nanophase Pt electro catalysts could be incorporated successfully in a composite electrode by sequential deposition, upon a suitable substrate and the catalysts in electrodes so formed proved to be stable and active under high-applied potential in high electrolyte environment for hydrogen production by electrolysis of water. This route to preparing a nanophase Pt OMC catalyst may be applicable to prepare active electro catalysts for polymer electrolyte fuel cells and solid polymer electrolyte electrolyzers.



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### 1. Introduction

Electrochemical production of hydrogen is possible by water electrolysis. Water electrolysis is a non-polluting process, if high current densities can be obtained for a low energy input and particularly if performed in low electrolyte environments using renewable energy. With the strong emphasis upon waste reduction and reuse, the development of suitable high activity electro cata-

lysts that can be incorporated into composite electrodes for water electrolysis has a large commercialisation potential.

Composite electrode surfaces containing catalytic nanophases should result in high activity because of geometry, electro conductivity, high surface area, enhanced porosity and transport of reagents and products. Application of highly dispersed nanoscale active components may reduce the over potential of electro catalytic reactions such as water electrolysis resulting in overall increase in energy efficiency of the processes.

The greatest challenge at present is to find effective nanosynthesis procedures [1]. Nanoparticles of catalytically active metals may be deposited on inorganic supports, such as mesoporous materials [2–4] in order to prepare nano-composite materials suitable for electro catalysis. Enhancement of catalytic reactivity can be expected by matrix support of ultra fine particles.

*Abbreviations:* BET, Brünauer–Emmett–Teller method; CVD, chemical vapour deposition; LPG, liquid petroleum gas; OMC, ordered mesoporous carbon; HMS, hexagonal mesoporous silica; SEM-EDS, scanning electron microscopy–energy dispersive X-ray spectroscopy; XRD, X-ray diffraction.

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Aggregation of the unstable highly dispersed nanophase state can be prevented due to the porous micro-texture and to interfacial interactions with the support.

In the surface coverage of a substrate with catalysts, the relatively low amount of active sites obtainable per unit area in a two dimensional plane has to date not resulted in sufficiently high catalytic activity for overcoming the barrier to producing cost competitive catalytic electrodes for hydrogen production or fuel cell applications. By use of porous three-dimensional supports, the highest number of active sites per unit volume may be obtained. Nanophases could be deposited on these high surface area three-dimensional mesoporous supports [5–9]. Metal salts may be impregnated in these inorganic silica-based porous materials for the preparation of supported metal nanoparticles. Inorganic hexagonal mesoporous silica (HMS) [10,11] and MCM-41 [12] materials have three-dimensional nanometer pores that are much larger (20–50 Å) than that typical for microporous zeolites (3–7 Å). Synthesis of Pt nanoparticles upon mesoporous materials may allow production of nanophase catalysts in a narrow nanoparticle size distribution, with a high stability. Recently, graphitic ordered mesoporous carbon (OMC) materials have been prepared using HMS as template via a chemical vapour deposition (CVD) route [13].

Synthesis of Pt nanoparticles within the matrices of mesoporous materials such as HMS or ordered mesoporous carbon materials as supports may allow production of nanophase catalysts in a narrow nanoparticle size distribution, with a high stability, in a three-dimensional array without pore blocking. Nanophases thus may be handled in bulk, and optimally dispersed and stabilized upon the mesoporous support for the exposure of the maximum number of active sites to the reactant. Since Pt is electro active and simultaneously conductive, the close proximity of such particles to each other upon the support pore walls would in theory provide an electron pathway for the applied electrical charge even on a non-conducting inert support as well as provide the required bare metal sites in close proximity for the dissociation of the reactant, H<sub>2</sub>O.

The aim of the study was to utilize the pore space of these ordered mesoporous materials as a high surface area support to stabilize uniformly sized, small and active nanoparticles of electro active metals. Prerequisites for such systems are complex. Firstly, the uniform, nano-sized pores of the mesoporous support matrix should act as a stable, constraining environment to prevent re-agglomeration of the highly dispersed, unstable, nanophase electro catalytic metals during water electrolysis for hydrogen production whilst also achieving the highest number of active sites per unit volume. The mesopores of the support should be large enough to accommodate Pt nanoparticles and yet enable diffusion of aqueous reactant through the porous matrix to the electro active metals encapsulated in the pore space, as well as allow product gas evolution. The composite catalysts should be electro catalytically active. Furthermore, it is not suitable to utilize these materials in powder form in electro driven reactions; therefore the composite electro catalyst would need to be stabilized upon a suitable conductive substrate in thin film format using binders in order to prepare a stable and durable thin film gas diffusion electrode whilst retaining sufficient electro activity. All these challenges were considered in this study.

## 2. Experimental

### 2.1. Synthesis and characterization of nanomaterials

HMS is not commercially available, therefore this material was synthesized and detemplated according to standard methods [10,11] and surface area characterization by N<sub>2</sub> BET was per-

formed upon the detemplated products obtained. The HMS was prepared at room temperature, using tetraethyorthosilicate as Si source and 1-dodecylamine as template. Pt was supported upon the mesoporous HMS by incipient wetness impregnation. 0.1545 M H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (hexachloro platinumic acid) solution was prepared by adding exactly 12.45 ml deionised water to 1.00 g PtCl<sub>6</sub>·6H<sub>2</sub>O. 1 g of the HMS support was impregnated with 2 ml of 0.1545 M H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O hexachloro platinumic acid solution. Reduction of Pt salts to form Pt metal nanoparticles on microporous or mesoporous materials can be achieved by thermal reduction using H<sub>2</sub> or in this study by various previously developed chemical means [14], namely the use of a methanol/formaldehyde reduction method, reduction by NaH<sub>2</sub>PO<sub>2</sub> and finally by carbonization with LPG. In the case of methanol/formaldehyde, the Pt seeding procedure was initiated by submerging the Pt impregnated sample in 2 ml of methanol/formaldehyde solution (20% deionised water, 27% methanol and 53% formaldehyde (37–40%)) for 60 min. The slurry was then dried in a hot-air oven at 100 °C for 60 min. The sample was removed from the oven, after which 6 ml of the methanol/formaldehyde solution was added and the formed slurry was left at room temperature (±32 °C for 24 h). Thereafter, the sample was heated again for 60 min at 100 °C, cooled, rinsed, filtered and dried. In the case of reduction by NaH<sub>2</sub>PO<sub>2</sub> a solution of 0.48 g of sodium hypophosphite was made in 10 ml H<sub>2</sub>O. 2.5 ml of this solution was added to 1.0 g of various Pt impregnated samples that had been impregnated by the incipient wetness technique. Samples were dispersed in the NaH<sub>2</sub>PO<sub>2</sub> solution and then placed in a hot air oven at 50 °C for 4.5 h. As no significant reduction was observed, the oven temperature was increased to 100 °C overnight in sealed containers. Thereafter the samples were thoroughly rinsed and dried at 80 °C.

In specified cases, the pre-reduced or unreduced HMS Pt electro catalysts were carbonized for various times using a chemical vapour deposition method with low cost commercial grade LPG as feed prior to incorporation of the powder electro catalysts into catalytic inks. For all CVD experiments done, the LPG was sourced from Afrox (South Africa). The LPG is a mixture of propane, butane, propylene and contains small amounts of ethyl mercaptan for odorizing the gas. The carbonization procedure was as follows: ceramic boats, each containing 1 g of the Pt impregnated and reduced or unreduced HMS starting material was placed in a flow through quartz tube furnace. From a starting temperature of 50 °C and subsequent heating rate of 1.67 °C min<sup>-1</sup>, the furnace was heated to a target temperature of 800 °C, under a constant flow of commercial grade liquefied petroleum gas (LPG). When the furnace reached the target temperature, the flow of LPG through the system was sustained from 15 up to 90 min. Thereafter, the LPG flow was stopped and the samples were allowed to cool to room temperature. After the carbonization process, a portion of each sample was treated with 50 ml of 1 M NaOH in solution at 75 °C under stirring in order to remove the HMS Si matrix. The resulting silica etched porous carbon analogue material was washed with ultra pure water and dried in an oven at 100 °C. Particle characterization of electro catalysts was performed using XRD, BET and TEM.

Carbonization was performed in order to investigate how long the CVD process should be and whether a carbon analogue of the parent HMS could be obtained by pore infiltration of the HMS with the carbon source followed by removal of the silica matrix. It was also of interest to ascertain whether different carbonization times would lead to improved electro conductivity or catalytic performance of Si containing samples because of an increase in the contact between the surface of the electro catalyst and the conductive carbon black phase added to the catalytic ink. This carbonization process could also replace the various metal reducing procedures described above.

## 2.2. Incorporation of nanomaterials by sequential deposition in thin films for electro active composite electrodes

Nanophase composite electrodes were formed by sequential deposition, through preparing admixtures of the prepared powder form, Pt nanophase-containing electro catalysts with dispersant ultra pure water and isopropanol and binder/proton conductive phase (Nafion® LIQUION 1100). Typically an ink was prepared as follows: the specified amount of electro catalyst was mixed together with ultra-pure water and isopropanol. Thereafter a binder solution was added, which was a 5% Nafion solution in most cases. The ink mixture was placed in an ultra sonic bath for an hour to disperse the particles and form a homogeneous ink. Prior to use, the ink was magnetically stirred continuously to prevent precipitating of the particles. The catalytic inks contained conductive phases in ratios of solids that took consideration of the percolation threshold. The micro-emulsion or ink so formed was coated upon a conductive substrate by deposition using spray coating or manual painting. The substrates that were used to support the ink layer to form the composite electrode was carbon black on carbon cloth (code: 6100–200 CB) supplier Lydall; carbon cloth, thickness: 500; (code: 6100–300) supplier Lydall, which is a typical fuelcell type of gas diffusion layer (GDL); or titanium fibre mesh (Bekenit, SaitamaKen, Japan) which is a suitable conductive substrate for high electrolyte environments.

## 2.3. Characterization of thin film gas diffusion electrodes and evaluation of their suitability for application in hydrogen production

Linear sweep experiments on all the powder form electro catalysts were conducted at 25 °C, in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The reference electrode was a Standard Calomel Electrode (SCE) in 3 M KCl and the counter electrode was platinum wire. The scanning range was 0.0 to –1.5 V at a scanning rate of 20 mV s<sup>-1</sup> with a step potential of 15 mV using a glassy carbon area of 0.8 cm<sup>2</sup> upon which the catalytic ink was deposited in thin film form.

Physical-chemical, and structural studies of prepared composite electrode materials containing the nanophase electro catalyst were performed using the dynamic analysis method of mapping from micro-PIXE data and stereo optical micrographs.

Electrochemical testing of composite electrodes prepared using HMS/Pt/LPG<sub>90</sub> were performed in order to determine the prepared electrodes' stability, durability and activity for hydrogen generation by water electrolysis in a high electrolyte environment. The composite electrodes, prepared in the manner specified, were suspended in 40% KOH in a two electrode configuration, one compartment cell, electrochemical analyses was performed on various samples by use of chrono amperometry. A large surface area circular basket Pt or Ni mesh counter electrode was used. These experiments were performed at 0–5 °C or at 60 °C whilst stirring magnetically. A geometric 1 cm<sup>2</sup> of each high surface area composite nanophase electrode sample was subjected to an applied potential in preset steps from 1 up to 6 V over 60 s. The potential was increased at the end of each time interval, at which time the current was sampled and a comparison of the activity for water electrolysis was made between the fabricated composite gas diffusion electrodes.

## 3. Results and discussion

### 3.1. Synthesis and characterization of nanophase electrocatalysts

The BET surface area of synthesized and detemplated HMS was 903 m<sup>2</sup> g<sup>-1</sup> and the average pore diameter was 2.7 nm. After

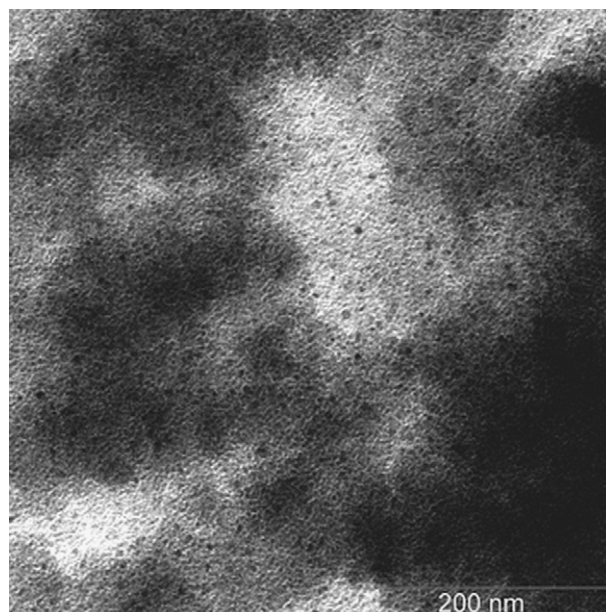
**Table 1**

Summary of particle size and catalytic activities towards the hydrogen evolution reaction (HER)

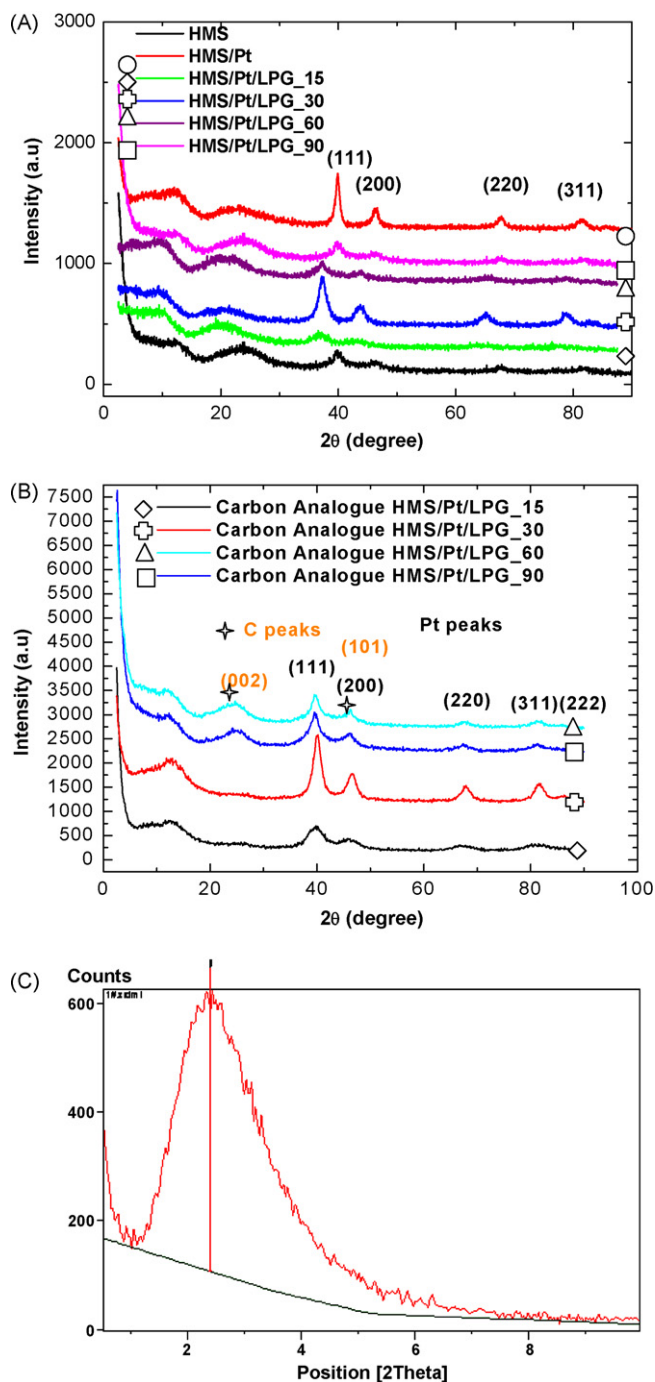
Material	LPG carbonization times (min)	Current density (J mA <sup>-1</sup> cm <sup>-2</sup> )	XRD particle size (nm)
HMS	0	0.7	–
HMS/LPG	15/30/60/90	0.6/0.5/0.6/0.6	–
HMS/Pt	0	5.0	8.37
HMS/Pt/LPG <sub>15</sub>	15/30/60/90	1.4/2.1/3.9/3.4	2.3/5.2/2.7/3.2
CA_HMS/Pt/LPG <sub>15</sub>	15/30/60/90	8.6/8.9/8.2/6.0	2.0/4.5/4.9/2.5/3.3
JM/Pt/C	0	9.70	4.2

impregnation of Pt salts upon HMS, reduction of Pt metal salts to form Pt nanoparticles included use of a methanol/formaldehyde reduction method, reduction by H<sub>2</sub> (thermal reduction) and reduction by NaH<sub>2</sub>PO<sub>2</sub>. Various Pt size ranges were achieved depending upon the reduction conditions applied. It was found that the CVD carbonization process using LPG could act simultaneously as reductant of Pt, LPG serving as an auto reduction agent, to reduce the Pt salt (Pt<sup>4+</sup>) to the metal (Pt<sup>0</sup>) whilst retaining a small nanoparticle size (Table 1) thus it was not necessary to pre-reduce the catalysts prior to the carbonization step. Table 1 shows the relative Pt particle sizes as determined by the Scherrer equation from XRD line broadening after carbonization for various times. Carbonization as reduction method was the simplest and most effective method to achieve the smallest particle sizes which ranged between 2.0 and 5.2 nm depending on the carbonization time. Fig. 1 shows the highly dispersed state of Pt nanophase metal that could be achieved on HMS supports using methanol/formaldehyde reduction, which shows that this may also be a suitable route for Pt reduction, to achieve small particle sizes. On the other hand, thermal reduction (at temperatures in excess of 400 °C) generally resulted in sintering of the nanoparticles on the mesoporous HMS matrix and some cluster formation and this route was not suitable for reduction of Pt upon a carbon matrix. The reduction by NaH<sub>2</sub>PO<sub>2</sub> resulted in agglomeration of Pt particles. Bare metal nanoparticle sizes ranged from below 8 nm or up to 60 nm when supported on HMS and reduced chemically with NaH<sub>2</sub>PO<sub>2</sub>.

XRD spectra of the Pt impregnated sample series denoted HMS Pt LPG (\_15, \_30, \_60, \_90 suffix denoting the time in minutes of



**Fig. 1.** TEM micrograph of HMS Pt LPG after methanol/formaldehyde reduction.



**Fig. 2.** XRD spectra of (A) HMS Pt LPG series compared to HMS and HMS Pt; (B) carbon analogues of the Si etched HMS/Pt/LPG series; (C) low angle XRD of Pt containing OMC.

carbonization) were compared to HMS Pt and HMS LPG as baseline materials (Fig. 2(A)). The XRD spectra shows the characteristic (111), (200), (220) and (311) peaks for fcc Pt in the HMS Pt LPG sample series. The Pt peak width broadening is characteristic of nano-sized particles. In the Pt impregnated and methanol formaldehyde reduced HMS sample (HMS Pt) these peaks are well resolved, and are absent in the sample without Pt (HMS). Graphitic carbon peaks (from the CVD carbonization process using LPG) that lie at  $2\theta$  values of  $25.6^\circ$  and  $43.7^\circ$  with miller indices (002) and (101), respectively could not be distinguished in the HMS/Pt/LPG series as the peak of amorphous Si in the pore wall of the meso-

porous material was superimposed and overlaps with the peak at  $25.6^\circ$  and that at  $43.7^\circ$  overlaps with the broad peak at  $46.22^\circ$  of Pt (200). Peak shifts for some samples are attributed to goniometer misalignment. In Fig. 2(B), the XRD spectra of the Pt containing carbon analogue samples are presented after removal of the HMS Si matrix by NaOH etching. Energy dispersive spectroscopy indicated less than 5% of Si remaining after etching away the Si matrix with NaOH.

Graphitic carbon peaks at  $2\theta$  values at  $25.6^\circ$  and  $43.7^\circ$  with miller indices (002) and (101), respectively, were obtained that indicates that in the case of the Pt containing samples carbonized for 60 and 90 min of CVD with LPG, and subsequently etched with NaOH, a Pt containing graphitic porous carbon analogue of the HMS substrate is formed. The crystalline fcc Pt catalyst nanoparticles are retained upon the carbon analogues with similar particle sizes to the size determined before etching. All the Pt peaks are still evident in the carbon analogues; for the latter carbon  $2\theta$  value, there was a significant carbon peak overlap with the Pt (200) peak.

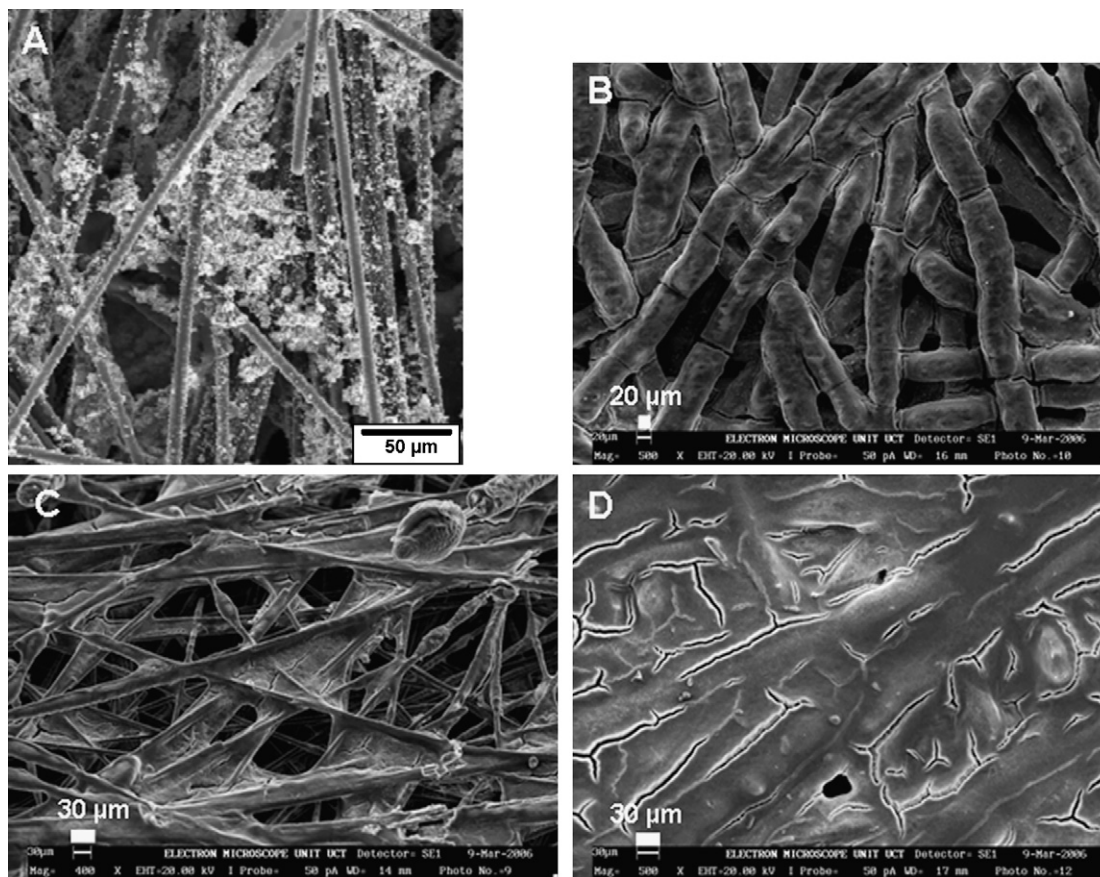
A Pt containing ordered mesoporous carbon was thus formed by removal of the porous Si HMS matrix. Moreover, these Pt containing carbon analogues or Pt OMC retained the nanoporous HMS structure as can be seen from the low angle XRD spectra in Fig. 2(C). Further investigation is underway in order to establish the degree of graphitization [13] and the porosity obtained once Pt is incorporated into OMC in this manner.

Table 1 shows the relative Pt particle sizes of the prepared powder form electro catalysts as determined by the Scherrer equation from XRD line broadening and also the electro activity of the electro catalysts powders towards the hydrogen evolution reaction (HER) were determined by linear sweep voltammetry. Current densities of the electro catalysts as presented in Table 1 were obtained at a potential of  $-1.5$  V (versus Standard Calomel Electrode in 3 M KCl).

HMS is generally non-catalytic. Yet, a reasonable current density at  $-1.5$  V of  $5 \text{ J mA}^{-1} \text{ cm}^{-2}$  was obtained for HMS/Pt. Since Pt is electro active and simultaneously conductive, the close proximity of Pt particles to each other upon the Si-based HMS support pore walls are thus shown to have provided an electron pathway for the applied electrical charge as well as provided the required bare metal sites for the dissociation of the reactant,  $\text{H}_2\text{O}$  even when Pt was supported on an inert non-conductive porous Si support such as HMS. Further studies are underway to optimize the degree of Pt loading necessary to obtain higher electro activity.

After carbonization, it is apparent in Table 1, that changes in HER current density, ranging between  $1.4$  and  $3.9 \text{ J mA}^{-1} \text{ cm}^{-2}$  at  $-1.5$  V were observed for HMS/Pt/LPG sample series upon increased carbonization periods in the case of carbonized samples, prior to removal of the HMS Si matrix. Increasing carbonization times resulted in an increase in the electro activity for HMS materials containing Pt (denoted HMS/Pt/LPG series in Table 1), indicating that the degree of carbonization improved electro activity by between 2 and 3 times, which electro activity however was low compared to the HMS/Pt sample without carbon and to the CA.HMS/Pt/LPG-series prepared. It is thus evident that prior to the removal of the HMS Si matrix the deposition of the CVD carbon layer coated the Pt nanoparticles and may have occluded the active sites, limiting their electro catalytic activity. However, these Pt containing samples were more active than the HMS and HMS/LPG samples.

Once the HMS Si matrix was removed by etching the carbonized samples with NaOH, and thus creating Pt containing OMC material (denoted CA.HMS/Pt/LPG-series in Table 1), the deposited Pt was again exposed and a significant increase of electro activity ranging between  $8.2$  and  $8.9 \text{ J mA}^{-1} \text{ cm}^{-2}$  at  $-1.5$  V was observed in the case of the Pt OMC catalysts so obtained. The electro activity of the prepared catalysts were only slightly lower than that of the industry standard carbon-based Johnson Matthey Pt/C electro catalyst



**Fig. 3.** SEM micrograph of substrate with catalytic ink (Nafion and Pt/C electrocatalyst from Johnson Matthey) deposited by (A) manual painting and (B–D) spraycoating; on Ti fibre mesh (B); on carbon cloth (A, C and D).

( $9 \text{ J mA}^{-1} \text{ cm}^{-2}$  at  $-1.5 \text{ V}$ ) when tested by linear sweep voltammetry under the applied conditions.

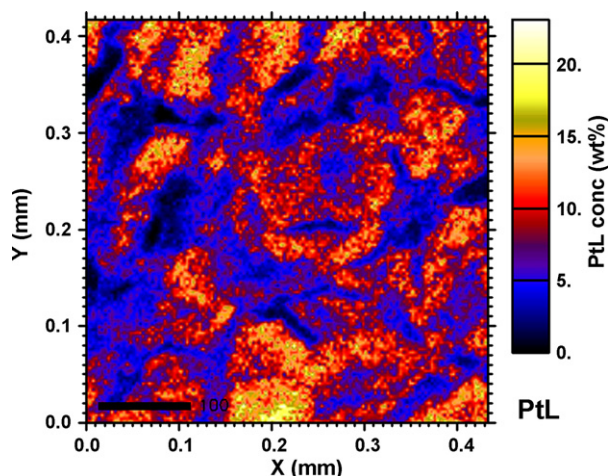
It is interesting to note that even on an insulating mesoporous substrate such as Si-based HMS it is possible to achieve electro catalytic activity by the incorporation of Pt nanoparticles, which was significantly enhanced by carbonization followed by removal of the HMS Si matrix. In this way a platinum containing ordered mesoporous carbon (Pt/OMC) analogue of HMS could be obtained and the OMC acted as a conductive and porous support or carrier for the active Pt nanophase electro catalyst.

The TEM micrographs and XRD results show that it was possible to successfully achieve high density and dispersion of Pt nanophases across the very high surface area of nanoporous HMS supports using relatively simple preparation procedures. It is particularly noteworthy that in the case of the Pt supported on HMS and reduced via the carbonization procedure, very small Pt nanoparticles are evenly dispersed upon the HMS or its carbon OMC analogue. The small Pt particle size was maintained after carbonization and removal of the HMS Si matrix as can be seen from XRD particle sizing results (Table 1). In the Pt/OMC samples (CA\_HMS/Pt/LPG\_series) the particle sizes ranged between 2.0 and 4.9 nm, whereas the particle sizes ranged between 2.3 and 5.2 nm in the case of the HMS/Pt/LPG series. Thus using this route nanophase Pt electro catalysts were successfully stabilized without agglomeration on both HMS and upon the carbon analogue OMC formed by carbonization of HMS and subsequent removal of the HMS Si matrix. A very uniform, three-dimensional nanoparticulate array of Pt metal nanoparticles was thus achieved in these porous materials with a size well below 8.4 nm, which was the particle size obtained in the case of HMS/Pt.

### 3.2. Incorporation of nanomaterials by sequential deposition in thin films for electroactive gas diffusion electrodes

Ink formulations that were used to prepare thin films were optimized using the commercial Pt/C electro catalyst. Optimized ink formulations were deposited upon the selected substrate (Section 2). The substrate material was firstly tested for any activity towards the hydrogen evolution reaction prior to deposition of catalytic thin films and was generally not active below an applied potential of 2 V. Lydall carbon cloth, thickness: 500 mm, 6100–300 was hydrophilic and showed the best and most durable performance as a substrate in hydrogen production. This material is suitable as a conductive gas diffusion layer in polymer electrolyte membrane (PEM) systems such as fuel cells and PEM electrolyzers. Fig. 3(A–D) shows SEM micrographs of carbon cloth and Ti substrates with catalytic ink deposited by manual painting or by spray coating. It is evident that good surface coverage of the support substrates could be obtained in the case of spray coating with the catalytic ink. The thickness of the catalytic film upon the substrate depended upon the desired catalyst loading which was optimized to between 0.03 and  $0.04 \text{ g geometric cm}^{-2}$ .

Spray coating was found to be the most suitable method for deposition of the ink upon the substrate but was laborious and time consuming. Some crack formation was observed in the electrodes (Fig. 3D). It was concluded that crack formation could be caused by excessive loading or by the different co-efficient of expansion between the thin film layers including the binder Nafion® and the conductive substrate, resulting from excessive shrinkage during drying after spraycoating.



**Fig. 4.** Elemental distribution map calculated by dynamic analysis method of mapping from micro-PIXE data of Pt gas diffusion electrodes (Pt/C electrocatalysts from Johnson Matthey).

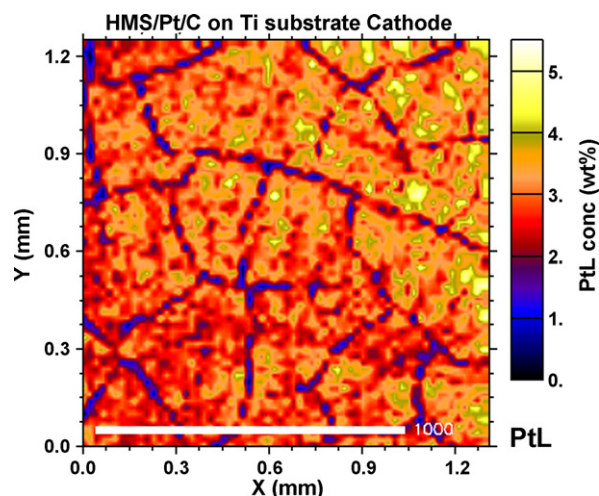
It was important to obtain the critical concentration of conductive phase to reach the percolation threshold, i.e., to enable an electronic long range (d.c.) charge transport. Electro catalyst loadings of 0.03 and 0.04 g geometric  $\text{cm}^{-2}$  of gas diffusion electrode showed an increase in current and conductivity. At these loadings the electronic conduction is assisted by the other components such as the carbon support, and the insulating effect of the binder Nafion<sup>®</sup> was found to be minimal after suitable electrode moisturization.

### 3.3. Characterization of thin film gas diffusion electrodes

Homogeneous distribution of nanophases was dependent upon the deposition method, the electro catalyst and the substrate type as well as the ink formulation. Fig. 3(A–D) shows the distribution of the ink on selected electrodes prepared on different substrates by different means as illustration. Distribution of nanophases upon the substrates was determined by the dynamic analysis method of mapping from micro-PIXE data. Selected results show that the electro catalysts were not homogeneously dispersed in the inks or on substrates in all cases. For instance, agglomeration of the commercial JM Pt/C electro catalyst particles was visible by PIXE when deposited upon the hydrophilic carbon cloth (Fig. 4), but much less agglomeration and a greater homogeneity was observed when HMS Pt was deposited upon Ti mesh although crack formation was still apparent (Figs. 5 and 6). The agglomeration of the ink contents could be caused by surface free energy or interfacial tension effects upon the substrate or interparticular attraction of electro catalysts or conductive phases in the ink. In future work this aspect will receive attention.

### 3.4. Evaluation of suitability for application in hydrogen production

The Pt-based composite electrodes were applied in electrochemical generation of hydrogen by water electrolysis in a high electrolyte (40% KOH) environment. Table 2 gives an example of electro activity for a composite gas diffusion electrode containing Pt HMS at 0 °C in 40% KOH during rapid screening using chrono voltammetry. The electrochemical response of the nanophase composite electrodes, prepared by sequential deposition, was evaluated. The relative electro activity of various combinations was initially determined at low temperatures in liquid electrolyte sys-



**Fig. 5.** Elemental distribution map calculated by dynamic analysis method of mapping from micro-PIXE data of HMS/Pt/LPG dispersed upon Ti fibre mesh electrode substrate.



**Fig. 6.** Stereo optical micrograph (150 $\times$ ) of HMS/Pt/LPG dispersed upon Ti fibre mesh electrode substrate.

tems in order to screen prospective candidate electro catalysts and optimize ink formulations as well as to reduce the effect of nuisance variables such as temperature changes during testing. Hydrogen production in the alkaline electrolyte was used as a simple and relatively rapid qualitative measure of the electro catalytic activity of the nanophase electro catalyst in this composite format. Because of the three-dimensional nature of composite electrodes (Fig. 3), it is necessary to remember that activity data presented during rapid screening have not been normalized for active surface area, but are based on a geometric 1  $\text{cm}^2$  of composite electrode, therefore the results of rapid screening in the high electrolyte environment are qualitative. Poor catalytic perfor-

**Table 2**

Rapid screening of composite gas diffusion electrode containing Pt HMS (carbonized) at 0 °C in 40%KOH using chrono voltammetry

Volts	Blank carbon cloth	Pt HMS carbonized
1	0	0.005021
2	0.000149	0.105672
3	0.00284	0.153824
4	0.1198	0.331765
5	0.3442	0.556639
6	0.58	0.813782

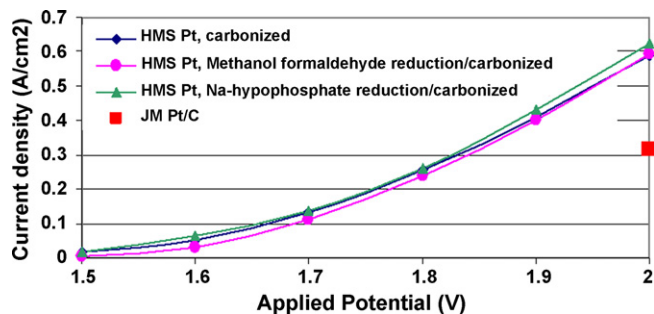


Fig. 7. Comparison of electroactivity of Pt on HMS composites prepared by sequential deposition with binder (Nafion), conductive phase and nanophase upon carbon-based support for high electrolyte water electrolysis (conditions: 60 °C; 40% KOH).

mance for hydrogen production was taken as a simple measure of the occlusion of catalytic sites by binders or the lack of adequate conductive pathways and was used as rapid indicator for optimization of formulations of micro-emulsions or inks. The expected high gas evolution under the applied potential (up to 6V) was used as an accelerated aging test of the stability and durability of the composite electrode components. Delamination of the catalytic component during high gas evolution was used as a simple measure of inadequate stabilization of the thin film upon the substrate.

Since initial rapid testing of the electro catalysts at 0 °C in 40% KOH (Table 2) did not allow a true comparison to be made with standard electrode materials working at the optimum electrolysis temperature of above 60 °C in 40% KOH, these electro catalysts were tested at higher temperatures using a Ni mesh counter electrode. Selected results are presented (Fig. 7 of chrono amperometric analysis of the activity of composite electrode materials for hydrogen production by electrolysis of water). The comparison of electro activity was performed with electrodes prepared by sequential deposition of the catalytic ink, containing binder (Nafion), conductive phase (carbon black) and nanophase HMS Pt that had been reduced by different methods (methanol formaldehyde or carbonization with LPG). The ink was deposited by spraycoating upon carbon cloth support substrate (carbon cloth, thickness: 500 mm, 6100–300). Electrodes prepared in the same way but using the commercial Pt/C (40%) from Johnson Matthey as electro catalyst were used as baseline comparison.

The conductive substrate itself showed virtually no activation below an applied potential of 2V under the conditions tested. At these higher testing temperatures composite electrodes, containing Pt on HMS reduced in different ways, achieved current densities of about 600 mA cm<sup>-2</sup> at an applied potential of -2V, which was higher than the performance of the electrode prepared with the commercial Johnson Matthey Pt/C catalyst which only achieved a current density of 317 mA cm<sup>-2</sup> under the conditions applied (Fig. 7).

### 3.5. Discussion

Although the commercial catalyst did not perform as well as the newly prepared electro catalysts once processed into composite form in the electrode configuration, it was slightly more active when tested by linear sweep voltammetry (Table 1). This could indicate that the method of electrode preparation could have negatively impacted on its activity due to occlusion of electro active metals by binders or due to the observed excessive agglomeration of the Pt/C catalyst in the composite (Fig. 4), making it difficult for all catalytic sites to be available for reaction. Homogeneity of elec-

trodes and high dispersion of the active component was improved by improving ink formulations, matching the substrate type and electro catalyst and improving the deposition methods.

Most recent efforts have focused upon the optimization of methods to prepare MEAs for the fuel cell and less effort has been aimed at optimization of electrodes for SPE electrolyzer systems. Because of the different reactions occurring in PEM electrolyzers compared to PEM fuel cells it is not possible to directly apply the advances made in one system to that of the other, and specific optimization of each electrode in each system is required. The electro catalyst configuration and type used for hydrogen production is somewhat different to that applicable in fuel cells. Electrodes for the electrolyzer systems are reversed compared to the fuel cell system. In electrolyzer systems, water splitting is achieved on the anode accompanied by evolution of O<sub>2</sub> and hydrogen being produced on the cathode; whereas in a fuel cell the oxidant (O<sub>2</sub>) and fuel (H<sub>2</sub> or hydrocarbon) fed to the cathode are recombined to form water on the anode. Thus accumulation of evolving gas on the electrodes can occlude the electrode surface in electrolyzer systems whereas water flooding is typically a problem of electrodes in PEM fuel cells. Hence, a different approach is required to preparing electrodes for each specific system. Hydrophobicity is required in a fuel cell to prevent flooding of the electrode, unlike in the case of a SPE electrolyzer, where hydrophilic catalyst layers, coatings or gas diffusion layers are required, in order to optimize the ingress of the reactant, water. Because the hydrophobic and/or hydrophilic properties of catalyst layers have a large impact on the water transport and on the performance of the PEMFC, these systems commonly have PTFE-bonded carbon electrodes, but it has been observed that when the hydrophobicity of the electro catalyst layer increased, the hydrogen chemisorbed Pt fraction and utilization of Pt decreased [15], which would have a negative impact on water electrolysis. Hence, depending on the application, the conditions for preparing composite gas diffusion electrodes should be further optimized with respect to ink formulation and hydrophilic/hydrophobic characteristics, to maximize catalyst utilization and minimize detrimental effects caused by surface free energy and interfacial tension.

### 4. Conclusions

This study has identified a new method for preparing highly active nanophase supported Pt electro catalysts based on mesoporous HMS or its carbon analogue, an ordered mesoporous carbon as support substrate, and also a sequential deposition method for incorporating these materials into composite electrodes that are active, stable and easy to prepare and upscale.

Nanophase Pt electro catalysts were prepared by impregnating a Pt salt containing solution upon a high surface area hexagonal mesoporous silica matrix, which was then carbonized to varying degrees by chemical vapour deposition of LPG. Thereafter the HMS Si matrix could be removed by chemical etching with NaOH to immediately form a porous Pt containing carbon analogue or ordered mesoporous carbon with a porous structure similar to the parent HMS.

Pt nanophases could be stabilized and dispersed upon both the parent HMS or an OMC based on HMS mesoporous supports, without agglomeration. Thus nanophase electro active metals incorporated on ordered mesoporous materials could be used to form active electro catalysts. Even on an insulating mesoporous matrix such as Si-based HMS it was possible to achieve electro catalytic activity by the incorporation of Pt nanoparticles.

The electro activity of the prepared Pt OMC catalyst series was only slightly lower (8.9 J mA<sup>-1</sup> cm<sup>-2</sup>) than that of the industry standard Johnson Matthey Pt/C electro catalyst (9.7 J mA<sup>-1</sup> cm<sup>-2</sup>) in linear sweep voltammetric analysis under the conditions tested.

Thin film composite nanophase gas diffusion electrodes were formed by deposition of catalytic inks containing new electro catalysts on conductive supports. Incorporating supported nanophase electro catalysts in composite electrodes resulted in production of electrodes capable of current densities for hydrogen production by water electrolysis of about  $600 \text{ mA cm}^{-2}$  at  $60^\circ\text{C}$  at an applied potential of  $-2 \text{ V}$  in a high electrolyte environment. The fact that the electrodes were able to withstand the very high degree of hydrogen gas evolution at an applied potential of  $6 \text{ V}$  showed that even under these aggressively accelerated testing conditions the nanophase catalyst containing thin films were stable and durable.

This route to prepare electro catalysts and composite electrodes may be suitable for application in polymer electrolyte membrane fuel cells or solid polymer electrolyte electrolyzers for hydrogen production.

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