Precipitation and calcination synthesis methods forming nano-sized platinum catalytic particles for methanol and hydrogen oxidation

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Abstract

Under varying experimental conditions of calcination and precipitation reactions, different particle sizes and levels of platinum on carbon supported (Pt/C) catalysts were obtained. Rapid precipitation following a chemical reaction ensured formation of nano-sized catalytic particles using super-saturated concentrations under controlled conditions was a significant contribution in understanding the synthesis process and how it relates to an increased number of catalytic reaction sites ultimately providing superior electrochemical (EC) activity. These conditions influenced nucleation and growth rates of the catalytic particles. The super-saturation concentrations of the reactants in the reaction vessel played a direct role in producing the desired morphology of the crystallites.

Keywords: nano-sized platinum catalyst, methanol oxidation, hydrogen oxidation, PEM fuel cells

Classification numbers: 4.02, 5.06

1. Introduction

All methods attempted in this study utilized varying parameter settings to ascertain trends in electrochemical (EC) activity; a comparison of the methods and subsequent EC activity allowed the identification of the most effective synthesis methods and with different kinetics of formation. To understand the precipitation kinetics which allowed the formation of nano-sized catalytic particles, previous studies conducted by the crystallization and precipitation unit based at the University of Cape Town's Chemical Engineering Department were incorporated to explain the kinetics of formation for these catalysts. The physical and chemical properties of nanoparticles of various elements are extremely sensitive to the number of atoms comprising the cluster when they contain less than a few dozen atoms. Furthermore, these variations in properties which are often manifested in a nonlinear fashion as the size of the cluster changes [1–7], may be attributed to electronic and/or structural changes. The interaction of small clusters of atoms with the surface of a support may result in alteration of the electronic state of the cluster, depending on the nature of the support material [8].

There are various reports in the literature showing that as the Pt cluster size reduces to below 3–5 nm, EC mass activity decreases [9–13]. However, large uncertainties exist due to the broad size distributions of most catalyst preparations analysed in the literature. Direct measurement of the size-dependent properties of small Pt clusters with narrow size distribution

Table 1. Summary of the synthesis parameters.

Catalysts	%Metal/support	Synthesis Parameters				
		RT (h)	TP ($^\circ$C)	RA	Volume (ml)	Flow rate (ml min^{-1})
A1	20%Pt/ Vulcan	5	650	H	150	3
A1R1	20%Pt/Vulcan	5	900	H	150	3
A1R2	20%Pt/Vulcan	5	700	H	150	3
A2	20%Pt/Vulcan	5	22	FA	150	N/A
A3	20%Pt/Vulcan	5	22	F	150	N/A
A4	20%Pt/Vulcan	5	22	H	150	3
A5	20%Pt/Vulcan	5	4	FA	150	N/A
A6	20%Pt/Vulcan	5	4	H	150	3
A7	20%Pt/Vulcan	5	4×80	F	150	N/A
A8	20%Pt/Vulcan	18	4×80	F	150	N/A
A9	20%Pt/Vulcan	18	4×80	F	150	N/A
A10	20%Pt/MWNT	18	4×80	F	150	N/A
JM	20%Pt/Vulcan	N/A	N/A	N/A	N/A	N/A

RA (reducing agent); F (40% formaldehyde); TP (temperature programme); H (hydrogen);
RT (reduction time); N/A (not available).

would enable design of optimized electro-catalysts for proton exchange membrane fuel cells (PEMFCs). Traditional bulk Pt/C electro-catalysts are typically prepared via impregnation or precipitation from solution phase of a Pt-salt onto a pre-formed carbon support, followed by thermal or chemical reduction of the Pt species to form clusters [14]. This yields Pt clusters spanning a range of sizes which are weakly attached to the carbon; stabilization of the active metal species on the carbon surface is reliant on the presence of surface functional groups [15]. An alternative approach, electrostatic adsorption of Pt complex ions from solution onto a support [16–19], can lead to highly dispersed Pt clusters. Dispersions of Pt as high as 50% ($\sim$2 nm) were reported for 9.4 wt% Pt/carbon (XC-72) prepared by this method [20]. Well-defined Pt clusters of narrow size distribution down to below 1 nm may be obtained in zeolite hosts under suitable conditions [21–25]. Due to their poor electrical conductivity, however, zeolite-supported clusters are not suitable as electrocatalysts. Several recent publications have described the preparation of mesoporous [26–29] or microporous pyrolitic carbons [30] through templating by mesoporous or microporous hosts, respectively. In some cases these carbons have been used as substrates for Pt clusters in the fabrication of fuel cell catalysts, however, only relatively large Pt clusters [31], or ones with a broad size distribution [32], were achieved.

2. Experimental

Here the Pt/C catalysts will be prepared using various methods including heat treatment, reducing agents and low temperature combined reducing agents to produce nanoparticle sized catalysts. This work will not include stabilizers or organic dispersants which require expensive and time-consuming post-synthesis treatments.

The reducing agents used were hydrogen, formaldehyde and formic acid. The temperatures at which the reduction processes were performed were selected after a series of temperature ranges were investigated. The temperatures ranged from 0 to 900 $^\circ$C. In table 1 only the parameters that showed trends and where further investigations were proving

fruitful were recorded. In other words, there were a number of investigations and experiments performed that did not provide any convincing results and thus did not warrant any further investigation.

The temperatures utilized were in the range of 400–900 and 22–400 $^\circ$C, not mentioned here are the results of the intermediate parameter settings, e.g. temperature ranges between 22–5; 22–400 and 400–650 $^\circ$C. These trend determining results (TDRs) were significant in producing and observing trends, but do not form part of the mentioned data. The TDRs were interpreted and used to arrive at the mentioned data. The mentioned data are the most reflective of the experimental analysis.

For the formaldehyde and formic acid reduction methods, the pH (will not be discussed here) was controlled using various strong acids and bases including HCl and ammonium hydroxide, respectively. The low pH was significant in producing an insoluble product.

Therefore 40–4–40 $^\circ$C would mean: the salt precursors including $H_2PtCl_6 : 6H_2O$ in 0.5 M HCl, multi-walled carbon nanotube (MWCNT) and 1:1 NaOH solution would be stirred for a specified time period at 40 $^\circ$C until dissolution of the salts is achieved. Once the salts have dissolved, the solution temperature was reduced to below 4 $^\circ$C. Whilst stirring add formaldehyde (reducing agent), previously cooled to 2 $^\circ$C, drop wise, maintaining the entire process and solutions involved at 4 $^\circ$C for 5 hours, and finally a post-reduction temperature treatment at 40 $^\circ$C. Controlling the post reduction temperature proved essential in controlling the particle size. The suspension was then filtered through a 0.45 μm membrane filter followed by 1:1 solution acetic acid and boiling purified water.

3. Results

The electrochemical (EC) activity was determined by cyclic voltammetric (CV) analysis of the different catalysts. By comparing the EC activity for each catalyst the reducing agents and other synthesis parameters can now be identified as effective contributors to synthesis routes. In table 2, the EC activity of the once-formed catalyst is analysed in an

Table 2. Comparing the EC by CV analysis.

Catalyst	Metal/support	T (°C)	I (A) at 0.5 V (versus Ag/AgCl)	I (A) at 0.6 V (versus Ag/AgCl)	EC status
A1	20%Pt/Vulcan	20	3.80×10^{-6}	4.98×10^{-6}	Not active
A1R1	20%Pt/Vulcan	20	5.79×10^{-9}	8.00×10^{-9}	Not active
A1R2	20%Pt/Vulcan	20	4.60×10^{-7}	0.96×10^{-6}	Not active
A2	20%Pt/Vulcan	20	4.25×10^{-5}	1.75×10^{-4}	Active
A3	20%Pt/Vulcan	20	4.59×10^{-5}	1.23×10^{-4}	Active
A4	20%Pt/Vulcan	20	0	0	Not active
A5	20%Pt/MWNT	20	0	0	Not active
A6	20%Pt/Vulcan	20	6.52×10^{-7}	6.46×10^{-7}	Not active
A7	20%Pt/Vulcan	22	1.02×10^{-4}	1.57×10^{-4}	Active
A8	20%Pt/Vulcan	22	1.43×10^{-4}	2.41×10^{-4}	Active
A9	20%Pt/Vulcan	22	1.13×10^{-4}	2.29×10^{-4}	Active
A10	20%Pt/MWNT	22	1.93×10^{-5}	2.29×10^{-5}	Active
JM	20%Pt/Vulcan	22	1.17×10^{-4}	1.82×10^{-4}	Active

MWCNT (multi-walled carbon nanotube); *I* (current); TP (temperature programme); *T* (temperature); EC (electrochemical); RT (reduction time); N/A (not available).

acidic medium (base analysis), followed by the addition of 1 M methanol which undergoes oxidation on the platinum surface as shown in the CV graphs below. The potential regions analysed are −0.2 V to 0.6 V and −0.2 V to 1.0 V (versus Ag/AgCl) and the scan rate used was 20 mV s^{-1}. The objective and application of the EC activity is mainly to determine the activity of the catalyst synthesized by different methods, and give an indication as to which method produces a catalyst with the highest EC activity at 0.5 V (versus Ag/AgCl), because it is at this potential that the direct methanol fuel operates optimally.

Table 2 compares the different catalysts, methods and EC activity. The table indicates the activity status, this indication refers to the increase in current (*I*) as and when methanol is added. If the current increases from the base line, the difference in current is calculated at a specific potential, where the two potentials of interest as mentioned earlier were 0.5 or 0.6 V (versus Ag/AgCl).

Poor EC activity is associated with larger catalytic particles and small surface areas. The poisoning effect is a well-studied phenomenon and to meet our objectives, the production of CO will be kept to a minimum. To enable the minimizing of CO formation, the number of scans will be limited to a maximum of two. The actual EC activity was the difference between the base line without methanol and after methanol addition calculated at 3.80×10^{-6} A cm^{-2} and this poor performance after the addition of 0.5 M methanol can be attributed to inadequate amounts of catalytic particles formed during the synthesis process, the lack of dispersion and the formation of a large particle comprising of different sizes with possible agglomerations.

Catalysts reduced at high temperatures were composed of particles with particle size distributions in the region of 50% < 3 nm. The concentration of particle formation in a specific surface area is less than that formed at sub-ambient temperatures. The formation of larger particles could be assigned to particle growth due to lack of dispersion during the metal formation process. The high temperature methods are limited with regards to the options for implementing dispersion techniques as the reduction takes place in a furnace where no physical or mechanical equipment at laboratory level can be installed to aid in particle dispersion without

adding immensely to the cost factor. This analysis applied to samples A1, A1R1 and A1R2 prepared under similar conditions with different pre-treatments, which had very little or no effect on the poor EC activity observed later.

Apart from increased dispersion, slowing down the particle growth rate was also attempted by exploring ambient and sub-ambient temperatures at which reduction could take place. TEM particle dispersion images for catalysts A2, A3 and A4 synthesized using formic acid, formaldehyde and hydrogen, respectively, as the reducing agents and synthesis route performed at 22 °C catalyst A2 showed the positive direct influence smaller particles and the resulting increased surface area have on the EC activity, although there is poor dispersion and formation of agglomerations of smaller particles (∼30% <3.5 nm) in the region of 10 nm, the EC activity at 0.6 V (versus Ag/AgCl) was significantly higher than the catalysts produced at high temperatures. There were further attempts to disperse the catalytic particles by using MWCNT supports and the resulting image observed for sample A5 showed an image with larger particles. To make the MWCNT support more effective required a series of pre-treatments to firstly remove impurities and secondly disperse the tubes themselves prior to the actual deposition of metallic particles.

The poor dispersion was noted once again for sample A3, and highlighted the need to introduce effective dispersion methods while slowing down and controlling the particle growth rate. From the XRD and SEM it was clear that the method employed to synthesize catalyst was able to synthesize platinum metallic particles from a chloroplatinic acid salt solution.

4. Conclusion

Two methodologies for catalyst formation were compared at lab scale, i.e. calcinations and precipitation methods. The particle morphology during the synthesis processes at high temperatures exceeding 80 °C proved more difficult to control. During the precipitation syntheses reactions, supersaturated precipitation reaction conditions played a significant role in controlling particle nucleation rates and stemming growth by controlling synthesis conditions and thereby enhancing their

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respective EC activity. The control of the occurrence of the particle sizes in the nanometer range was an important finding where super-saturation and conditions supporting minimizing the growth and formation of stable structures using fast kinetic formation instead of growth was a key aspect for their synthesis and controlling particle size, positively influencing the electrochemically active surface area.

The formation of Pt/C catalytic particles at high temperatures produced catalysts with lower EC activities than those synthesized at supersaturated concentrations and supporting conditions, including sub-ambient temperatures and increased pH produced effective high surface area and high EC activity catalysts. In all cases where lower or no activity was recorded, the particle size distributions were in the region of 80–90% > 4 nm and the amount of platinum formed was less than 15%.

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