Tailoring Pt-Alloy Cluster Nanoparticles for Enhanced Electrocatalytic Activity

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ABSTRACT

Polymer electrolyte membrane fuel cell, PEMFC is an electrochemical energy conversion device that has the potential to be an alternative to internal combustion engines. However, the complexity and slow oxygen reduction reaction (ORR) kinetics on the catalyst surface are among the most limiting factors in the energy conversion efficiency of the state-of-the-art PEMFCs. For large scale and wider application of fuel cells it is estimated that an approximately five-fold reduction in the amount of Pt-loading in membrane-electrode assembly (MEA) to << 0.15mgPt/cm^2 MEA is envisaged, while maintaining high power density at high cell voltage. In this work, we demonstrate a facile fabrication method using biomimetic protein directed self-organization followed by reducing of the corresponding precursor salt/s to prepare shape and size controlled Pt and Pt-alloy nanoparticles (<<5nm) with precise control over size, shape, compositions and morphology. It is demonstrated that the Pt-heterostructures so produced are highly active towards ORR and methanol oxidation reaction; electrochemical stability is significantly better than commercially available catalytic systems (Pt supported on carbon black). The improvement in catalytic activity is attributed to the narrow size distribution, high surface area of Pt NP and porous nature of the catalyst system.

Keywords: Electrocatalyst, Fuel cell, nanoparticles, proton exchange membrane fuel cell, oxygen reduction, hydrogen oxidation

1. INTRODUCTION

A continuation of current trends in energy use puts the world on track for a rise in temperature of up to 6°C and poses serious threats to global energy security [1]. However, the worldwide energy consumption is projected to grow by 40% between now and 2030 and about 13 terawatts (TW) of energy is currently needed to sustain the lifestyle of 6.5 billion people worldwide. It is predicted that an additional 10TW of clean energy will be essential to maintain the current lifestyle. Furthermore, the energy poverty challenge also remains unresolved with 1.5 billion people still without electricity. A growing population with higher energy demand and push toward renewable and less polluting resources are driving the development of a wider range of methods for energy generation [2]. Therefore, development of a renewable energy technology platform that can start to compete with traditional energy sources at an economic level, without subsidies is urgent and of critical importance. Among the various energy conversion and storage technologies now being seriously considered; electrochemical energy-conversion [ECV] and storage devices are anticipated to play a major role and contribute to mitigate global warming and reduce our dependence on fossil fuels.

Among different ECVs' fuel cells have been recognized as one of the most promising candidate for the future in stationary, automotive and mobile applications because of their high energy density, high conversion efficiency and low pollution level [3]. The potential influence of fuel cells on cleaning the air and improving human health has also been clearly identified [4,5]. After decades of evolution, fuel cells of various types have been proposed and developed including alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and proton exchange membrane fuel cell (PEMFC). Amongst different types of fuel cells, in the past few decades, PEMFCs have attracted wide interest due to their demonstrated advantages including rapid start up and high power density, which is particularly suitable for vehicle applications [6,7]. PEMFC are now attracting enormous interest as one of the most promising clean power generation technologies for their potential use as an environmentally benign and a highly efficient electric power generation technology for various applications, including low/zero-emission vehicles (replace the internal combustion -IC engine) and utility sector.

A hydrogen-oxygen (H_2/O_2) fuel cell converts hydrogen and oxygen into water and, as part of the process, produces electricity. The combination of anode/membrane/cathode in PEMFC is referred to as the membrane/electrode assembly (MEA) and is considered as the heart of the fuel cell. In hydrogen fuelled PEMFC, hydrogen is delivered to the anode side of the MEA and oxygen/air to the cathode side.

At the anode side, the supplied hydrogen is catalytically split into electrons and protons (hydrogen oxidation); whereas, at cathode side, oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules (oxygen reduction) [4]. Although they are promising, demonstration fleets and prototypes aside, wider market penetration of PEMFCs has not materialized [8]. Besides the high cost of membranes, this is due mainly to the (i) dependence on platinum-based (an expensive and scares resource) electrocatalyst (used in anode and cathode), (ii) sluggish oxygen reduction reaction (ORR) kinetics, and (iii) CO related poisoning of the catalyst. To achieve the goals scientific breakthroughs in novel electrocatalyst layer are critical [9]. To enhance the effectiveness and utilization effciency of the electrocatalyst significantly we have focused our research on the fundamental understanding of the design principle and on developing approaches to create predetermined nanostructures with a high-level of control in size, shape, composition and morphology using facile nanotechnology approach.

2. ELECTROCATALYST FOR PEMFC

Electrocatalyst layers in fuel cell are complex and heterogeneous forming a three-phase interface that is in direct contact with the electrolyte membrane and the gas diffusion layer (GDL) of the fuel cell. In hydrogen fuelled PEMFC, HOR at the anode involves two electrons. The H-H bond is relatively easy to break catalytically and the HOR mechanism undergoes three stages. Among the electrocatalytically active electrode materials for the HOR, platinum exhibits the highest exchange current density, making it one of the best electrocatalysts for HOR.[8,9] The mechanism for the HOR on a platinum electrode in acid electrolyte are reported to proceed through two pathways, followed by a fast charge-transfer step:[8]

$Pt + H_2 \rightarrow 2Pt–H_{ad}$ (rate determining step, Tafel) (1)

$Pt + H_2 \rightarrow H^+ + Pt–H_{ad} + e^-$ (rate determining step, Heyrosky) (2)

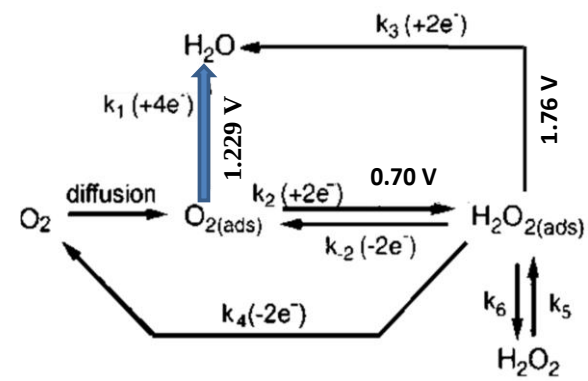
$Pt–H_{ad} \rightarrow Pt + H^+ + e^-$ (fast charge-transfer, Volmer) (3)

For the hydrogen oxidation, the charge-transfer reaction (Volmer expression):[4]

$$i = k_f[H]e^{\frac{\alpha_v FE}{RT}} - k_b[H^+]e^{\frac{-(1-\alpha_v)FE}{RT}} \quad (4)$$

where, 'i' is the net current density, 'k_f' and 'k_b' are the rate constants of current densities in the anode and cathode, [H] is the surface concentration of atomic hydrogen, $[H^+]$ is the surface concentration of protons; 'α_v' is the charge-transfer coefficient, 'R' is the gas constant, 'T' is the temperature; and 'E' is the electrode potential. With respect to the above mechanisms the kinetics of the HOR is mainly determined by the interaction between H_{ad} and the platinum surface atoms. Markovic et al.[10] and Jerkiewicz et al.[11] demonstrated two adsorbed states of hydrogen on platinum single crystals : respectively, the strongly adsorbed states of hydrogen as the underpotentially deposited hydrogen (H_{upd}), and the weakly adsorbed states as the reactive intermediate or overpotentially deposited hydrogen (H_{opd}).The H_{upd} is strongly dependent on the crystallographic orientation of the platinum surface.

The ORR is relatively more complex than HOR involving multi-electron process with a number of elementary steps and reaction intermediates. In a typical ORR pathway O_2 can be electrochemically reduced either directly through a four-electron process to water with the rate constant k_1 without intermediate formation of H_2O_2(ads) or a less efficient two-step two electron pathway involving the formation of H_2O_2 as an intermediate with the rate constant k_2. The pathway of the reaction depends on the adsorbed states of oxygen and the structure of the catalyst surface i.e. crystallographic orientations.



Scheme: Reaction pathways of ORR in hydrogen fuelled PEMFC

The mechanism of ORR on platinum is still not well understood. According to a dissociative mechanism [8]

$Pt + 1/2O_2 \rightarrow Pt–O$ (5)

$Pt–O + H^+ + e^- \rightarrow Pt–OH$ (6)

$Pt–OH + H^+ + e^- \rightarrow Pt + H_2O$ (7)

O_2 adsorption breaks the O-O bond and forms adsorbed atomic O, which further gains two electrons in the two consecutive steps, forming water. For metal electrocatalysts like platinum, different planes show different behaviour for oxygen reduction pathways. Incomplete reduction of oxygen to hydrogen peroxide not only leads to low energy conversion efficiency, but also produces reactive intermediate that can further convert to harmful free radical species. The current-overpotential relationship of ORR is given by:

$$I_c = i_0 \left(e^{\frac{n_{a0}\alpha_0 F\eta_c}{RT}} - e^{-\frac{n_{a0}(1-\alpha_0)F\eta_c}{RT}}\right) \quad (8)$$

where, 'I_c' is the oxygen reduction reaction current density, 'i_0' is the exchange current density (electrochemical reaction rate at equilibrium); '$n_{\alpha o}$' is the number of electrons transferred in the rate determining step, 'α_o' is the transfer coefficient (defines the extent to which the free energy change contributes to a change in the activation energy, which ranges in value from 0 to 1) ,' η_c' is the overpotential of ORR, 'F' is the Faraday constant, 'R' is the gas constant, and 'T' is the temperature in Kelvin. If the overpotential is large, the backward reaction is negligible and Eq 8 can be simplified as:

$$I_c = i_0 \, e^{\frac{n_{a0}\alpha_0 F \eta_c}{RT}} \qquad (9)$$

The plot of η_c vc log(I_c) gives a linear relationship and the slope ($2.303RT/n_{\alpha o}\alpha_o F$) is called the Tafel slope. Thus, for an electrochemical reaction to obtain a high current at low overpotential, the reaction should exhibit a low Tafel slope. Among all the noble metals, platinum shows the lowest overpotential for ORR with the reaction proceeding via the four electron route majorly. Thus, a platinum-based electrocatalyst is the most preferred and Pt or Pt-alloys supported on high surface area carbon is the only feasible electrocatalysts for PEMFC systems [9]. However, according to the cost breakdown of fuel cell components, the cost of catalysts in manufacturing fuel cells is the highest (30%) for small production volume, and remains very high with increasing production volume. Intensive research efforts are ongoing to reduce or replace Pt-base electrodes [12,13]. Current targets for transport PEMFC fuel cells are below 0.2 g/kW Pt – which is a factor of 5 decreases over current loadings.

In a highly efficient electrocatalyst structure most of the Pt-sites should be at the triple-phase boundary (TPB) structure formed by the electron path, the ion path, and the access site for the fuel gas which correspond to the carbon, electrolyte, and Pt, respectively. Despite many advances, existing fuel-cell electrocatalyst technology still has many drawbacks including lower catalytic efficiency, higher cost, durability, and loss of platinum cathode electrocatalysts, which can be as much as 45% over five days. [13].

3. TUNING THE CHARACTERISTICS OF PtNPs ELECTROCATALYST

To achieve high ORR activity synthesis of uniform and high-yield nanocrystals of well defined faces is essential but a challenging task. For a size controlled synthesis of NPs we have develoed and used directed molecular self-assebly to create templates/nanoreactors for confined synthesis and stabilization of metallic/bimetallic nanoparticles(M-NPs) using colloidal techniques. The process involves loading of relevant metal precursor salts into pre-organized block copolymer/biomimetic polymer microcompartments followed by reduction and stabilization of resulting NPs.

It is quite versatile and can be employed for a large number of precursor/polymer/solvent systems. The incorporation of inorganic materials into polymer domains is not trivial, since most polymers are low surface energy materials the adhesion between metals and polymers is poor. Only through tuning specific interactions like dipolar interactions and hydrogen bonding complex formation can inorganic materials be incorporated into polymers [14]. However, thermodynamic and kinetic factors need to be precisely tuned to control the shape of the bimetallic nanoparticles. In colloidal synthesis, the shape is dictated both by the intrinsic structural properties of the nanoparticle and reaction systems such as solvent, capping agent, and reducing agent. The reaction conditions including concentration, time and temperature are also critical. Introducing defects can break down the crystal symmetry resulting in the formation of shape with reduced symmetry such as nanorods, plates, planner tripods and multipods.

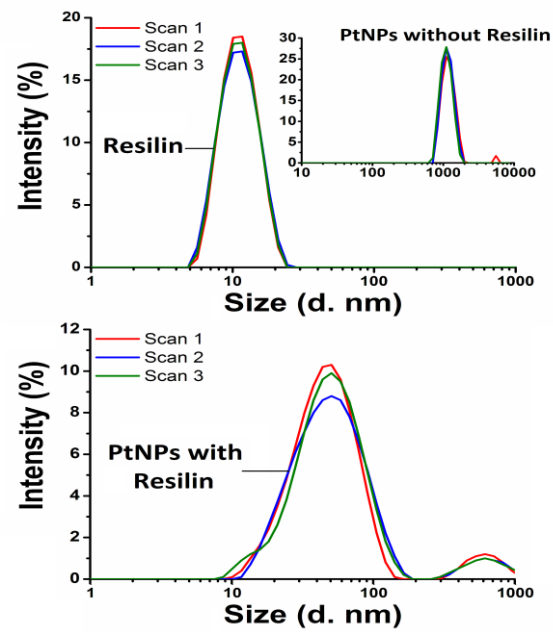


Figure 1: Hydrodynamic diameter, D_h and its distribution observed for neat BMP solution and BMP-NP composite sol using dynamic light scattering (DLS). The consequence of the interaction and complexation on the sols alters the D_h and its distribution dramatically.

The composition of the templating polymer used can play a pivotal role in shape control of colloidal bimetallic nanoparticles; since such nanocrystals will have different electronic structures and atomic arrangement for various facets and the different polymer segments will absorb onto these surfaces differently. One key criterion in selecting the proper templating polymer for shape control is controling the interaction between the host micelle molecule segment and various nanoparticle facets. In our very recent work for

the first time we have demonstrated the power of guided co-assembly of block copolymer(BCP) to synthesize Pt

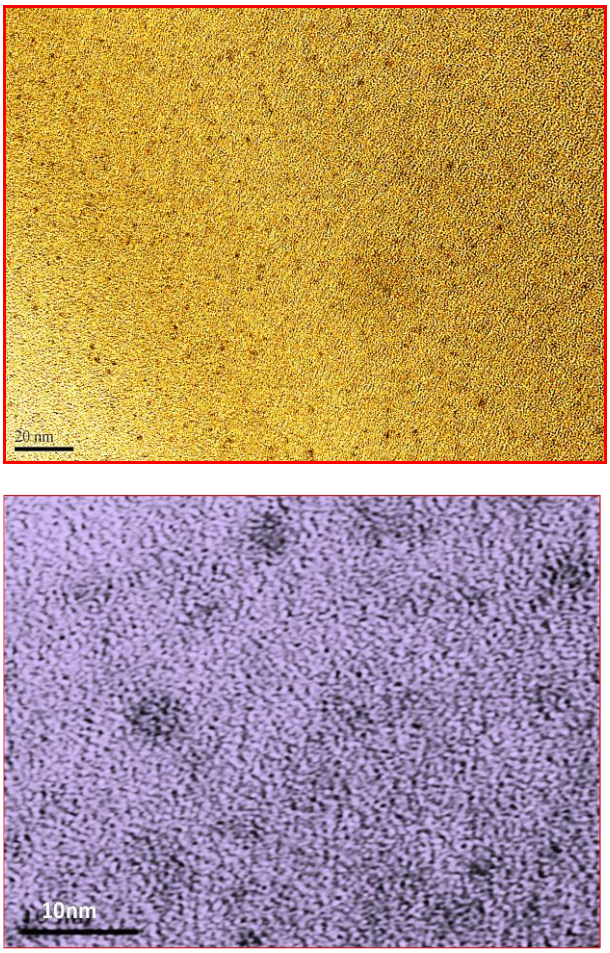


Figure2: TEM image of the Pt-nanopaarticles: (a) overall view display uniform distribution of particles (b) close view of particle of <<5nm in size.

and Pt/Co nanparticles[14]. We have also reported use of biomimetic responsive protein polymers (BMP), *rec1-resilin* [15-17] to synthesise AuNPs of controled size, (<5nm), interparticle distance, and aggregation[18]. Resilin, is a member of the family of natural elastic proteins that includes elastin, gluten, gliadin, abductin and spider silks. Recently, we have reported the synthesis of the biomimetic polymer *rec1-resilin* from the repeat sequences of the first exon of the *Drosophila melanogaster* CG15920 gene using recombinant DNA technology [19]. The composition of the protein is dominated by 18 copies of a 15-residue repeat sequence: GGRPSDSYGAPGGGN. It contains a very high content of glycine (~35 mol %) and proline (~14 mol %). We have been successful in using BMP to stabilize Pt and Pt-alloy nanoparticles (Figure 1) and to enable synthesis of Pt and Pt-alloy NPs of size <<10nm (Figure 2).

Pt and Pt-alloy NPs so synthesised–without futher treatment- when supported on carbon nanotubes exhibit significantly improved electrocatalytic activity and stability relative to traditional NPs. The process is scalable giving high yields. This is to note that traditionally in ECLs, the NPs are generally embedded on to a carbon support for electron transport. The functional role of the carbon support is to provide electrical connection between the widely dispersed Pt catalyst particles and the porous current collector. However, significant oxidation of the carbon support and poor long-term durability is considered to be one of the most critical issues for wider application of PEMFCs. Moreover the impermeability of the carbon support to reactant gases and its lack of proton conductance reactants (oxygen/hydrogen), water and proton transport limit the efficiency of the electrocatalyst that can be achieved. In our work we address this issue by using functionalized carbon nanotubes as catalyst support materials due to their unique structural, electrical and mechanical properties and a wide electrochemical stability window and very high surface area.

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