Li, J Material Sci Eng 2017, 6:3
DOI: 10.4172/2169-0022.1000337

Journal of Material Sciences & Engineering

Research Article OMICS International

Pt-Shell Nanowires for Fuel Cell Electrodes

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Abstract

Gibbs idea of surface excess is reexamined to discover that the surface excess is not the same as surface enrichment. This finding could help us design Pt shell nanowires for fuel cell electrodes which should have the best performance than any other kinds of Pt catalysts. All the reasons behind this possibility are collected and discussed. It is hoped that this analysis will convince you to make such wires as fuel cell electrodes.

Keywords: Pt-shell nanowires; Fuel cell electrodes; Gibbs surface excess; Surface enrichment; Fuel cell cars; Self driving cars; Pt price

Introduction

As analyzed by Ugurlu and Oztuna [1], fuel cells definitely can be used in automobiles. In fact the Toyota Mirai and Hyundai ix35 FCEV are already fuel cell cars. They can be driven 250 miles between fueling and the fueling takes only about 5 minutes. Currently $1 worth of hydrogen can drive 146 miles while $1 worth of gasoline can only drive 10 miles. The source of hydrogen is unlimited but gasoline will one day be gone. With hydrogen the exhaust is only water, no pollution of air as with gasoline. Hence fuel cells are the future for ground transportation.

In a fuel cell, hydrogen flows at one electrode and air flows at the other. With a catalyst the hydrogen ionizes into H^+ and an electron which flows through the external circuit to the other side. The H^+ diffuses through a PEM (Proton Exchange Membrane) to the other side and reacts with oxygen and an electron to form water. The second catalytic reaction is 6 orders slower than the first catalytic reaction.

The catalyst is Pt and the price of Pt can increase as much as 4% a day. If we produce more fuel cells, the price of Pt will increase rapidly. Zhu et al. [2] found a correlation between oil prices and Pt prices. They did not know why. But this is probably the reason. Luckily we need Pt only on the surface. The question is how to make a catalyst with Pt only on the surface. To increase the surface/volume ratio, we have been using Pt nanoparticles which need a support structure. The support is usually carbon. But the adhesion between Pt and C is not so good and the Pt particles can agglomerate and grow. The carbon can be oxidized also. We are looking into the self-supporting nanowires. The question is whether we can make Ni (or other metal) nanowires with only one atomic layer of Pt on the surface. The radius of a Pt atom is 135 pm and the atomic weight is 195 so a close packed layer of Pt atoms is 5 mg per square meter area, the lowest possible Pt loading achievable. This paper is to try to shed some light on this question. We are going to try to make it. You should try it too.

Gibbs Surface Excess

Gibbs started with two homogeneous phases 1 and 2 and then let them touch each other to form an interface. Consider phase 1 of energy U_1, entropy S_1, volume V_1, chemical components n_{i1} (i=1 to c, c being the number of components):

$$dU_1 = TdS_1 - PdV_1 + \sum_{i=1}^{c}\mu_i dn_{i1} \quad (1)$$

This equation just says for phase 1 at constant temperature T, pressure P and all the chemical potentials μ_i (i=1 to c) the reversible heat absorbed is TdS_1, the reversible mechanical work done is PdV_1 and the reversible chemical work is $\mu_i dn_{i1}$ (i=1 to c) by diffusing in the component i. Similarly for phase 2:

$$dU_2 = TdS_2 - PdV_2 + \sum_{i=1}^{c}\mu_{i2} dn_{i2} \quad (2)$$

Now at the same temperature, pressure and all the chemical potentials, combine the two phases to form an interface. All the energy, entropy, volume, and the chemical components may change. Gibbs defined them as excess quantities due to the interface: Let U, S, V and n_i be the total energy, entropy, volume and the number of moles of component i of the combined system:

Excess energy $U_{xs=}U\text{-}U_1\text{-}U_2$ (3)

Excess entropy $S_{xs=}S\text{-}S_1\text{-}S_2$ (4)

Excess volume $V_{xs}=V\text{-}V_1\text{-}V_2$ (5)

Excess i^{th} component $n_{ixs}=n_{i1}\text{-}n_{i2}$ (6)

These excess quantities may be negative. The system now also has an interface of area A and energy γ per unit area.

So for the combined system

$$dU = TdS - PdV + \gamma dA + \sum_{i=1}^{c}\mu_i dn_i \quad (7)$$

Hence $$dU_{xs} = TdS_{xs} - PdV_{xs} + \gamma dA + \sum_{i=1}^{c}\mu_i dn_{ixs} \quad (8)$$

As you may remember from your thermodynamics course, Gibbs integrated this equation by adding small quantities together into the big system at the same temperature, pressure, and all the chemical potentials. So,

$$U_{xs} = TS_{xs} - PV_{xs} + \gamma A + \sum_{i=1}^{c}\mu_i n_{ixs} \quad (9)$$

He then differentiated this equation and compared with eqn. (8) to obtain:

$$S_{xs}dT - V_{xs}dP + Ad\gamma + \sum_{i=1}^{c} n_i d\mu_i = 0 \quad (10)$$

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Received May 06, 2017; **Accepted** May 16, 2017; **Published** May 26, 2017

Citation: Li JCM (2017) Pt-Shell Nanowires for Fuel Cell Electrodes. J Material Sci Eng 6: 337. doi: 10.4172/2169-0022.1000337

At constant temperature, pressure and the chemical potential of all other components, the surface excess of component *i* is:

$$\frac{n_{ixs}}{A} = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{T,P,\mu_j} \quad (11)$$

Which is the famous Gibbs adsorption equation. It is applicable to interfaces, grain boundaries and free surfaces.

Surface Excess and Surface Enrichment

While thermodynamics is never wrong, the prediction may not be exactly what you expected. Let us look at some of the PtNi alloys. Gauthier et al. [3,4] studied the {111} surface of 50-50 NiPt alloy. They found the surface layer contains 88 ± 2% Pt, the second layer 9 ± 5% Pt, the 3rd layer 65 ± 10% Pt and the 4th layer and inside 50% Pt. Since they started with 50% Pt and the bulk is 50% Pt, the three surface layers averaged 54 ± 7% Pt so the surface excess was 12 ± 7% Pt if concentrated on the surface. Yet there was actually strong surface enrichment of Pt (88%). For the {111} surface of 50-50 NiPt alloy Van et al. [5] also found Pt enrichment on the surface. The Gibbs eqn. (11) predicts only the surface excess, not the surface enrichment. But the catalytic properties depend on the surface enrichment, not the surface excess.

For the {111} surface of an 22-78 NiPt alloy, Gauthier et al. [3,4] found the first layer 1 ± 1% Ni, the second layer 70 ± 5% Ni, the 3rd layer 13 ± 10% Ni and the 4th layer and inside 22% Ni. So the surface excess is 18 ± 6% Ni but the surface enrichment is 99 ± 1% Pt. Based on the surface excess, this alloy may not be a good catalyst. But based on the surface enrichment, it is an excellent catalyst.

Similar results were found by computer simulation as reported by Wang et al. [6]. At 600 K, a nano particle (2 to 5 nm) of 25-75 Ni-Pt alloys has Pt strongly enriched on the surface layer and the third layer and the Ni enriched on the second layer. For a nano particle of 25-75 Re-Pt alloys, a nearly pure Pt shell surrounds a more uniform Pt-Re core. For a nano particle of 20-80 Mo-Pt alloys, the facets are fully occupied by Pt atoms, the Mo atoms are at the edges and vertices. The amount of Pt atoms on the surface increases with the size of the particle. So when it is a flat surface it will be pure Pt.

Experimentally by using LEIS (Low Energy Ion Scattering) in the same system $Pt_{75}Ni_{25}$, Stamenkovic et al. [7] found pure Pt on all 3 surfaces, (100), (110) and {111}. Their CTR (Crystal Truncation Rods) analysis for the {111} surface showed the second layer to consist of 45% Pt, the third layer 82% Pt and the fourth layer and inside were normal (75% Pt). Since the average of the first 3 layers was about 75% Pt, there was no surface excess yet there was strong surface enrichment of Pt (100%).

Gallego et al. [8] deposited Mn on Pt {111} by evaporation and did prolonged annealing at 950 K. LEED analysis showed first layer 100 ± 1% Pt, 2nd layer 75 ± 4% Pt, 3rd layer 100 ± 10% Pt, 4th layer 75 ± 10% Pt and 5th layer and inside 100% Pt. So the surface excess is 50 ± 8% Mn but the surface enrichment is 100 ± 1% Pt. The surface Pt atoms have the ability to push Mn atoms inside even though Mn atoms were coated on the Pt surface.

Some Properties of Pt Shells

Shui et al. [9] made $PtNi_5$ nanowires by electro spinning and then treated in 0.001 M sulfuric acid for 8 minutes and heated to 60°C for 4 minutes to remove the Ni atoms and Ni oxides on the surface. Then the nanowires were cleaned several times in deionized water and ethanol before they were heat treated in a hydrogen (5 vol%) argon (95 vol%) mixture at 300°C for 15 hours to allow Pt atoms to reach the surface to replace Ni atoms. Sure enough the Pt atoms can protect Ni in hot (60°C) 1 M sulfuric acid for hours.

Even for an alloy with 90% Ni, Tammermann et al. [10] and Gauthier et al. [11] still reported Pt enrichment on the surface. Hebenstreit et al. [12] suspected that Pt atoms on the (100) surface tend to be reconstructed into a close-packed surface layer.

For Ni-core Pt-shell nanoparticles of about 7.5 nm size, Godinez-Salomon et al. [13] made Ni core by colloidal reduction of $NiCl_2$ with $NaBH_4$ and coated with Pt by subsequent reduction of H_2PtCl_6. Cyclic voltammetry on thin film rotating disk electrode revealed that these particles had a more than twice enhanced catalytic activity than Pt nanoparticles synthesized by the same way.

Pt-skin surfaces were fabricated on Pt-Ni nanoparticles (2-3 nm) by Jung et al. [14] by using chemical deposition. They found that the chemically tuned Pt skin had a higher Pt coordination number and surface crystallinity which resulted in better oxygen reduction reaction activity and durability compared to the Pt-skin formed by heat annealing.

Pt-shell Ni-core nanoparticles supported on C were prepared by Kang et al. [15] with either an amorphous or crystalline Ni core while the thickness and structure of the Pt shell were similar. They compared the methanol oxidation activities by using cyclic voltammetry and chrono-amperometry and found that the amorphous core had better performance. Ni nanowires can be made by electro-spinning [9,16] and these wires can be made amorphous by straining [17].

Serra et al. [18] made mesoporous CoNi and Pt Nano rods by electrochemical synthesis and then coated the mesoporous CoNi Nano rods with a layer of Pt shell by interfacial replacement reaction. They found the later was better than the mesoporous pure Pt Nano rods. In fact they found the best ones were obtained from the water-in-ionic liquid micro emulsion which gave a mass activity of 1.3 A/mgPt.

From these considerations we suspect that Pt can protect a pure Ni wire by depositing on the surface.

Stability of the Surface Layer

Recently, Tao et al. [19] observed compositional changes near the surface of a nanoparticle for a free surface (in vacuum) and for surfaces in different environments. So the surface layer is the most important part of the surface which is affected by the environment and can be treated as a thermodynamic phase in equilibrium with the bulk and with the environment. The Gibbs equation of state and the associated Helmholtz and Gibbs free energies are:

$$dU_S = TdS_S - PdV_S + \gamma_S dA_S + \sum_i \mu_{iS} dn_{iS} \quad (7.1)$$

$$dF_S = d(U_S - TS_S) = -S_S dT - PdV_S + \gamma_S dA_S + \sum_i \mu_{iS} dn_{iS} \quad (8.1)$$

$$dG_S = d(U_S - TS_S + PV_S) = -S_S dT + V_S dP + + \gamma_S dA_S + \sum_i \mu_{iS} dn_{iS} \quad (9.1)$$

Unlike the Gibbs excess quantities which belong to the geometric surface, the surface quantities here are for the surface layer atoms including the surface energy γ_s which is not the usual surface energy but the energy for the surface layer atoms. At constant temperature, pressure, surface energy and all the chemical potentials, eqn. (7.1) can be integrated by putting small systems together and give:

$$U_S = TS_S - PV_S + \gamma_S A_S + \sum_i \mu_{iS} n_{iS} \quad (10.1)$$

Which can be differentiated and compared with eqn. (7.1) to give:

$$A_S d\boldsymbol{\gamma}_S = -S_S dT + V_S dP - \sum_i n_{iS} d\boldsymbol{\mu}_{iS} \quad (11.1)$$

At constant temperature and pressure, the surface composition still can be found from the following equation:

$$\frac{n_{iS}}{A_S} = -\left(\frac{\partial \boldsymbol{\gamma}_S}{\partial \boldsymbol{\mu}_{iS}}\right)_{T,P,\boldsymbol{\mu}_{jS}} \quad (12)$$

but this is no longer the Gibbs adsorption equation since γ_s is not the usual surface energy and n_{iS} is no longer the surface excess quantity. However now n_{iS} is the real surface composition. So the surface layer is like another phase (a homogeneous part) in equilibrium with the rest of the system. The equilibrium with the interior could be an exchange equilibrium in a substitutional binary alloy of A and B such as Pt-Ni:

A (on surface)+B (inside) ↔ B (on surface)+A (inside) (13)

This exchange equilibrium can be described by:

$\mu_{AS}+\mu_B=\mu_{BS}+\mu_A$ or $\mu_{AS}-\mu_{BS}=\mu_A-\mu_B$ (14)

So the difference between chemical potentials of any two components is a constant throughout the system.

At constant temperature, pressure and the area of the surface layer, eqn. (9) can be integrated by adding up small systems and then differentiated to compare with eqn. (9) to obtain the Gibbs-Duhem type equation:

$$\sum_i n_{iS} d\boldsymbol{\mu}_{iS} = 0 \quad (15)$$

For any changes of surface composition, for a binary alloy A and B, this equation can be re-arranged into:

$$x_{BS} = \frac{n_{BS}}{n_{BS}+n_{AS}} = \left[\frac{\partial \mu_{AS}}{\partial(\mu_{AS}-\mu_{BS})}\right]_{T,P,A} = \left[\frac{\partial \mu_{AS}}{\partial(\mu_A-\mu_B)}\right]_{T,P,A} \quad (16)$$

Where μ_A and μ_B are the chemical potentials for A and B in the bulk, respectively. So by changing the bulk alloy composition and examining the effect on the surface composition, it is possible to calculate the change of chemical potentials on the surface.

However, it is possible that A prefers to stay on the surface and B has zero solubility in the surface layer so that eqn. (13) is an inequality:

B (on surface)+A (next layer) → A (on surface)+B (next layer) (17)

This inequality can be described by:

$\mu_{BS}+\mu_{A1}>\mu_{AS}+\mu_{B1}$ or $\mu_{AS}-\mu_{BS}<\mu_{A1}-\mu_{B1}$ (18)

Then the surface layer may not respond to the change of bulk composition. It is possible that for Pt-Ni alloy, the Pt surface layer is a stable layer obeying the inequalities represented by eqn. (18).

However, the surface layer may be in equilibrium with the surroundings such as the fluid in contact with the surface. If C is such a component, then:

$\mu_{CS}=\mu_{CF}$ (19)

Where μ_{CF} is the chemical potential of C in the contacting fluid. For a two-component system, A and C, the Gibbs-Duhem eqn. (15) shows:

$n_{AS}d\mu_{AS}+n_{CS}d\mu_{CS}=n_{AS}d\mu_{AS}+n_{CS}d\mu_{CF}=0$ (20)

So by changing the composition of the fluid phase in contact, the surface composition or the chemical potentials could be affected.

The Stable Surface Layer

Which atoms should be enriched on the surface and form a stable layer? The usual finding is that the metal with lower surface energy or the larger atoms are enriched on the surface. Ma and Balbuena [20] collected data for some Pt_3M systems and compared with their theoretical predictions with two notable exceptions, Pt_3Mn {111} and Pt_3Ti {111}. While their theory predicts Mn and Ti segregation, experiments showed Pt segregation [8,21]. So the surface segregation is governed, not by the atomic size mismatch and the surface energy differences but by the subsurface atomic arrangement, namely the shell structure. In other words, the shell free energy determines the surface composition.

Li et al. [22] discovered in the oxidative steam reforming of methane, a Pt coated Ni catalyst was better than a Pt-Ni alloy catalyst. Comparing to the activity in the steam reforming of methane without oxygen, the presence of oxygen led to decreased reforming activity in both pure Ni (2.6 wt% in catalyst) and Pt (0.1)+Ni (2.6) alloy due mainly to the oxidation of nickel, whereas Pt (0.1) coated over Ni (2.6) exhibited a high resistance to oxidation and maintained the activity even in the presence of oxygen. The mole ratio of Pt (0.1) to Ni (2.6) is only 0.01 and yet it was sufficient to protect Ni from oxidation. Considering the fact that the catalyst was calcined in air at 573 K for 3 hours and the bed temperature went as high as 1123 K in the oxidative steam reforming of methane we suspect that Pt segregates over the Ni surface and may not diffuse in as an alloy element.

Similarly Mukainakano et al. [23] found in the same steam reforming of methane, hysteresis with respect to the addition and removal of the methane oxygen mixture was clearly observed on a Pt (0.1)+Ni (2.6) alloy catalyst and pure Ni (2.6) catalyst but no hysteresis was observed for a Pt (0.1) coated Ni (2.6) catalyst. They also believed that the Pt coated Ni catalyst had Pt segregated on the surface which enhanced the reducibility of Ni drastically and eliminated the hysteresis behavior.

For steam reforming of ethanol, Soyal-Baltacioglu et al. [24] found the best catalyst was 0.3 wt% Pt-15 wt% Ni over δ-Al_2O_3. Here the Pt/Ni atomic ratio was only 0.006. It shows the importance of understanding the surface enrichment rather than the surface excess.

Pt-Shell Co-Core Nanoparticles

For Co core, Pt shell nanoparticles prepared by electroless deposition, Beard et al. [25] found that the lower Pt:Co ratio (monolayer Pt on Co) Pt-Co/C catalysts outperformed a commercial Pt/C catalyst.

Wang et al. [26] made ordered Pt_3Co intermetallic particles coated with 2-3 atomic layers of Pt. These nanocatalysts exhibited over 200% increase in mass activity when compared with the disordered Pt_3Co alloy nanoparticles.

So the monolayer Pt shell over Co nanowire is a distinct possibility. The size effect is shown by Frankenburg et al. [27]. Larger wires have better surfaces.

Pt-Shell Pt-Cu Nanoparticles

Strasser et al. [28] made $Pt_{25}Cu_{75}$, $Pt_{50}Cu_{50}$ and $Pt_{75}Cu_{25}$ nano particles and annealed them at 800°C and 950°C and then dealloyed electrochemically to remove Cu from the surface. They found a Pt-enriched surface layer (about 0.6 nm thick) in all these 4 nm particles. The fcc unit cell parameter for Pt on the surface (0.388 nm for $Pt_{75}Cu_{25}$, 0.382 nm for $Pt_{50}Cu_{50}$ and 0.375 nm for $Pt_{25}Cu_{75}$) was smaller than the

bulk Pt (0.392 nm) and they attributed the superb catalytic activity of these particles for the oxygen reduction reaction in fuel cell electrodes to the reduction in atomic spacing. For a thin layer of Pt on Cu the Pt spacing would be the smallest and the catalytic activity would be the best.

Yeh et al. [29] found that the oxygen reaction reactivity of the Pt-Cu nanorods was 2.2 times higher than that of the Pt nanoparticles after 1000 potential cycles. They attributed this to the 1-D morphology and the low Pt unfilled d-states by alloying.

Pt Shell Ag Core Nanoparticles

Wojtysiak et al. [30] tried to cover Ag particles with Pt shell by the galvanic replacement reaction between Ag and $PtCl_4^{-2}$. However, the coverage was not good and the shell had a lot of holes. To improve the integrity of the shell, seeded growth of Pt on the surface of Ag by the reduction of $PtCl_4^{-2}$ with ascorbic acid was used at room temperature. To cover the surface of an 11 nm Ag particle, the number of atoms of Pt in the final Ag@Pt core-shell particle must be at least the same as that of Ag.

Abkhalimov and Ershov [31] coated 6.3 nm Ag nanoparticles with Pt by treating with aqueous K_2PtCl_4 with hydrogen. The Ag/Pt atomic ratio ranged from 1/9 to 9/1. They used these particles to catalyze the reduction of methyl viologen with hydrogen in an alkaline solution. They found a critical thickness of about 1 nm for Pt below which no catalysis will take place. This critical thickness can be reduced when the nanoparticles are replaced by nanowires of large diameters.

Pryadchenko et al. [32] made C supported PtAg nanoparticles by the chemical reduction of H_2PtCl_6 and $AgNO_3$ in a mixture of water: ethylene glycol=5:1. A 0.5 M $NaBH_4$ solution was used as reducing agent. If both Ag and Pt salts were used together, the particles were solid solutions. But if the Ag salt was reduced first to form Ag nanoparticles and then Pt salt was added to be reduced, the nanoparticles had a core-shell structure. The shell had a thickness of at least 3 atomic layers of Pt.

Pt Shell Ag Core Nanotubes

Kim et al. [33] made Ag nanowires by heating 20 mL ethylene glycol (EG) to 151.5 C and adding 4 mM $CuCl_2{\cdot}2H_2O$ in 0.16 mL EG, 147 mM polyvinyl pyrrolidone (PVP, MW 55,000) in 6 mL EG, and 94 mM $AgNO_3$ in 6 mL EG and maintaining at this temperature for one hr. resulting in a gray solution of Ag nanowires. See Korte et al. [34] for more details. To coat the Ag nano wires with Pt, the Ag nanowire solution (32.16 mL) was cooled to 100 C, added slowly 20 mM K_2PtCl_4 in 6 mL EG and heated for 1 hr. The Pt shell Ag core nanotubes were obtained by centrifuge and washing several times with water and ethanol and NH_4OH to remove AgCl precipitates. To make pure Pt nanotubes, the Pt coated Ag nanotubes were treated with 6 M HNO_3 solution to remove Ag. In alkaline media, the Pt coated Ag nanotubes showed 50% better activity than pure Pt nanotubes and Pt/C.

Pt Shell Au Core Nanoparticles

Min et al. [35] overgrew Pt on the surface of Au nanocrystals of cubic, octahedral and spherical shapes. Different modes of overgrowth were observed depending on the shape of the gold core. It occurred on the planar surfaces of Au cubes, at the vertices of the Au octahedral and over the entire surface of the Au spheres.

Banerjee et al. [36] made 5 nm gold particles by the reduction of chloroauric acid with tannic acid and coated these particles by Pt using different amounts of chloroplatinic acid and hydrazine. For Pt/Au ratios of 0.19, 0.39, 0.58 and 0.88, the Pt thickness was half a monolayer, 1, 1.5 and 2 monolayers, respectively. The electrochemical activity was the best for the 2 monolayers with a mass activity 3 times better than the pure Pt nanoparticles.

Roy et al. [37] used 40 nm Au nanocrystals with extensive {111} facets and deposited 5 atomic layers of Pt on the surface by reducing hexachloroplatanic acid with ascorbic acid. Electrochemical evaluations revealed a compact Pt shell with a mass activity 4 times better than Pt black and comparable to that of Pt bulk metal.

Hartl et al. [38] used commercial 30 nm Au particles, highly crystalline and stably dispersed. To the dispersion they added hexachloroplatinic acid (mass of Pt=20% of Au), heated to 70-80°C, added 0.01 M ascorbic acid to reduce Pt to coat on Au particles. The Pt shell was about 3 atomic layers thick. The electrocatalytic activity for the oxygen reduction reaction using these core-shell particles equals that of bulk Pt.

Xiao et al. [39] fabricated nanoporous film of 100 nm thick by dealloying $Au_{50}Ag_{50}$ leaf at room temperature for 8 hours, rinsed and treated with 0.31 mM H_2PtCl_6 and 0.13 mM HCOOH in the dark to deposit Pt on Au. The catalytic activity of the nanoporous AuPt film towards electrochemidal oxidation of methanol increases with the loading level of Pt, resulting in the highest electochemical area of 70.4 m^2/g Pt, about 3 monolayers. Compared to the Pt nanoparticles supported in C, this self-supporting film uses much less Pt.

Kulp et al. [40] made Au nanoparticles by adding 1 mL of 1 wt% solution of $HAuCl_4{\cdot}3H_2O$ to 250 mL water with vigorous stirring. Then 1 mL of 1 wt% $Na_3C_6H_5O_7{\cdot}2H_2O$ in water was added and after 1 min, 1 mL of 1 wt% $NaBH_4$ and 1 wt% of $Na_3C_6H_5O_7{\cdot}2H_2O$ was added. The color change of the solution from light yellow to orange red indicated the formation of Au nanoparticles. The solution was stirred for another 10 min followed by adding 90 mg of Vulcan XC72 with continued stirring for 45 more min. The solution was filtered yielding a clear colorless filtrate which was dried for 3 hours at 90°C. TEM images showed homogeneously distributed colorless Au particles of about 5.5 nm adsorbed on C. To coat Pt shells on these particles, they used glassy carbon electrode in a solution of Pt $(NO_3)_2$ and $NaNO_3$ by pulsed electro deposition. See paper for details.

Zhang et al. [41] coated 6 nm Au particles with Pt resulting in particles of 9.0 ± 2.4 nm, 10.4 ± 2.8 nm and 13.0 ± 3.2 nm sizes. These particles stabilized by polyaryl ether trisacetic acid ammonium chloride dendrons and had higher catalytic activity than monometallic Pt nanoparticles. They attributed this to the fact that Au core attracts electrons from Pt.

Li et al. [42] made 55 nm Au particles by reducing $AuCl_4^-$ with sodium citrate. Then different amounts of 1 mM of H_2PtCl_6 were added and the mixture was heated to 80°C. Then while stirring, a solution of 10 mM of ascorbic acid was slowly dropped into the mixture until half of the volume of H_2PtCl_6 was added. The mixture was stirred for another 30 min. and should change from red brown to dark brown indicating the coating was complete. The final diameter of the core-shell particle can be estimated from the volume ratios of Au and Pt. The mixture was then centrifuged 3 times before coated on a smooth and clean glass carbon surface for testing.

Gao et al. [43] coated only 2 monolayers of Pt on 16 nm Au particles by reducing H_2PtCl_6 with ascorbic acid. The uncoated Au nanoparticles exhibited a strong localized surface Plasmon resonance (LSPR) peak at 520 nm. After coating, the LSPR peak shifted to 508 nm.

Zhang et al. [44] made 55 nm Au particles by reducing $HAuCl_4$ with sodium citrate. Then 30 mL of sol containing the 55 nm Au seeds were mixed with 0.76 mL of 1 mM H_2PtCl and heated to 80°C for a few minutes. Ascorbic acid (0.4 mL, 10 mM) was slowly dropped into the mixture with vigorous stirring. Th coated Pt shell over the Au surface was about 0.7 nm thick. The coated Au particles were almost spherical. The sol was centrifuged 3 times to remove excess reactants.

From these observations, it seems likely that gold wires can be coated with only one mono layer of Pt to increase its catalytic activity.

Pt and Pt Alloy Nanowires

Higgins et al. [45] made Pt-Co alloy nanowires by mixing 0.001 m Pt acetylacetonate and 0.001 m Co carbonyl, dissolved in ethylenediamine under nitrogen protection and transferred to an autoclave reactor at 160°C for 1 hour under 600 W powers. Pt-Co alloy nanowires of about 35-60 nm diameters were formed and collected by filtration and washing followed by annealing at 600°C in Ar for 1 hr. These nanowires were found much more stable catalytically than Pt nanoparticles supported on C.

Yaipimai and Pornprasertsuk [46] made Pt, Pt-Cu and Pt-Sn alloy nanowires by electro spinning using the salts and PVP, Poly (vinyl pyrrolidone) with molecular weights 1.3×10^6 and 4×10^4 g/mole.

Pt Shell Pd Core Nanoparticles

Cao et al. [47] made the Pd core Pt shell nanoparticles by using an area selective atomic layer deposition method. The Pt shell thickness could be monitored by an in-situ quartz crystal microbalance. The catalyst with one monolayer Pt shell showed the best mass activity and selectivity and the lowest barrier for CO oxidation.

Choi et al. [48] did electro less deposition of Cu on Pd Nanoparticles and galvanic displacement of Cu by Pt. The catalyst is active toward electro-oxidation of methanol and is more stable against CO poisoning than a commercial Pt/C catalyst.

D'Souza and Sampath [49] made highly uniform, stable Nano bimetallic dispersions using organically modified silicates as the matrix and the stabilizer. They found that the structure of the particles consists of a Pt shell and a Pd core. No aggregation or segregation of the particles was observed after prolonged storage of several months.

Shao et al. [50] found that the specific oxygen reduction reaction activity of Pt shells over Pd octahedra enriched with {111} facets was 28 times higher than that of Pd octahedral without Pt. It was only 3 times better than Pt coated Pd cubes enriched with {100} facets. The Pt coated Pd octahedra also showed excellent durability during potential cycling suggesting their great potential for application in fuel cells.

Wongkaew et al. [51] made electro less deposition of Pt on Pd surfaces of 30 wt% Pd/C. Pt loadings of 6.0, 11.7, 17.2 and 22.7 wt% corresponded to Pt shells of 0.9, 1.7, 2.7 and 3.4 monolayers on Pd. These core/shell catalysts were very active, especially the sample of 0.9 monolayer coverage which had a mass activity of 329 A/gPt as compared to 183 A/gPt for a conventional 50.5 wt% Pt/C sample.

Li et al. [52] synthesized C supported Pd_3Au@Pt core-shell electrocatalyst by chemical reduction of K_2PtCl_4, K_2PdCl_4 and $NaAuCl_4$ with ascorbic acid. The resultant particles (3.4 nm diameter core) had a thin layer (less than 1 nm) of Pt shell. They had a mass activity of 939 A/gPt for oxygen reduction reaction, 4.6 times that of commercial Pt/C (203 A/gPt). But the durability was about the same. They proposed that the tension in the Pt shell and the electron transfer from the core to the shell contributed to the improved electrocatalytic activity.

Pt Shell Ru Core Nanoparticles

Chen et al. [53] coated Ru nanoparticles (3.2 nm diameter) with 1.5-3.6 atomic layers of Pt. The sample with 1.5 atomic layers showed a 3.2 fold improvement in CO tolerance and 2.4 fold current enhancements during methanol oxidation as compared to the commercial Pt/C.

Yang et al. [54] found that the Pt shell grew on <111> radial facets and <200> face facets of the Ru core if the incubation time was short. For 2 hours incubation, severe chemical etching occurred prior to shell growth. So the dynamic rearrangement at the core-shell interface is important for the final structure.

Wang et al. [55] made Pt shell (0.42 nm thick or about 1.5 atomic layers) and Ru core (3.18 nm diameter) nanoparticles (4.02 nm diameter total). Compared to the pure Pt nanoparticles of 4.38 nm diameter, these Pt-shell Ru-core nanoparticles showed 4.5 fold more power density for the direct methanol fuel cell. The open circuit voltage was improved by 0.18 V (from 0.49 to 0.67 V). They attribute the improvement to the lattice compression in the Pt shell due to the core.

Huang et al. [56] made 15 wt% $Pt_{50}Ru_{50}$/C nano particles (2 nm) by the method of incipient wetness impregnation and activated by hydrogen reduction at 620 K. The reduced catalyst with Pt rich in the shell and Ru rich in the core was subsequently modified by oxidation in air. This oxidation enhanced significantly the electrochemical activity of Pt-Ru/C for electro-oxidation of methanol. Such enhancement was attributed to the segregation of Ru and the formation of RuO_2.

Pt Shell Pd Core Nanowires

Guo et al. [57] started with Te nanowires (11 nm diameter) produced by a hydrothermal route and used them as both reducing agent and sacrificial template to make Pd nanowires in aqueous solution at room temperature in less than 5 min. The Pd nanowires were used as seeds to direct dendritic growth of Pt upon the reduction of K_2PtCl_4 with ascorbic acid in aqueous solution.

Liao and Hou [58] made Pt-on-$Pd_{0.85}Bi_{0.15}$ nanowires by a facile, one pot, wet-chemical and templateless method in the presence of oleylamine and NH_4Br. These nanowires had 8.3 ± 1.1 nm diameters and 387 ± 105 nm length. Small Pt nanobranches (5 nm) grew on the Pd nanowires at the end of which Pt nanoflowers grew. They could see also about 2 nm thick of amorphous C on the nanowires. Depending on the composition and the ratio of Pd/Bi/Pt they could grow nanowires, nanoflowers, nanoparticles or nanoplates. They all demonstrated high electro-chemical activity and durability for the oxygen reduction reaction.

Xia et al. [59] reported a facile solvothermal synthesis of nanowire assemblies composed of ultra-thin (3 nm) and ultra-long (10 μm) Pt, Pt-Au and Pt-Pd nanowires without involving any template. These nanowires can be easily cast into a free-standing membrane which exhibits excellent electro catalytic activity and very high stability for formic acid and methanol oxidation and the oxidation reduction reaction.

Pt Shell Cu Core Networks

Feng et al. [60] made nanoporous Cu by electrodepositing Zn on a 0.1 mm Cu plate, making Cu-Zn alloy by heating and then removing Zn by HCl. They followed the method described by Leaman [61].

Then they deposited Pt onto the Cu surfaces by electroless plating. This NPCu-Pt catalyst can reduce CO_2 in the ionic liquid $BMIMBF_4$ (1-butyl-3-methyl-imidazolium-tetra-fluoborate) with more stable current, higher current density and efficiency compared to the pure Pt catalyst.

Pt Shell Cu Core Nanowires

Alia et al. [62] and Wittkopf et al. [63] already made Pt shell (14 monolayers) over Cu core nano wires with mass activities of 0.1-1.0 A/mgPt which may be improved by reducing the number of monolayers of Pt on the surface.

Conclusions

It is seen that there are many possibilities to make a single layer Pt Shell over large nanowires of a cheaper metal so a commercial catalyst for a fuel cell can be made to make self- driving automobiles widely used soon. It is anticipated that we will have cheaper and safer ground transportation available in the very near future.

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Citation: Li JCM (2017) Pt-Shell Nanowires for Fuel Cell Electrodes. J Material Sci Eng 6: 337. doi: 10.4172/2169-0022.1000337