

The Role of Water-Surface Interactions of Platinum Based Catalysts in Electrochemical Methanol Oxidation

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Study focuses on the impact of potential of zero total charge (PZTC) determined with N₂O reduction on different Pt-based catalysts in three important proton exchange membrane fuel cell (PEMFC) reactions, namely oxygen reduction (ORR), CO oxidation and methanol oxidation (MOR). The catalysts activities are correlated with a change in PZTC, hence with a change of structure and surface coverage of adsorbed water (and other adsorbed species). These correlations indicate that adsorbed water and its dissociation products (OH_{ad}) together with other adsorbed species govern the trend in the rates of the above reactions.

1. Introduction

Rapid growth of population together with our current unsustainable lifestyle requires progressively increasing amounts of energy which is still based on un-renewable natural sources like natural gas, oil and coal. Many scientists and technology developers are focusing their interests towards energy conversion, which enables us to transform chemical energy to electricity or to produce molecules that can be stored and later when necessary transformed back to electricity in a non-polluting way. Two prospective energy cycles are lately being studied intensively: carbon (CO₂ to mainly hydrocarbons and also methanol and back) and water cycle (H₂O to O₂ + H₂ and back) (Markovic, 2013).

Fuel cells like PEMFC and direct methanol fuel cells (DMFC) directly convert chemical energy from hydrogen or methanol to electricity at temperatures below 100 °C with relatively high efficiencies (not limited by Carnot cycle like combustion engines). Methanol has some important advantages over hydrogen in replacing it as a fuel. It gives 6 electrons per molecule, it can provide high current densities, it is in liquid form therefore it is more convenient for storage and transportation. However it has huge polarisation losses mainly due to the poisoning of the electrode by CO (intermediate) which in reality only provides half of the thermodynamic voltage (1.23 V). Besides it also tends to form stable intermediates like formic acid or formaldehyde that lower the efficacy. One of the solutions is to make new multifunctional catalysts that can fix all of the polarisation and poisoning issues. For this one need to study fundamentals in the platinum based surface and water interface. This must come together with strong design and optimisation engineering (S. Basri, 2009).

In this study I extend our previous short communication (Hodnik et al., 2012) with results on the Pt nano-particle size dependant MOR activity and explain in more depth our basic approach for the explanation of MOR activity of the Pt-based catalyst. Evidence from the literature and our measurements indicate that the water-surface interactions (like shifts in PTZC and OH_{ad} formation) govern the availability of Pt surface active sites (surface coverage, Θ) and therefore directly the rates of the above reactions.

2. Theory

2.1 PZTC

In interfacial electrochemistry the potential of zero charge (PZC) is a potential, related to the phenomenon of adsorption, where net electrical charge on a surface equals zero. It was treated both theoretically and experimentally by Frumkin (Frumkin and Petrii, 1975). In real systems only potential of zero total charge (PZTC) or also closely related potential of maximum entropy (PME) (Harrison et al., 1973) can be

accessible, since the real PZC is shifted by the free charge induced by adsorbed mono-poles and the charge corresponding to the formation of chemical bonds (for example, the electrosorption of hydrogen atoms at platinum). From here on I use the term PZC although it would be more correct to use PZTC. Trasatti found a parallel between metals work functions and PZC (Trasatti, 1971). They best correlate when the degree of water orientation was included through the effective electronegativity derived from plots of work function and the chemical electronegativity given by Pauling ("more electropositive the metal the stronger the adsorption of water"). The theoretical calculations and experimentally observed results both show negative shift of PZC by solvation (lower cca. 1 V from vacuum to the 2/3 water mono-layer) (Jinnouchi and Anderson, 2008). It was also concluded that the charge redistributions due to the adsorption of water molecules is the main reason for this negative shift of the PZC. At a charged surface a strong electric fields (cca. 10^7 V or several V/Å) orients the first mono-layer of water molecules with the strong electrostatic interactions with water dipoles (water orients with H-down or O-down). Fields of this magnitude can distort molecules, induce ionization and break bonds, thus play a vital role in interfacial chemistry. The effect is similar as in the electric fields around solvated ions (Conway, 1992). At the PZC the first layer density has minimum and increases as the potential is changed in both to the positive or negative direction (Toney et al., 1994). Therefore at PZC the surface (in the inner Helmholtz plane) is relatively easily accessible by the neutral molecules whose interaction with the Pt is weaker than water (N_2O (Climent et al., 2002) or peroxodisulfate (Climent et al., 2008) molecules). In theory the highest adsorption coverage of non-ionic species is around PZC (Vielstich et al., 2003) and this is also where the pick current density for N_2O reduction is measured (Climent et al., 2002). More common way to determinate PZC is to measure the displaced charge with the introduction of CO (Climent et al., 2002, Mayrhofer et al., 2005). With increasing the potential in the positive direction the increasing H_2O -metal interaction is observed and at the potentials roughly around 0.50 V vs. RHE the H_2O dissociation start to occur with formation of adsorbed OH_{ad} , where water can bond on platinum even more strongly than CO (Giz et al., 2007). Climent et al. showed with a nanosecond-laser-pulsed experiments that the potential at which water reorientation occurs (PZC) shifts in different directions, depending on the relative values of the electronegativity of the ad-atom and the substrate (García-Arárez et al., 2008). If ad-atom is electropositive it retains the surface local positive charge density. The effect on the electronic density on the surface is important to understand the so-called "ligand and strain effect" platinum based alloys electro-catalysts (Stamenkovic et al., 2007, GreeleyJ et al., 2009, Strasser et al., 2010, van der Vliet et al., 2012). Nørskov et al. showed that different Pt alloys have different adsorptive energies for the oxygenated species (oxygen binding energy) (Nørskov et al., 2004) and for CO (Ruban et al., 1997). They used the density functional theory (DFT) to predict the position of d-band centre that as they say has the decisive influence on an adsorptive energy. Similar adsorption properties of Pt-alloys were obtained by Linic's group with a relatively simple model (without DFT) using only electronegativity, atomic radius, and the spatial extent of valence orbitals) (Xin et al., 2011). The different electrochemical adsorption properties of different types of Pt-based surfaces were experimentally confirmed by van der Vliet et al. (van der Vliet et al., 2012). They show that the adsorption of hydrogen and oxide species potential is shifted and reduced in magnitude compared to monometallic Pt in the same potential region.

2.2 ORR

Oxygen reduction on Pt can occur by two general reaction pathways (Wroblowa et al., 1976): the dissociative pathway, in which oxygen dissociates upon adsorption and the associative pathway, in which reaction proceeds through a peroxy intermediate which received much attention lately since its stability determines the reaction pathway (Katsounaros et al., 2012). For the purpose of this paper it is however not important to deduce which pathway is the dominant one as the rate loss in ORR on our samples is a consequence of a loss of active sites that get blocked with oxygen containing species like water and its dissociation products in 0.1 M HClO_4 (Stamenkovic et al., 2007, GreeleyJ et al., 2009). These capacitive reactions are occurring also in the absence of O_2 (Figure 1). The extent of this passivatization of surface is governed by nature of the catalyst surface like work function and electronegativity that is closely related to PZC (Trasatti, 1971). The passivation of the surface by water or the inability of oxygen to displace the strongly adsorbed water molecules was already suggested in the 60s and 70s by authors like Hoar (Hoar, 1967), Evans (Evans, 1971) and Burke and O'Meara (Burke and O'Meara, 1972). In the absence of strongly adsorbing anions it is basically the competition between water (and its dissociation products) and reactive species (like oxygen or methanol) for a spot on the platinum surface (water concentration is high; approximately. 55.5 M). This was elegantly shown by Strmčnik et al. with different cations in the alkaline electrolyte. They prove that OH_{ad} that is stabilised by cation-water cluster covers the Pt (111) and lowers the activity of the reactions of ORR, hydrogen oxidation reaction and MOR (Strmčnik et al., 2009). And that the extent of the coverage increases with the hydration energies of the cations: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$.

With the effects like *ligand* and *strain* in Pt-alloy one can also see the changed affinity and/or coverages of surface blocking species (water or OH_{ad} – depending on the position on the volcano curve or also referred as Sabatier principle) and therefore changed ORR activities (Mavrikakis et al., 1998, Stamenkovic et al., 2007, Zhang et al., 2005, Greeley et al., 2009, Strasser et al., 2010, van der Vliet et al., 2012). Similar was observed also by Mayrhofer et al. for different Pt particle sizes (in 0.1 HClO_4). They got a clear correlation between PZTC and ORR specific activity where more active catalyst has more positive PZTC. The same trend was also shown Pt-alloy nanoparticles (Hodnik et al., 2012). This implies a general rule that the water surface interaction (coverage) governs platinum's ORR specific activity. Similar effect was already nicely explained by Parsons in the 60s: “The effect of the nature of the electrode on the kinetics of electrode reactions is considered. This effect may be primary in the sense that the electrode exerts a direct influence on the state of the reactants or may itself be a reactant. On the other hand, secondary effects occur when the nature of the electrode affects the state of non-reactants which then influence the rate or course of the reaction.” (Parsons, 1964). However, it must be noted that the electrode processes of heterogeneous reactions at a metal-solution interfaces are more complex (like Frumkin effect) (Timmer et al., 1969) and here I only provide a simplified description that fits to all of our experimental data.

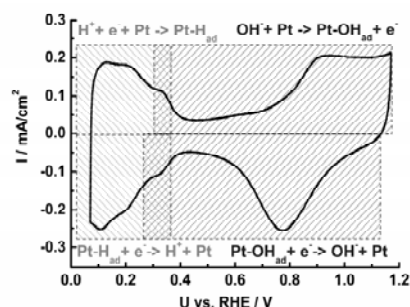


Figure 1: Cyclic voltammogram for PtCu/C nanoparticles in 0.1 M perchloric acid 0.2 V/s.

2.3 CO oxidation

Proceeds through Langmuir–Hinshelwood reaction mechanism or as it was called in the 60s the “reactant-pair” mechanism (Gilman, 1964) where CO reacts with OH_{ad} to form CO_2 in the whole potential region (Marković et al., 1999). The adsorbed OH group is formed by dissociation of water in which an applied field stretches an H–O bond leading to dissociation and removal of a hydrated proton. This leaves an OH_{ad} group that can react directly with CO to form solvated hydronium ion and CO_2 . Due to high reactivity and sensitivity between CO and OH_{ad} , CO oxidation can be elegantly used as a probe for the origin of the formation of the OH species on the surface. Like ORR, CO-stripping (oxidation of one monolayer of pre-adsorbed CO) was also proven to be Pt particle size dependant (Arenz et al., 2005) where the bigger particles burn CO at lower potentials (in 0.1 HClO_4). I must also note that CO can also convert to CO_2 without adsorbed partner (OH_{ad}) with Eley–Rideal mechanism (Urchaga et al., 2012). However for the present study this is not relevant since it only occurs to minor extent at almost full CO coverage’s.

2.4 MOR

Methanol electrooxidation (like ORR) has a very rich history with a numerous papers published with its share of controversy. However the community seems to agree that the reaction has two pathways: a direct route to CO_2 and an indirect route through an adsorbed CO intermediate, which poisons both the direct and indirect routes (Parsons and VanderNoot, 1988, Sriramulu et al., 1999). Ferrin et al. (Ferrin et al., 2008) examined both pathways computationally for a variety of catalysts. They found that the indirect route could be characterized by two descriptors: the free energies of CO_{ads} and OH_{ads} . However, the reaction on a Pt surface was most sensitive to the OH_{ads} free energy. Stuve’s group showed by mathematical modelling and by experiments that the formation of CO_2 through the CO_{ad} intermediate is significantly slower than the parallel dehydrogenation pathway in 0.1 M methanol on a Pt(111) electrode at 0.6 V (Sriramulu et al., 1999). However the formed CO passives the surface and consequently influences the direct route. MOR was like ORR and CO-oxidation found to be Pt particle size dependant (in 0.1 HClO_4) where larger particle give higher current densities (Takasu et al., 2000).

In the 70s Watanabe and Motoo provided a proof of concept for an ad-atom bi-functional mechanism of MOR with the bi-functional catalyst (Ru ad-atoms on Pt surface) (Watanabe and Motoo, 1975). The high activity of Pt surface with small percentage of ruthenium was already known (Petry et al., 1965). Since then it is well established that ruthenium based catalyst have better MOR activity than pure platinum. This is due to the enhanced rate of CO_{ad} oxidation for which some say that it changes CO_{ad} from spectator to a

reaction intermediate (Marković et al., 1995). In our opinion the principal effect of opening the dehydration channel at steady-state (via the presence of Ru in the surface) is to lower the coverage of CO_{ad} and permit the oxidation of methanol to go through the dehydrogenation path. In other words, we get more free surface sites to run the reaction through the direct pathway to CO_2 . This is because OH_{ad} that is formed on Ru sites spills over to Pt site where CO_{ad} can be oxidized at lower potentials.

3. Experimental

Experimental setup has been explained in our previous publication (Hodnik et al., 2012). The new carbon-supported Pt nanoparticles samples with mean diameters of 1 nm and 5 nm in this study were supplied by TKK (Tokyo, Japan). The pure platinum sample Pt Black was provided by Umicore AG.

4. Results and discussion

In Figure 2c one sees N_2O reductions curves. Potential at the minimum coincides with the PZTC. In the Figure 2b there is a correlation between the activities of ORR and MOR at 0.9 V and PZTC. This implies that water surface coverage (it decreases with the increase of PTZC) governs the ORR and MOR activity.

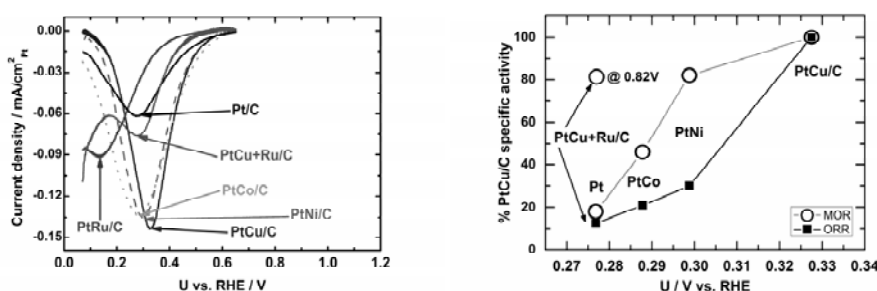


Figure 2: a) N_2O reduction on different Pt-based catalysts. b) Relation between PZTC and normalized ORR and MOR specific activities at 0.9 V.

With the measurements of ORR and CO-stripping (Figure 3a) on samples with different Pt sizes (1, 5 and 30 nm) and highly active PtCu/C sample one can simulate and predict (as we already did for Pt polycrystalline and Pt-alloy nanoparticles: interested reader is invited to read the reference (Hodnik et al., 2012)) the correct trend for MOR (Figure 3b). As was already shown in the literature bigger particles show better specific activities (Takasu et al., 2000). I must note that in the case of 1 and 5 nm samples the calculated coverage is below 0 which is impossible. However this is just a simulation that sums two separately measured coverages (CO and ORR measurements). From these new results one can again confirm the two important findings from our previous publication (Hodnik et al., 2012):

- The adsorbed spectators and reactive intermediates regulate the surface occupancy, which directly influences the kinetic currents in ORR and MOR.
- The MOR current is directly influenced by the potential window in which the surface is least occupied by adsorbed spectators and reactive intermediates for CO oxidation and oxygen reduction.

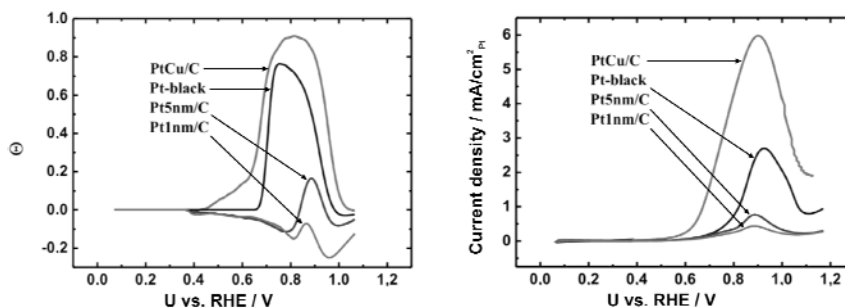


Figure 3: a) Simulated surface coverages and b) polarization curves for MOR of platinum samples.

5. Conclusions

Climent and Feliu wrote in their conclusion remarks in the review about PZC and more (Climent and Feliu, 2011): "Finally, I want to stress the importance of the properties mentioned above, such as the PZTC,

PZFC and the PME, energies and entropies of adsorption and orientation of adsorbed water as key properties giving clues to understand the reactivity of platinum with unprecedented detail.”. With that in mind I want to stimulate the reader to construct his or her own picture of the platinum-water based electrolyte interface and its electrocatalytic activities. And further to spark new fundamental research on the influence of the water in electrocatalysis.

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