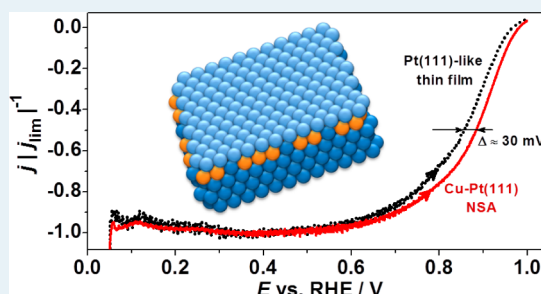# Thin-Film Cu−Pt(111) Near-Surface Alloys: Active Electrocatalysts for the Oxygen Reduction Reaction

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Ⓢ *Supporting Information*

ABSTRACT: A simple method is presented for the formation of thin films of Cu−Pt(111) near-surface alloys (NSA). In these thin films, the solute metal (Cu) is preferentially located in the second platinum layer and protected by a Pt surface layer. The NSA-films act as active and fairly stable electrocatalysts for the reduction of oxygen with the activity and stability which approach those for bulk single crystalline Pt-alloy surfaces and ~5 times more active than state-of-the-art Pt thin films.

KEYWORDS: *near-surface alloys, ORR, electrocatalysis, Pt(111)-like thin films*

Alternative energy sources continue to attract significant attention because of concerns about fossil fuel supply and numerous ecological and environmental factors.[1,2] Proton exchange membrane fuel cells (PEMFCs) are promising clean power sources for both automotive and stationary applications. However, high cost of state-of-the-art Pt catalysts which are currently used at the cathode side of the fuel cells, where oxygen reduction reaction (ORR) takes place, prohibit wider commercialization of PEMFCs.[3] Further technological advances are necessary to improve stability and increase the activity of Pt catalysts toward the ORR. For PEMFCs to be economically viable, the ORR-activity should be improved 4−10 times compared to that of Pt(111) surfaces.[4,5]

A viable route to improve the catalytic activity of Pt is to benefit from so-called strain and ligand effects[6−8] and use Pt alloys with other less noble metals, such as Y, La, Ni, Co, and Cu. The electronic structure, and hence, catalytic activity of the surface Pt layer can be efficiently tailored with the solute metals.[6−8] Recent density functional theory (DFT) calculations have shown that for Pt alloys, to optimize the ORR-activity, the electronic structure of the Pt surface should be modified to bind weaker ORR-intermediates such as *OH, *OOH, and *O (where "*" denotes an adsorbed species).[3,8,9]

Figure 1 summarizes literature data for the experimentally measured ORR-activity as a function of the calculated *OH-binding energy for some state-of-the art catalysts.[3,8−11] It can be seen from Figure 1 that Pt₃Ni(111) surface demonstrates the best known ORR-activity.[10] This alloy binds *OH ~0.12 eV weaker than Pt(111) and is close to the theoretical DFT-predicted optimum (Figure 1).

While the best-known bulk metal alloys (such as Pt₃Ni and Pt₃Y) use both strain and ligand effects, Cu−Pt(111) near-
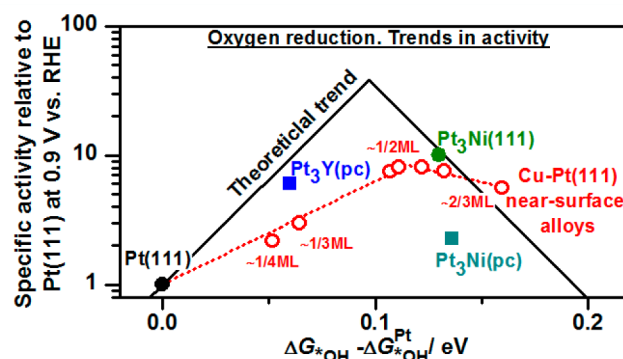

Figure 1. Experimental ORR-activity plotted as a function of *OH-binding energy for some single crystal and polycrystalline (pc) catalysts. The data are taken from refs 3, 8−11.

surface alloys (NSAs) show improved ORR-activity mostly because of the ligand effect.[8] Submonolayer amounts of Cu are stabilized preferentially in the second Pt layer and effectively modify the electronic structure of the Pt surface layer.[7,8,12−14] As can be seen from Figure 1, Cu-NSAs show ORR-activity close to that observed for Pt₃Ni(111).

There are several technological advantages to the use of Cu-NSAs in fuel cell applications compared to other active alloys: (i) Cu is more stable against electrochemical oxidation than other solute metals, for example, Ni, (ii) DFT calculations and experimental measurements suggest that Cu is stabilized in the

second Pt layer to such an extent that it should survive in the electrode potential region relevant for PEMFC applications, (iii) it is supposed to be considerably easier to reactivate the catalyst by using the catalyst formation process introduced in this paper than to reactivate a full alloy electrode.

However, in real fuel cell applications, optimization of the ORR-activity is not the only concern. Currently, highly dispersed Pt nanoparticles on carbon supports are widely used as the state-of-the-art commercial catalysts for PEMFC cathodes. Figure 2A schematically shows the contact between a
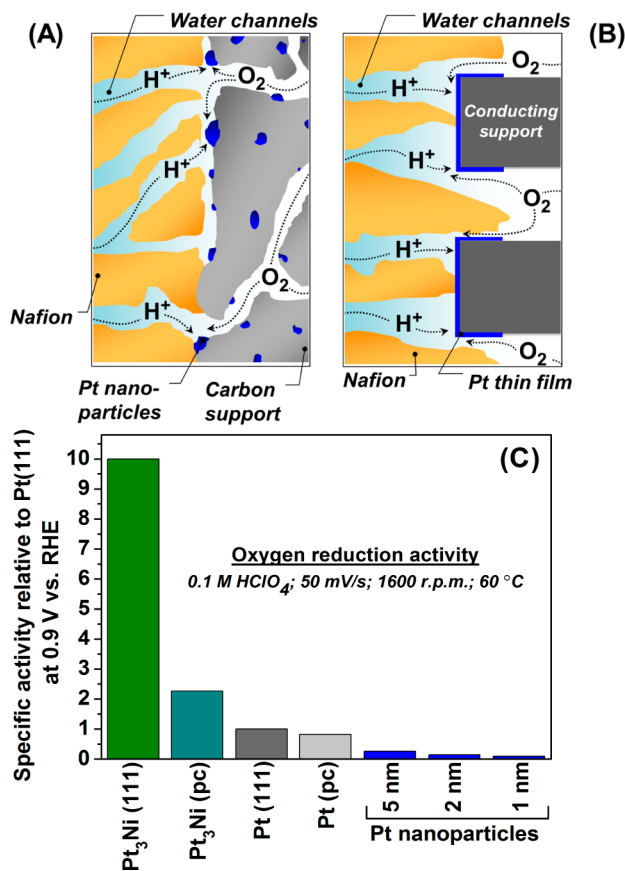

Figure 2. Schematics of the contact between a catalyst and a proton conducting Nafion membrane in PEMFCs for the cases of carbon supported Pt-nanoparticles (A) and an idealized thin-film catalyst (B). ORR-activity for some (111)-single crystalline surfaces, polycrystalline surfaces, and nanoparticles (C). The data in (C) are taken from refs 10,11, and 15.

proton-conducting Nafion membrane and a carbon supported Pt-nanoparticle catalyst. While the use of nanoparticles significantly increases the Pt surface area, there is a considerable amount of catalyst which is not involved in the electrochemical reaction.

Ideally, Pt-nanoparticles should be located at the boundary between the proton conducting Nafion membrane and electron conducting support where both protons and O_2 from the gas phase are easily accessible (Figure 2A). Large amounts of nanoparticles loaded to PEMFCs do not satisfy these criteria, hence decreasing the catalyst utilization. Moreover, Pt nanoparticles are largely nonstable when compared to bulk materials and thin films.[3]

Attempts were undertaken to overcome the aforementioned complications by using specially designed polycrystalline thin

films[16] to approach a more ideal situation (Figure 2b) where the Pt-catalyst is used precisely at the required boundary and provides improved stability.[16] However, these technological advances meet complications related to the ORR-activity. As the ORR-activity of Pt and Pt-alloy nanoparticles as well as polycrystalline materials are drastically reduced compared to single crystalline (111) surfaces, as shown in Figure 2C.

In this communication, we report a simple method to form thin films of Cu−Pt(111) NSA which demonstrate activity and stability approaching those for bulk single crystalline alloy surfaces. Also, we investigate model continuous Cu−Pt(111) NSA thin films as a potentially promising catalyst material with improved activity and stability.

The procedure to form Cu−Pt(111) NSA thin films is schematically presented in Figure 3. Thin Pt(111)-like films,
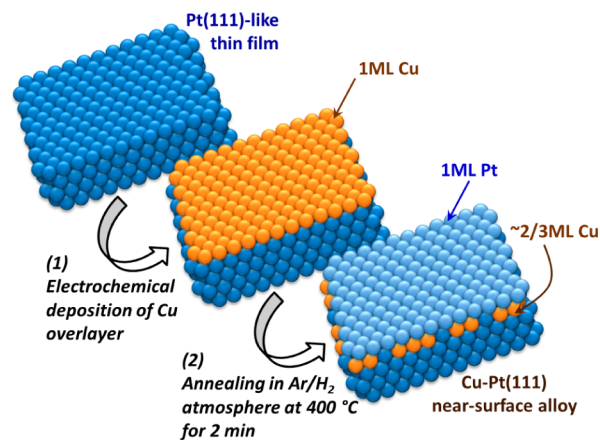

Figure 3. Procedure for Cu−Pt(111) NSA film formation.

formed through a simple preparation procedure that we reported recently,[17] on a conducting support are used as the starting material. To form the NSA, a monolayer of Cu is initially deposited onto the Pt(111)-like thin film via electrochemical undepotential deposition (UPD). In UPD, metal deposition is limited to monolayer quantities by ensuring the electrode potential remains too anodic for bulk metal deposition. To form a compact monolayer of Cu on the Pt(111)-like thin film, the potential is held at 0.33 V (RHE) for 3 min in an electrolyte containing 1 mM Cu^{2+} + 0.1 M $HClO_4$. The sample is then annealed under a reducing Ar/H_2 (5%) atmosphere at 400 °C for 2 min in a tube furnace (see Supporting Information for further details). This reductive annealing forces the Cu to move into the second Pt-layer as shown schematically in Figure 3. Previous studies have shown that approximately 2/3 ML of Cu is stabilized in this second layer while the rest migrates into the bulk Pt-phase.[3,8,12−14] It should be noted here that this NSA-approach is very different from the Cu−Pt nanoparticle catalyst formation reported by Strasser et al.[18] The Cu−Pt nanoparticle catalyst is prepared from a chemically synthesized alloy with subsequent electrochemical oxidation of Cu available at the surface Pt layers. This procedure results in the formation of a thick protective layer of Pt which is active toward the ORR predominantly because of the strain effect.[18]

The resultant cyclic voltammogram (CV) of the formed NSA film is markedly different than that of the Pt(111)-like thin film (Figure 4A): for example, *OH-adsorption starts at more anodic potentials. This voltammogram is in excellent agreement
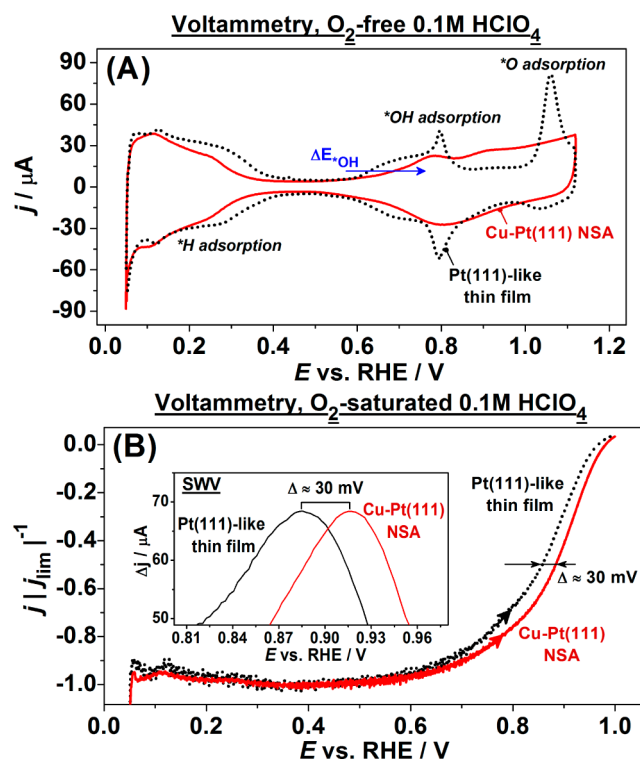
Figure 4. CVs of Pt(111)-like thin films and Cu−Pt NSA formed on Pt(111)-like thin film in (A) O$_2$-free and (B) O$_2$-saturated 0.1 M HClO$_4$. T = 295 K, dE/dt = 50 mV/s. Inset of (B) shows corresponding square-wave voltammograms.

with the voltammograms of Cu-NSAs formed on Pt(111) single-crystals reported in refs 8 and 14.

The usual method to test the ORR-activity of Pt-based catalysts is to use a rotating disk electrode (RDE). However, the use of commercial RDE-equipment with the large thin-film substrates was prohibitively difficult. We, therefore, utilized cyclic voltammetry and square-wave voltammetry (SWV) to elucidate the activity of the formed NSA (see experimental details in Supporting Information).

The results of these experiments are shown in Figure 4B. It can be seen that the "half-wave" potentials for the ORR in the CVs and the peaks in SWVs for ORR show the same anodic shift of 30 ± 3 mV. This confirms that the Cu-NSA is significantly more active than the initial Pt(111) surface. The half-wave potential for the Pt(111)-like thin film is in excellent agreement with that observed on Pt(111) bulk single crystals (∼0.86 V).[3,8,10,14] To the best of our knowledge, this is the highest ORR-activity reported for Pt thin films up to date and measured under similar conditions. The observed half-wave potential for the NSA-films is approximately 0.89 V, which is slightly lower than that reported for the same Cu-NSA prepared on Pt(111) single crystals (∼0.9 V, measured at 60 °C, see Supporting Information for further discussion on reproducibility).[8,14] Nevertheless, the developed NSA thin-film catalyst shows the activity which is ∼5.5 times better than for the state-of-the-art Pt nanostructured thin films and ∼3.6 times better than bulk Pt(pc) measured under the same conditions at 0.9 V (RHE) in ref 15. This corresponds to the turnover frequency ∼17ē/s per active site of Cu−Pt(111) NSA surface at room temperature at 0.9 V. However, further optimizations of the Cu content in the second layer are necessary to achieve

the optimum activity which is likely possible in this system (Figure 1).

The formed NSA thin film and ORR-activity were stable for at least 3 h [Figure 4B shows voltammograms taken after the sample was scanned in the potential region between 0.05 V and 1.0 V for ∼3 h (see Supporting Information for further details related to stability, reproducibility and the ORR-activity issues)] while the activity of the thin film was investigated by cycling the potential between 0.05 and 1.0 V vs RHE. Further studies are required to fully evaluate the stability of such NSA thin films. However, it is important to note, that whereas the degradation of nanoparticles in conventional PEMFCs would necessitate a complete replacement of the cathode material, thin-film NSAs would be degraded by loss of submonolayer amounts of Cu, without serious contamination of the PEMFC working parts. The thin-film catalyst could then be simply regenerated with the procedure described in Figure 3. This would lower the total operational cost over the lifetime of PEFMCs.

In conclusion, we have developed a quick and simple method to form Cu−Pt(111) NSA thin films. This method provides a promising route to fabricate in the future active and stable cathodes with maximum utilization of the catalyst at the boundary between the catalyst and a proton conducting Nafion membrane in PEMFCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and comments on reproducibility, ORR-activity, and stability of Pt(111) thin films and Cu-Pt(111) NSA samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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