Application Note

Significance of SKP and SECM Integration in the Study of Noble-Metal-Based Electrocatalytic Materials

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The work function (WF), a crucial factor in the charge transfer process, is correlated with catalytic activity.[1,2] This discovery, combined with the use of scanning Kelvin Probe (SKP) to measure contact potential difference and generate high-resolution maps of work function or potential distribution, has opened new avenues for our understanding of metal-catalyzed reactions.

These reactions, also known as electrochemical promotion of heterogeneously catalyzed reactions, depend exponentially on catalyst work function. In this application note we explore the significance of combining SKP with in-situ scanning electrochemical microscopy (SECM) for studying noble metal based electrocatalytic materials. This technique provides valuable insights into the underlying correlation between electronic and electro-catalytic characteristics of recently developed noble-metal-based electrocatalytic materials.

Pt- and Pd-based alloys, have shown significantly high electrocatalytic activity for water electrolysis and proton exchange membrane fuel cell (PEMFC), in both acidic and alkaline media when compared to pure, noble metal catalysts. This has been attributed to reduced binding energy when the noble metals are alloyed with more oxophilic elements. Nevertheless, it should be noted that either too strong or too weak M-H (M stands for metal surface) binding energy may result in poor catalytic behavior. According to the free energy of activation (ΔG^*) for proton (H^+) reduction, work function may be directly correlated with the strength of the M-H bond. However, the reported trends are inconsistent or even contradictory. A significant concern is the degradation and dissolution of catalysts and carbon support under operating conditions, which determines fuel cell performance in addition to catalyst chemistry. The majority of investigations on electrocatalysts have been limited to crystalline materials.

Moreover, a novel finding has emerged in the field, revealing an inverse correlation between the electrocatalytic behavior of polycrystalline Pt-based nanoparticles and the work function for oxygen reduction. This discovery was published as “Noble-Metal based Metallic Glasses as Highly Catalytic Materials for Hydrogen Oxidation Reaction in Fuel Cells” in Scientific Report, (2019) 9:12136, https://doi.org/10.1038/s41598-019-48582-7 by Vahid Hasannaeimi and Sundeep Mukherjee at the Department of Materials Science and Engineering at the University of North Texas.[5] They reported the electrocatalytic activity of a series of Pd- and Pt-based metallic glasses using SECM and SKP for hydrogen oxidation reaction (HOR). This innovative approach of using metallic glasses in electrocatalysis opens up new avenues for research. The synergistic effects of Pt/Pd toward HOR were demonstrated for alloys containing both noble metals.

The study was conducted using a VersaSCAN system. The tip of the SKP probe was moved laterally over the surface of the specimen at a fixed distance of 50 µm from the surface. The vacuum levels are the same, while the Fermi levels differ for each material. When the tip and sample are connected electrically, electron flow results in Fermi energy alignment, and the system reaches equilibrium. However, a contact potential difference (V_{CPD}) is formed between the tip and sample. The external opposite potential (V_{SKP})

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that nullifies V_{CPD} is proportional to the relative work function difference between the tungsten tip and sample (V_{SKP} ~ Φ_{sample}-Φ_{tip}, in which Φ represents the work function). Positive values for the samples indicate their higher work function compared to tungsten.

$$V_{CPD} = \frac{\phi_{sample} - \phi_{tip}}{-e}$$

The alloys containing both Pt and Pd exhibited significantly lower work function values, approximately 150 mV lower than pure Pt. This lower work function translated into a more favorable Standard Kinetic Potential (SKP) than pure Pt alone. The rate of metal-catalyzed reactions in solid oxide fuel cells exhibited an exponential dependency on the average catalyst work function across a broad range of work function values (0.3–1 eV). In this particular study, the work function (WF) of all Bulk Metallic Glasses (BMGs) was found to be notably lower compared to that of pure Pd and Pt. (Fig. 1) This decrease in work function likely contributed to higher electronic conductivity, resulting in enhanced reaction rates over the catalyst surface due to facilitated electron transfer, which were further supported by X-ray Photoelectron Spectroscopy (XPS) analysis. This analytical approach verified the observed correlations between alloy composition, work function, and catalytic performance in the studied materials.

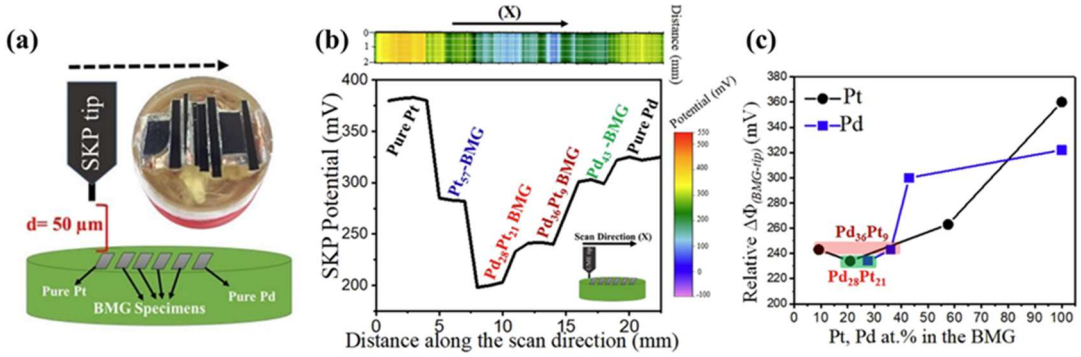


Figure 1. (a) The experimental setup and a schematic showing the array of amorphous alloys and pure Pt and Pd mounted side by side in a non-conductive resin. (b) SKP map/line scan of the BMGs along with pure Pt and Pd measured over an area of 2mm×25mm with a tungsten micro tip and the inset showing tip scanning direction over the array of amorphous alloys; (c) Relative work function difference of the BMGs as a function of Pt and Pd content with alloys containing both Pd and Pt marked with two separate boxes. Reprinted Fig. 1 and 2. Reproduced from Ref. [1] by permission of Springer Nature.

Scanning Electrochemical Microscopy (SECM) imaging was utilized to investigate the electro-catalytic activity of amorphous alloys compared to pure, noble metals, explicitly focusing on the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER). In this experimental setup, a platinum (Pt) tip, polarized at -1.2V, was used to scan over all the alloys at a fixed tip/substrate separation of 5 µm within an aqueous electrolyte. The variation in the current recorded at the Pt tip was directly proportional to the catalytic rate constant of the amorphous alloys. More negative current values corresponded to higher reactivity of the substrate. The SECM map and the corresponding Pt tip current line scan are depicted in Fig. 2(a), illustrating the spatial distribution and intensity of catalytic activity across the studied alloys. This method allowed for a detailed analysis of the electrochemical performance of the amorphous alloys in

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comparison to pure noble metals, providing insights into their catalytic behavior under specific electrochemical conditions.

Chronoamperometry experiments were conducted for all samples to assess the stability of the amorphous catalysts towards the hydrogen oxidation reaction (HOR). All the alloys achieved steady-state current densities in these experiments within approximately 200 seconds, as depicted in Fig. 2(b). Notably, the current densities observed for the amorphous alloys containing both Pd and Pt were significantly higher compared to the other alloys tested. This finding suggests that the presence of both Pd and Pt in the alloy composition enhances the catalytic activity and stability of the catalyst towards the HOR. The higher current densities indicate more efficient hydrogen oxidation, highlighting the potential of these specific amorphous alloy compositions for electrocatalytic applications involving hydrogen oxidation reactions.

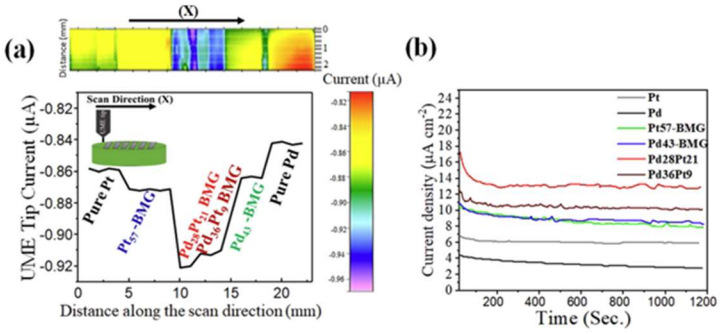


Figure 2. (a) Pt UME reduction current distribution map along with a single line scan over the BMGs in 0.01M H2SO4+0.1M Na2SO4 solution at a fixed tip/substrate distance of 5 μm, the tip potential was held fixed at −1.2V (vs. Ag/AgCl), while the sample was at OCP; the inset shows the tip scanning direction over the array of amorphous alloys; (b) Chronoamperometric plots of the metallic glass catalysts and pure Pt and Pd at a potential of −1100 mV (vs Ag/AgCl) in 0.01M H_2SO_4+0.1M Na_2SO_4. Reproduced from Ref. [1] by permission of Springer Nature.

Integrating SKP with SECM offers valuable insights into the relationship between electronic properties and electrocatalytic behavior of recent Pd- and Pt-based metallic electrocatalysts for fuel cells and water electrolyzers. SKP analysis was employed to investigate the impact of electronic structure on the electrochemical reactivity of the amorphous alloys. This approach helps in understanding how variations in electronic properties influence catalytic performance. SECM, on the other hand, was utilized to evaluate the catalytic activity of these alloys directly, providing spatially resolved information on their performance.

Additionally, Optical Surface Profiling (OSP) techniques can be instrumental in experiments conducted in atmospheric or electrolyte environments. OSP minimizes the influence of surface topography on the experimental outcomes, ensuring more accurate and reliable measurements of electronic and catalytic properties. This technique enhances the precision and reproducibility of studies investigating the electronic and electrochemical characteristics of catalyst materials under realistic conditions.

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Summary – This application note illustrated the application of SKP and SECM mapping for evaluating the catalytic performance of Pd- and Pt-based amorphous alloys toward hydrogen oxidation reaction. The work function for the metallic glasses was lower by 75 mV to 175 mV compared to pure Pt. This resulted in higher catalytic activity for the amorphous alloys, which was attributed to the ease of charge transfer on the surface.

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