



# Palladium/nickel bifunctional electrocatalyst for hydrogen oxidation reaction in alkaline membrane fuel cell



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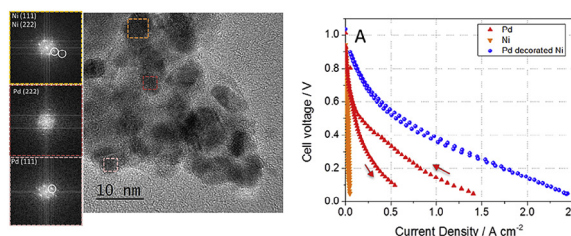
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## HIGHLIGHTS

- Best reported power in AMFCs for non-Pt catalyst (anode and cathode).
- Detailed structural characterization (HRTEM and EDS mapping).
- Electrochemical measurements in RDE and AMFCs to propose a mechanism.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Investigation of the hydrogen oxidation reaction (HOR) in alkaline media has been pursued in the past few years side by side with the development of alkaline membrane fuel cells (AMFCs), also called anion exchange membrane fuel cells (AEM-FCs). In this communication, we present the synthesis, electrochemistry and AMFC test of a platinum-free HOR catalyst. The anode catalyst is prepared by growing palladium nanoparticles onto nanoparticles of an oxophilic metal (nickel), resulting in nano-dispersed, interconnected crystalline phases of Ni and Pd. When used in the anode of a hydrogen/air AMFC, such Pd/Ni catalyst exhibits high HOR activity, resulting in record high performance for a platinum-free AMFC ( $0.4 \text{ A cm}^{-2}$  at  $0.6 \text{ V}$  vs RHE). The enhancement of HOR catalytic activity vs. that observed at Pd (or Ni) alone is revealed directly in rotating disc electrode tests of this Pd/Ni catalyst that shows a significant negative shift ( $200 \text{ mV}$ ) of the onset potential for the HOR current vs. the case of Pd.

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## 1. Introduction

Alkaline membrane fuel cell (AMFC) technology has received significant interest in recent years, because it has the potential of overcoming cost barriers of polymer electrolyte fuel cells [1], as the basic environment of the anion exchange membranes allows the use

of less expensive electrocatalysts and low-cost metal hardware [2]. While research on oxygen reduction reaction (ORR) catalysts in alkaline medium has been ongoing for many years [3,4], studies on hydrogen oxidation reaction (HOR) catalysts for AMFCs constitute a practically new field of investigation. In contrast with the very fast kinetics of the HOR on Pt catalysts in proton exchange membrane fuel cells (PEMFCs), resulting in negligible anode losses [5], it has been argued that the HOR activity of Pt in AMFCs is apparently the result of an intrinsic HOR kinetic barrier in alkaline media which, having been found to be significant even for Pt, does not bode well for the AMFC's hydrogen anode performance in general.

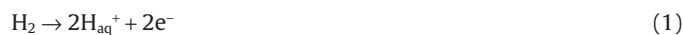
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In a study investigating the HOR activity of platinum in both acidic and alkaline media, Sheng et al. [6] reported that the HOR kinetics are at least two orders of magnitude slower in alkaline electrolyte than in acidic electrolyte. Recently, this finding has been confirmed and quantified by Rheinländer et al. [7] who reported that ultra-low anode loadings of Pt in alkaline medium may result in a prohibitive potential loss of about 150 mV.

Whereas the overall hydrogen anode reaction in acidic medium has as product a hydrated proton:



the product of the overall anode reaction in alkaline medium is water:



With the addition of an OH moiety to an adsorbed  $\text{H}_{\text{ads}}$  atom required to complete the latter process, it can be understood why unalloyed Pt could fail to provide the required HOR catalytic activity, as the metal has no substantial tendency to form  $\text{OH}_{\text{ads}}$  species from the  $\text{OH}_{\text{aq}}^-$  anion (or from water) at the negative potentials corresponding to satisfactory anode performance. The need of such chemisorbed  $\text{OH}_{\text{ads}}$  species for a fast, bimolecular, oxidative surface reaction is well documented; for example in the oxidative removal of  $\text{CO}_{\text{ads}}$  from Pt, facilitated by adding Ru which serves as the oxophilic component of a PtRu active binary catalyst. This bifunctional catalytic effect was argued recently for platinum-based HOR catalytic bimetallic surfaces [8–10], examined with rotating disk electrode (RDE), where significantly higher HOR catalytic activity in alkaline medium was shown for bimetallic surfaces vs. platinum alone.

In the search for Pt-free catalyst candidates for HOR in alkaline media, a first natural target would be a less expensive catalyst which is still derived from the platinum group metals. With palladium a possible such candidate, it was found that (unalloyed) Pd follows the same trend as Pt and Pd/C exhibits 20 times lower exchange current density than Pt/C in alkaline medium [11]. This HOR activity of unalloyed palladium is insufficient for reduction to practice.

A pioneering study investigating non-Pt-group metal (non-PGM) catalysts for HOR in  $\text{H}_2/\text{air}$  AMFCs, was carried out by Lu et al. [12] In that study, the decoration of Ni nanoparticles with Cr was reported to generate HOR activity in an AMFC generating an initial maximum peak power density of ca.  $70 \text{ mW cm}^{-2}$ , at  $60^\circ\text{C}$  [13]. Other recent reports described nickel-based catalysts in alkaline media, for example for alkaline electrolyzers (*i.e.* hydrogen evolution reaction) [14–17], and for hydrazine anodes [18]. Also in a recent contribution, Ni was combined with Mo and Co in ternary alloys of NiMoCo, which were tested for HOR in alkaline conditions [19]. The latter ternaries were shown to improve strongly the HOR activity vs. the case of Ni alone, however the high HOR activity recorded could be sustained only at anode potentials lower than 0.1 V, apparently because of excessive surface oxidation above that potential. All the above studies of HOR catalysts for AMFCs have left a remaining need for a demonstration of a low-cost, active and highly dispersed HOR catalyst, building on the understanding of the role of enhancing the HOR rates in the AMFC by the use of metal binaries.

In previous work, Dekel and Gottesfeld reported for the first time that a mixture of Ni and Pd nanoparticles exhibit a favourable metal–metal interaction that enhances the AMFC anode HOR reactivity as compared with an anode using same loading of Pd alone [20]. In this communication, we report the best performance yet achieved (as far as we know) in liquid electrolyte-free AMFCs based on Pt-free electrocatalysts, using a bimetallic Pd/Ni electrocatalyst. The synthetic approach yields nano-islands of Pd supported on nanoparticles of Ni, chosen for displaying oxophilicity in the relevant potential range, good electronic conductivity and low cost. Based on the present study, we argue that the specific role of Ni in this bifunctional catalyst is to bond hydroxyl surface species, which in

turn improves the reactivity of the hydrogen atom intermediates adsorbed onto the neighbouring Pd surface site towards the formation of the water product molecule.

## 2. Experimental

Catalyst nanoparticle preparation: doubly deionized water (18 M $\Omega$  cm, 50 mL) was adjusted to pH=12, pre-heated to  $60^\circ\text{C}$  and purged with  $\text{N}_2$  gas for 30 min to remove most of the dissolved oxygen. Then, Ni(0) nanopowder (QSI, 0.69 mmol) was added dropwise and after 5 min stirring,  $\text{Na}_2\text{PdCl}_4$  (STREM, 0.23 mmol) was introduced under vigorous magnetic stirring. The reaction was conducted under inert atmosphere of  $\text{N}_2$  for 1 h at  $60^\circ\text{C}$ , whereupon the resulting colloidal dispersion was centrifuged (3500 rpm, 15 min, RT) and subsequently washed three times with doubly deionized water.

The morphology and elemental compositions of bimetallic NPs reported in this work were visualized using scanning electron microscopy (SEM, FEI Magellan equipped with an Energy-Dispersive X-ray (Oxford 80 mm<sup>2</sup>) spectroscopy attachment), transmission electron microscopy (TEM/HR-TEM: FEI Tecnai-12 at 120 kV and JEOL JEM-2100 (LaB6) at 200 kV for high resolution imaging). Fourier transform analysis (FFT) of high-resolution images technique was used for structural analysis. High Resolution Transmission Electron Microscopy (HRTEM) images together with energy dispersive X-ray spectroscopy (EDS) were obtained by a JEOL JEM-2100F Field Emission Electron Microscope operated at 200 kV. The crystalline phases and crystallinity of the prepared powders of final products were examined by XRD using Cu Ka (0.1541 nm) radiation (Bruker D8).

Fuel Cell Testing: 5 cm<sup>2</sup> Catalyst-coated membranes (CCMs) for AMFCs were prepared by CellEra's standard methods [20,21]. Catalyst inks were prepared by mixing the dispersed catalyst in a solution of a quaternary ammonium-functionalized polyhydrocarbon ionomer, and applied onto an anion exchange membrane, also quaternary ammonium-functionalized, as commonly described in the literature [2]. Ni and Pd nanopowders in the inks were used as purchased, and the Pd/Ni nanocomposite catalyst was synthesized as described above. One CCM version was prepared using the Pd/Ni catalyst bimetallic nanoparticles (1.5 mg cm<sup>-2</sup> total metal loading, or 0.3 mg<sub>Pd</sub> cm<sup>-2</sup>) as the catalyst for the anode electrode, and a silver-based alloy (3.0 mg cm<sup>-2</sup>) as the catalyst for the cathode electrode. Another CCM version was prepared using the same metal loading, 1.5 mg cm<sup>-2</sup>, but with Pd nanoparticles only (~5 nm diameter) as the anode electrocatalyst, resulting in an otherwise identical CCM for comparison. The CCMs were pressed between polytetrafluoroethylene (PTFE) sheets to 4 tons for 3 min, and then pre-hydrated and ion-exchanged to hydroxyl form by soaking for 30 min in NaOH (3 mol L<sup>-1</sup>), followed by exhaustive rinsing in deionized water, ensuring no NaOH remained in the system. The CCMs were then combined with gas diffusion layers (carbon cloth with microporous layer, CeTech, Taiwan) to give membrane-electrode assemblies (MEAs), assembled into 5 cm<sup>2</sup> test cells (Fuel Cell Technologies, AZ, USA), sealed with perfluoroalkoxy (PFA) copolymer resin gaskets (250  $\mu\text{m}$  thick). The cells were then activated by operating at 50 mV in humidified, CO<sub>2</sub>-free air (1.0 standard litres per minute (sLPM), 200 kPa, 100% RH) and dry hydrogen (0.2 sLPM, 400 kPa, room temperature), while heating the cell from room temperature to  $73^\circ\text{C}$ . Following temperature and current density stabilization, polarization curves were measured at a scanning rate of 100 mV/min, from 0.05 V to open-circuit voltage (~1.0 V), then to 0.05 V.

The electrochemical measurements were collected in a polypropylene cell in a three electrodes configuration, with a polished 0.196 cm<sup>2</sup> glassy carbon disk as working electrode, glassy carbon rod as counter electrode and reversible hydrogen electrode (RHE)

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