



Full paper

Nickel-based electrocatalysts for ammonia borane oxidation: enabling materials for carbon-free-fuel direct liquid alkaline fuel cell technology



Anicet Zadick^{a,b}, Laetitia Dubau^{a,b}, Kateryna Artyushkova^c, Alexey Serov^c, Plamen Atanassov^c, Marian Chatenet^{a,b,d,*}

^a University Grenoble Alpes, LEPMI, F-38000 Grenoble, France

^b CNRS, LEPMI, F-38000 Grenoble, France

^c Department of Chemical & Biological Engineering and Center for Micro-Engineered Materials (CMEM), The University of New Mexico, Advanced Materials Laboratory, Albuquerque, NM 87131, USA

^d French University Institute (IUF), Paris, France

ARTICLE INFO

Keywords:

Alkaline fuel cells
Ammonia borane oxidation reaction (ABOR)
Identical-location transmission electron microscopy (ILTEM)
Nickel
Activity
Durability

ABSTRACT

This paper introduces a new class of carbon-supported nickel-based electrocatalysts (Ni₃Ag/C, Ni₃Pd/C and Ni₃Co/C) for the direct electrooxidation of ammonia borane (AB) in alkaline medium. The enabled anodic process opens the opportunity to build a novel concept of carbon-free-fuel energy conversion devices. Promising performances are reported for every studied catalyst. A trade-off is observed between the activity for the direct electrooxidation of AB and its decomposition (and related hydrogen release), as well as hydrogen oxidation reaction (HOR). The direct AB oxidation reaction (ABOR) onset is lower for the least noble materials (Ni₃Co/C), due to its smaller catalytic activity for AB decomposition and hydrogen evolution, combined with a non-negligible activity for AB oxidation. On the contrary, on Ni₃Pd/C, the noblest material, the onset of the ABOR is higher, because this material decomposes AB into hydrogen and evolves hydrogen, and then valorizes it. Moreover, Ni₃Co/C exhibits a better durability than Ni₃Ag/C, Ni₃Pd/C, and than what is reported for Pt/C and Pd/C nanocatalysts in the literature in the same experimental conditions: identical-location transmission electron microscopy (ILTEM) investigations demonstrated no significant morphological degradations after accelerated stress tests (ASTs) in alkaline medium. This study therefore demonstrates that a carbon-supported nanostructured noble-free catalyst (Ni₃Co/C) is both active and durable for the AB direct electrooxidation in alkaline medium. This result opens the way to direct liquid alkaline fuel cells fed with boron based fuels, a technology that could be both economically and industrially viable if noble-free catalysts are used.

1. Introduction

Despite great improvements in the last decade, the existing fuel cell technologies still present drawbacks that limit their deployment in the energy market. For instance, the PEMFC (Proton Exchange Membrane Fuel Cell) technology is still too expensive (the electrodes are composed of platinum group metal (PGM) catalysts and the perfluorosulfonated proton-exchange membrane is inherently costly to produce) and insufficiently durable in long-term operation because of the degradation of the membrane-electrode assembly (MEA). Moreover, PEMFC are fueled with gaseous hydrogen, which implies technical issues in terms of hydrogen production, purification, transportation, storage and safety.

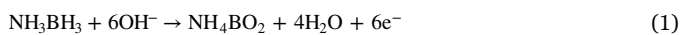
Alkaline Fuel Cells (AFCs), used with success in the space odyssey since the 1960s, have gained an increasing interest lately, because the

alkaline technology positively addresses many of the issues encountered in acidic medium, even though (i) anion-exchange membranes that are as stable and conductive than their acidic counterparts are yet to be developed and (ii) issues with carbonates (formed from interaction of the atmospheric CO₂ with the alkaline electrolyte) could impede the long-term operation of AFCs. Concerning the electrode materials, a wider range of base metals (and base metal oxides) are stable at high pH, while they suffer from massive dissolution in acidic electrolytes [1]. This larger material selection allows investigating the electrocatalytic performance and durability of platinum group metal-free catalysts, which could potentially resolve the issues in cost and longevity of the present PEMFC electrodes [2,3]. Furthermore, the alkaline medium allows to directly electrooxidize in AFC systems some chemical compounds that are high-energy density chemical hydrogen storage fuels: boron based materials (BBMs), such as sodium borohydride or

* Corresponding author at: University Grenoble Alpes, LEPMI, F-38000 Grenoble, France.
E-mail address: marian.chatenet@lepmi.grenoble-inp.fr (M. Chatenet).

boranes (ammonia borane, dimethylamine borane and hydrazine borane), are typical examples. Introduction of such fuels in main stream fuel cell technology is game-changing, potentially disruptive technology turn that can introduce carbon-free fuels into energy conversion practices along or even earlier than mass adoption of hydrogen. In addition to “boutique” applications in close systems such as autonomous vehicles and robots, these non-carbon fuels can find breather applications at industrial or macroeconomic scale provided a materials set of efficient catalyst is being developed and deployed, and provided their potential drawbacks (*e.g.* accumulation of boron oxides in the anode, toxicity of some of these fuels) are addressed. While addressing the last point is beyond the point of the present paper, one notes that it is of particular interest to evolve such catalysts from earth-abundant elements in order to allow broader technology impact since inception.

It should be noted that BBMs are thermodynamically expected to be electrooxidized at lower potential than hydrogen with appropriate electrocatalysts [4–9], opening the way to the development of fuel cells having an operating voltage beyond 1 V. For instance, the ammonia borane oxidation reaction is expected to start around -0.4 V *vs.* RHE (Reversible Hydrogen Electrode) at pH 13, following the 6-electron anodic reaction (Eq. (1)):



Direct electrooxidation of borane compounds has been studied to this date exclusively on platinum group metal catalysts, yet the electrocatalytic performances reported were far from impressive [4–9]. A notable exemption is a palladium electrocatalyst, reported elsewhere [10]. In this latter study, the onset of ammonia borane direct electrooxidation almost reached its thermodynamic value on a bulk Pd electrode, but the performances of a direct ammonia borane fuel cell (DABFC) using a Pd/C electrocatalyst at the anode were similar to a Pt/C-based DABFC. This means that the increase in operating voltage anticipated with borane electrooxidation on a bulk Pd electrode was not effective in fuel cell, and that the DABFC systems still need improvements to diminish the overpotential at the anode and reach the thermodynamic value for the ammonia borane electrooxidation reaction.

Then, recent studies have demonstrated that certain precious metals were not as stable as expected in alkaline medium; huge instability of carbon-supported platinum, and to a minor extent palladium, nanoparticles electrocatalysts was demonstrated even for mild accelerated stress tests in 0.1 M NaOH solution at $T = 25$ °C [11–14]. In addition to their inherent drawbacks (low abundance and high cost), this instability of carbon-supported noble electrocatalysts drives intense research to find active and durable electrocatalysts for the alkaline oxidation of liquid fuels, that do not belong to the platinum group metals (PGM-free). This search was rather successful lately, in particular for compounds capable to oxidize hydrazine hydrate [15–22] and sodium borohydride [23–29]. In this context, the present study aims to discover noble-free electrocatalysts for the AB electrooxidation that are both active and stable in practical operating conditions. The study focuses on carbon-supported nickel-based electrocatalysts ($\text{Ni}_3\text{Co}/\text{C}$, $\text{Ni}_3\text{Ag}/\text{C}$ and $\text{Ni}_3\text{Pd}/\text{C}$). At first, these materials are fully characterized using a broad set of advanced techniques: X-Ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), Transmission Electron Microscopy (TEM), High Angle Annular Dark Field Scanning Transmission Electron Microscopy (STEM-HAADF) coupled with X-Ray Energy Dispersive Spectrometry (XEDS). Then, their activity towards the AB oxidation reaction (ABOR) is characterized and their durability evaluated by accelerated stress tests; in particular, possible morphological degradations are investigated by Identical-Location Transmission Electron Microscopy (ILTEM) performed prior/after aging on the same regions of the electrocatalyst materials.

2. Material & methods

2.1. Material synthesis

The carbon-supported nickel-based nanoparticles were synthesized by thermal reduction of nickel, cobalt or palladium nitrates ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) on the surface of a commercially available carbon support (KetJen Black 600J, KB600J, AkzoNobel). The loading of the final catalyst was calculated to be 50 wt%, while the desired atomic ratio between Ni and the second metal ($M = \text{Co}$, Ag and Pd) was kept constant at 75:25. The calculated amounts of metal nitrates were dissolved in 5 mL of de-ionized (DI) water and KB600J was added to transparent solution under stirring. The water was evaporated on a heat plate pre-set to $T = 85$ °C. The dry composite mixture was loaded into an agate jar (volume of 50 mL) with 10 agate balls (diameter 10 mm) and was ball-milled in a planetary ball-mill at $\omega = 450$ rpm for 60 min. The resulting powder was placed into a porcelain boat and reduced for 2 h at $T = 400$ °C in a tube furnace under a flow of 7 at% H_2 at $100 \text{ cm}^3 \text{ min}^{-1}$. After natural cooling down to room temperature, the hydrogen gas was switched to a 1 at% O_2 stream, and the $\text{Ni}_3\text{-M}/\text{C}$ materials were passivated at $T = 25$ °C for 6 h. Extreme caution must be taken while removing the samples from the tube furnace without passivation: non-passivated nano-dispersed $\text{Ni}_3\text{M}/\text{KB600J}$ materials are pyrophoric and can self-ignite upon contact with air. The synthesized samples are denoted below as $\text{Ni}_3\text{M}/\text{C}$ ($M = \text{Co}$, Ag and Pd).

2.2. Material characterizations

Powder X-ray diffraction patterns were obtained using a Rigaku Smartlab diffractometer with a Cu anode X-ray source operating at 40 kV and 40 mA. A graphite monochromator was used to remove Cu K- β radiation. The crystallite size and relative phase composition were determined through Whole Pattern Fitting (WPF) in the MDI JADE 2010TM software.

Brunauer-Emmet-Teller (BET) surface area was calculated from a four-point measurement using a Gemini 2360 surface area analyzer. All samples were outgassed with N_2 at 120 °C for at least 8 h prior the measurements.

Surface chemical analysis was completed with X-ray photoelectron spectroscopy (XPS). The spectra were acquired using a Kratos Axis Ultra X-ray photoelectric spectrometer with an Al K α X-ray source operating at 225 W. High resolution spectra (O 1s, C 1s, Ni 2p, Ag 3d, Co 2p, Pd 3d) were collected at 20 eV pass energy. Three areas per sample were analyzed.

Transmission Electron Microscopy (TEM) and identical-location TEM (ILTEM) analyses were performed to investigate the morphology of the electrocatalysts in their initial state (pristine), and also after accelerated stress tests (ASTs). The electrocatalysts were directly immobilized on gold Lacey-carbon TEM grids. A JEOL 2010 TEM apparatus, equipped with a LaB₆ filament and operating at 200 kV (point to point resolution 0.19 Å), has been used. The TEM micrographs were used to calculate the number-average (d_N), surface-average (d_S) and volume-average (d_V) mean diameters, based on the enumeration of several hundred isolated (spherical-shaped) nanoparticles, as previously done in [14].

The local chemical composition of the $\text{Ni}_3\text{M}/\text{C}$ samples was further studied at the nm-scale using High Angle Annular Dark Field Scanning Transmission Electron Microscopy (STEM-HAADF) coupled with X-Ray Energy Dispersive Spectrometry (XEDS) mapping. These observations were performed on a Jeol 2100F apparatus operating at 200 kV equipped with a field emission gun (FEG); its point-to-point resolution in high-resolution TEM mode (HRTEM) is 0.23 nm, and the apparatus is compatible with Z contrast imaging (resolution 0.2 nm) thanks to a High Angle Annular Dark Field detector (HAADF) that can be operated in Scanning Transmission Electron Microscopy (STEM); besides, it is equipped with a diode for XEDS chemical analysis and mapping.

Download English Version:

<https://daneshyari.com/en/article/5452331>

Download Persian Version:

<https://daneshyari.com/article/5452331>

[Daneshyari.com](https://daneshyari.com)