Enhanced electrocatalytic nitrate reduction by preferentially-oriented (100) PtRh and PtIr alloys: the hidden treasures of the 'miscibility gap'

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ABSTRACT

Bimetallic alloys of Pt and Rh or Ir were prepared with pulsed laser deposition (PLD) on a well-ordered MgO (100) substrate, leading to epitaxial growth along the [001] plane, as confirmed by surface analysis techniques. The out-of-equilibrium conditions of PLD allowed the exploration of a range of compositions for which phase separation would instead be expected. The electrochemistry of a series of PtRh and PtIr (100) alloys was investigated in 0.5 M H_2SO_4, showing a surprisingly intense electrocatalytic activity towards the reduction of nitrate for a Pt content of 21–42%. These alloys feature a lower reaction overpotential with respect to Rh and Ir while outperforming the pure metals in terms of reduction current. A detailed analysis of the voltammetric features with respect to alloy composition highlighted a correlation between hydrogen desorption and nitrate reduction activity. In addition, an optimal potential range for nitrate reduction, common to PtRh and PtIr alloys, was observed, corresponding to the potential window in which nitrate adsorption coincides with fast reduction of the key reaction intermediate NO_{ads}.

1. Introduction

Bimetallic bulk, surface, and near-surface alloys, have attracted growing attention with an eye to their applications as electrocatalysts [1–3]. Their unique features [4] are explained [2] in terms of an interplay between bifunctional catalysis, the dynamic formation of highly active surface domains, and radical alterations in the electronic structure. In fact, alloying enables one to tune the density of states (DOS) at the Fermi level and the shape of the *d*-band, which determine the chemical properties of the alloy. The rational design of alloys from first principles [3] can be implemented, provided that the alloyed elements are fully miscible. In this respect, pulsed laser deposition [5] (PLD) has emerged as a convenient, reliable approach to obtaining kinetically stable alloys at room temperature in the "miscibility gap" of the alloy phase diagram [6–10], a range of compositions in which the elements are expected to segregate. As an additional advantage, epitaxial growth on single-crystal substrates (usually metal oxides) can easily be achieved by PLD [11–13]. In this study, we combine these two features of PLD deposition to grow thin-film epitaxial (100) alloys of Pt and either Rh or Ir, showing that Pt-poor alloys display a remarkable electrocatalytic activity towards the reduction of NO_3^- in H_2SO_4.

NO_3^- reduction has a considerable significance in the electrochemical nitrogen cycle [14], both for its intriguing mechanistic

underpinnings and its implications for applied technology (wastewater remediation and the treatment of low-level nuclear waste) [15,16]. The reaction pathways at transition metal electrodes can be briefly described as a rate-determining step ($NO_3^- \rightarrow NO_2^-$) followed by ensuing selectivity-determining reactions, such as the formation of strongly-adsorbed NO [17,18]. Adsorbed nitrate is the actual species involved in the rate-determining step [19,20]; unfortunately, the preliminary adsorption of NO_3^- is known to be weak and heavily inhibited by other co-adsorbates such as H or HSO_4^- [15,20]. Therefore, performing NO_3^- reduction in H_2SO_4 poses significant challenges for metal electrodes, which strongly adsorb HSO_4^-. In this respect, Pt(100) is of particular interest: when free of interfering adsorbates, this surface is able to reduce NO_3^- at a lower overpotential than the other basal planes [21]. The interplay of the requirement of fast removal of adsorbed NO and sufficient nitrate coverage (discussed in details later in the paper) is strongly evident for this surface: nitrate reduction at single-crystal Pt(100) in 0.5 M $HClO_4$ occurs in a sharp spike at 0.32 V [21], a potential region close to the peak potential for the reduction of a NO adlayer [22]. The interest in Pt(100) is further motivated by the absence of poisoning upon adsorption of NO (an intermediate of nitrate reduction), thanks to the rapid hydrogenation of N_{ads} at Pt(100), as recently suggested by computational studies [22,23].

Among the noble metals, Rh is arguably the most active electrode

material for the reduction of nitrate [15], in particular because it does not require the presence of available protons to reduce NO_3^- [24]. In addition, Rh features an easier adsorption of anions owing to its low potential of zero charge (pzc) [25]. From a more fundamental point of view, Rh has a number of valence electrons which can effectively stabilise N-containing intermediates [26]. Therefore, a preferentially-oriented (100) PtRh alloy represents, in theory, 'the best of both worlds' for the promotion of electrocatalytic nitrate reduction, combining the activity of Rh with the peculiar nitrate reduction reactivity of the (100) crystal plane. PtRh alloys have been widely investigated for electrocatalytic reactions of the nitrogen and the carbon cycle, such as nitrate reduction [27] and the oxidation of small organic molecules [27–31]. However, Pt and Rh are immiscible over an ample region of the alloy phase diagram (approx. between 20% and 80% Pt below 600 °C) [32].

Electrode materials (co-deposits, alloys) combining Pt and Ir have long been investigated as catalysts for electrochemical ammonia oxidation [10,33–35] and for nitrate reduction [36]. A polycrystalline $Pt_{70}Ir_{30}$ alloy has been reported to be more active than both pure metals for the reduction of NO_3^- in 0.5 M $HClO_4$ [36]. On the other hand, pure Ir does not match the catalytic activity of Rh, suffering from severe poisoning during the reduction of both NO and NO_3^- [20,37]. Experimental [37,38] and theoretical [26] studies have shown that Ir binds N adsorbates more strongly than Pt, and hence a Pt-Ir combination could be beneficial, so long as it does not induce increased poisoning [37]. By alloying varying amounts of Pt and Ir, the electronic structure may be fine-tuned and the catalytic response optimized; however, the Pt-Ir system features extensive phase segregation at low temperature: its miscibility gap spans the range $0 < \%\,Pt < 65$ at temperatures below 600 °C [9,10,39].

This survey of the literature on PtRh and PtIr alloys shows that large regions of the Pt-M phase diagrams remain unchartered territory. Therefore, we decided to take full advantage of the PLD technique to prepare a series of a thin-film PtM alloys characterised by a well-defined (100) crystal orientation and a range of compositions including the Pt-poor region. Electrochemical tests for NO_3^- reduction unveiled surprising features: when Rh or Ir is alloyed with $21 < \%\,Pt < 42$, nitrate reduction occurs at a lower overpotential than for each of the pure metals, and larger reduction current densities were recorded. Additionally, the deactivation during nitrate reduction at PtRh and PtIr alloys could be reversed by CO adsorption, as shown for the specific case of $Pt_{25}Ir_{75}$. These features were rationalised within the framework of the mechanism of nitrate reduction and of the electronic and structural properties of bimetallic alloys.

2. Experimental

Pulsed laser deposition (PLD) was used to prepare thin films of Pt, Rh, Ir and their alloys with a preferential (100) orientation. The procedure for Pt has been extensively described in previous publications [8,11]; specific details concerning the preparation of bimetallic alloys, Rh and Ir are as follows. The deposition was performed under low pressure ($3 \cdot 10^{-5}$ mbar) in a custom-made vacuum chamber, with a KrF laser beam (248 nm, 17 ns pulse width, 20 Hz, power density 3 J cm^2), at a temperature of 600 °C for Ir and the PtIr series, and of 400 °C for Rh and the PtRh series.

MgO(100) substrates (10 mm × 10 mm, epi polished, MTI Corporation) were previously cleaned by sonication in acetone (15 min) and in isopropanol (15 min) and dried under an argon stream.

Firstly, a nickel buffer layer was deposited on MgO by the ablation of a Ni foil (99.994%, 0.1 mm, Alfa Aesar) for 2000 pulses, corresponding to a thickness of approximately 1 nm. This preliminary step was found to enhance adherence and epitaxial growth of Pt films [8,11], and this strategy was also used for all other bi- and monometallic samples. PtIr and PtRh were deposited by focussing the laser on a custom-made iridium or a rhodium target, respectively, partially covered by a platinum foil. The target was kept in continuous rotational

and translational motion to ensure that the laser beam alternates between the Pt and the Ir or Rh domains. The ratio between the geometrical surface area of the platinum foil (99.99%, 0.1 mm, Alfa Aesar Company) and iridium (99.9%, Kurt J. Lesker Company) or Rh (99.8%, Kurt J. Lesker Company) target allowed control of the final alloy composition. For PtIr, the number of laser pulses was fixed at 20 000. Instead, 80 000 pulses were employed for PtRh: for this specific alloy, it was observed that thicker deposits were required to obtain a conductive film.

2.1. Physical characterization

Scanning electron microscopy (SEM, JEOL JSM 6300F) was used to image the surface morphology of the alloys. The bulk composition of the alloys was obtained by energy dispersive X-ray spectroscopy (EDX, Oxford Link ISIS, ATW2) at low magnification (150 ×). The composition, expressed as atomic %, was obtained from an average over 5 measurements performed at different locations on each sample (typical standard deviation 2–4%).

The crystallographic structure of the alloy was determined by X-ray diffraction (XRD) measurements (PANalytical X'Pert Pro diffractometer), using a Cu Kα source (average λ is 1.54184 Å). The diffractograms were recorded in the Bragg-Brentano configuration (θ–2θ mode) from 20° to 90° with a step size of 0.02° and a counting time of 0.5 s per step. Finally, the thicknesses of the films were evaluated by X-Ray Reflectivity (XRR) measurements performed by varying the incidence angle from 0.1° to 4°, with a step size of 0.005° and a counting time of 1 s per data point.

2.2. Electrochemical characterisation

All electrolytes were prepared with ultrapure water (Millipore Gradient, MilliQ, resistivity > 18.2 MΩ cm). High-purity reactants were obtained from various suppliers: H_2SO_4 (TraceMetal grade, Fisher), $NaNO_3$ (99.995%, Aldrich) and used as received. Prior to electrochemical measurements, the electrolyte solutions were purged by bubbling Ar (AirLiquide, UHP, 5.0) for at least 10 min. Argon blanketing was maintained over the solution during the experiments. A BioLogic VSP potentiostat, equipped with a low-current option, was used throughout this work. The low-current option allowed us to reduce the experimental noise; all voltammograms are plotted as recorded. A mercury-mercury sulfate reference electrode (MMSE) was employed for all experiments. To convert the potentials to RHE scale, the potential difference between the MMSE reference and a RHE electrode was measured in 0.5 M H_2SO_4, and it was found equal to 700 mV. A Pt wire was used as counter electrode throughout this work, and it was flame-annealed and quenched in MilliQ water prior to immersion into the working electrolyte.

The thin films were studied in a one-compartment small-volume electrochemical cell as previously described [40]. All glassware was cleaned following a standard protocol: first, it was left in a $KMnO_4$ + H_2SO_4 solution overnight; then, it was thoroughly rinsed with MilliQ water. Traces of MnO_2 were removed by rinsing the glassware with a H_2O_2 + H_2SO_4 solution. Finally, traces of sulfate were removed by boiling the glassware in MilliQ water repeatedly.

As a pretreatment step, all thin-film electrodes were subjected to cycling in 0.5 M H_2SO_4. We have previously shown that, for epitaxial (100) Pt films, such a pretreatment is required to clean the surface and obtain a stable voltammogram; potential cycling does not induce surface reconstruction leading to the appearance of crystal orientations other than Pt(100) [8]. The potential limits for Pt were 0.05–1.50 V vs RHE. On the other hand, a more restricted potential window was chosen for Ir, Rh and for most of their alloys with Pt.

Concerning Ir and all PtIr alloys, the upper potential was restricted to 1.10 V vs RHE to avoid loss of Ir. This value was reported in the literature for blank voltammograms of PtIr bulk alloys [36] and for the