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Mechanically activated Pt–Ni and Pt–Co alloys as electrocatalysts in the oxygen reduction reaction

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ABSTRACT

Mixtures of powders of platinum with nickel or cobalt to obtain Ni_{0.75}Pt_{0.25} or Co_{0.75}Pt_{0.25} were mechanical alloyed by high energy ball milling. The results of crystal structure, morphology and electrocatalytic performance are presented for mechanically activated powders after 3 and 9 h of ball milling. Total solid solutions of Ni and Co with platinum were analyzed by X-ray diffraction after 3 h of ball milling. After 9 h of ball milling, in both cases, the total solid solution was accompanied by the appearance of NiO or CoO and ZrO associated with a redox reaction with the milling media. The presence of zirconium monoxide was confirmed by energy dispersive spectroscopy analysis. In both cases, an amorphization was detected. X ray absorption spectroscopy measurements showed changes in atomic and electronic environment of platinum, a reduction of the distance to the first coordination sphere and increased d-band vacancy vs pure Pt and Pt nanoparticles were observed for both studied systems. The electrocatalytic activity was determined using cyclic and linear voltammetry. The Co_{0.75}Pt_{0.25} alloy milled for 9 h showed a higher electrochemical activity for the oxygen reduction reaction (ORR) compared with the other samples, including Pt-Etek. The degree of the ORR electrochemical activity was correlated with the presence of ZrO, which could affect the oxygen adsorption and improve the catalytic activity for the oxygen reduction reaction.

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Introduction

Intense efforts have been made to develop new materials for electrocatalysis in low temperature polymer electrolyte fuel cells (PEMFCs) [1,2]. Both anode and cathode electrocatalysts require low platinum content in order to reduce costs. At the same time, it is intended to have high activity towards the oxygen reduction reaction (ORR), i.e. fewer kinetic limitations; to achieve low cathodic overpotential and to reduce the CO poisoning effect. Anode and cathode electrodes made of nanosized materials have shown the best activity towards the ORR. The electrocatalytic activity is strongly influenced by its particle size, the nature of the support and the preparation method [12]. To achieve an effective reduction in platinum content and poisoning effect, some transition metals have been used [3–16]. However, preparation of transition metal particles with a diameter size of only a few nanometers i.e. large surface areas is a challenge. Many researchers have employed different methods of synthesis to obtain novel nano-electrocatalyst of transition metals. Among these methods of synthesis, the mechanical milling (also known as ball milling) has been recently used [17–20]. With this technique, it is possible to obtain alloys, metastable phases, solid solutions, amorphous phases, nanocrystalline structures or composites. The mechanical milling can be used to prepare advanced materials that are difficult to produce by conventional fusion techniques. This work presents the mechanical synthesis of nano-sized Pt alloys (Pt–Ni and Pt–Co) and evaluates their physical properties and electrocatalytic activity towards the ORR in an acid medium.

Materials and methods

Elemental powders of Pt (Sigma–Aldrich, >99.9%), Co (Sigma–Aldrich, >99.9%) and Ni (Sigma–Aldrich, >99.9%) were used as precursors. The raw materials Co and Ni were mixed in the appropriate weight ratio to obtain two different alloys: $\text{Co}_{0.75}\text{Pt}_{0.25}$ and $\text{Ni}_{0.75}\text{Pt}_{0.25}$. A total amount of 1 g of powder mixture together with 6 zirconia (ZrO_2) balls, 11 mm in diameter, were loaded into a zirconia vial. The ball-to-powder weight ratio was 25:1. The mechanical alloying process was carried out at room temperature in air atmosphere using a shaker mixer/mill machine. To prevent excessive overheating of the vials, all experiments were carried out using cycles of 60 min of milling and 15 min of resting. The milling time spanned from 0 to 9 h to evaluate the effect of this parameter on the particle size distribution and the synthesis of the metallic alloy. X-Ray diffraction (XRD) patterns of the milled powders were used to study the phase transformations as a function of the composition and milling time, using a Bruker D2 Phaser. Diffraction parameters were the diffracting angle, 2θ , ranging from 20° to 90° . Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used in all experiments. The morphology and composition of the milled powders were analyzed using a FEI Quanta 3D FEG scanning electron microscope under high vacuum.

X-ray absorption spectroscopy (XAS) spectra were taken at the I811 beamline of MAX-Lab synchrotron facility, Sweden [21,22]. XAS at Pt $L_{2,3}$ -edge, Ni K-edge and Co K-edge of the 9-h

ball milled samples were collected. 1 mg of the sample was distributed over a 1.5 cm^2 area of the glue-side of Kapton tape. The samples over Kapton were placed inside a He-filled chamber. The sample-side was oriented at 45° with respect to the incident beam, then XAS spectra were taken in fluorescence mode. Pt L_3 -edge spectra were taken between -100 and $+900 \text{ eV}$ vs $E_0 = 11564 \text{ eV}$ energy, with a step = 0.4 eV . Pt L_2 -edge spectra were taken between -100 and $+450 \text{ eV}$ vs $E_0 = 13273 \text{ eV}$ energy, with a step = 0.4 eV . A Zn filter was used before the Lytle detector during Pt $L_{2,3}$ -edge spectra collection, 5 scans were averaged. Ni K-edge spectra were taken between -50 and $+600 \text{ eV}$ vs $E_0 = 8333 \text{ eV}$, with a step = 0.4 eV . A Co filter was used before the Lytle detector during Ni K-edge spectra collection, 5 scans were averaged. Co K-edge spectra were taken between -100 and $+800 \text{ eV}$ vs $E_0 = 7709 \text{ eV}$, with a step = 0.4 eV . Fe filter was used before the Lytle detector during the Co K-edge spectra collection, 5 scans were averaged. Data were processed with the Athena program [23]: proper calibration with Pt, Ni and Co foil respectively was performed, background removal and normalization was performed before whiteline area integration.

Electrochemical evaluation was carried out using a conventional three-electrode electrochemical cell. The electrodes were: 1) glassy carbon covered with a thin electrocatalyst film as working electrode (0.196 cm^2 geometric area), 2) $\text{Hg}/\text{Hg}_2\text{SO}_4$, $0.5 \text{ M H}_2\text{SO}_4$ ($E = 0.680 \text{ V/NHE}$) as reference electrode and 3) platinum mesh as counter electrode (with more than 10 cm^2 of surface area). A $0.5 \text{ M H}_2\text{SO}_4$ (Merck, p.a.) solution was used as electrolyte.

The working electrodes were prepared according to the methodology reported elsewhere [17]. Briefly, the as milled electrocatalysts were supported in carbon Vulcan to a load of 10 wt% Pt/C: 5 mg of electrocatalyst, 24 mg of Vulcan and $200 \mu\text{L}$ of ethanol were sonicated for 20 min. Then the powders were dried at 40°C and placed in a closed glass container until their utilization.

A catalytic “ink” of each electrocatalyst was prepared by mixing $60 \mu\text{L}$ of ethanol, $6 \mu\text{L}$ of Nafion[®] (5 wt%, Du Pont 1000 EW) and 1 mg of electrocatalyst supported on carbon Vulcan (10 wt% Pt/C). $8 \mu\text{L}$ of the $\text{Ni}_{0.75}\text{Pt}_{0.25}$ or $\text{Co}_{0.75}\text{Pt}_{0.25}$ catalytic “ink” was uniformly dispersed over the surface of a glassy carbon electrode. After drying a thin film of electrocatalyst was formed.

The rotating disk electrode (RDE) electrochemical characterization technique was performed by means of a 263 A potentiostat/galvanostat (EG&G PAR). The rotating rates were fixed at 100, 200, 400, 900, 1600 or 2500 rpm; the scan velocity was set at 5 mV s^{-1} . Previous (and necessarily) electrochemical activation was carried out by 20 successive potential sweep cycles at 50 mV s^{-1} in a potential window of 0 – 1.2 V/NHE to eliminate impurities. Potentials are reported with respect to the normal hydrogen electrode unless otherwise specified.

Pt mass-specific activity (I_m) was calculated at $E = 0.90 \text{ V/NHE}$ for an ORR polarization curve measured at a scan rate of 5 mV s^{-1} . The mass activities are estimated via calculation of j_k (kinetic current) and normalization to L_{Pt} (the working electrode Pt loading). Catalyst electrocatalytic activity towards the ORR is quantified at $E = 0.90 \text{ V}$ because interferences from mass-transport losses cannot be completely excluded at higher current densities observed below $E = 0.90 \text{ V}$ [24].

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