



Comparative assessment of synthetic strategies toward active platinum–rhodium–tin electrocatalysts for efficient ethanol electro-oxidation



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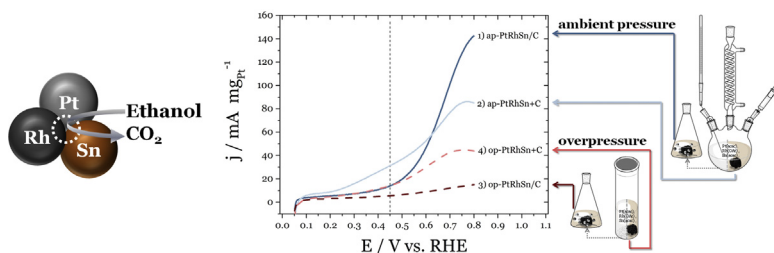
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HIGHLIGHTS

- The electrooxidation of EtOH on PtRhSn/C catalysts was investigated in acidic media.
- Small metal nanoparticles with sizes in the range of 6–12 nm were synthesized.
- Variation of pressure and carbon supporting conditions during polyol synthesis.
- Ambient pressure conditions result in catalysts with higher EOR mass activities.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work explores the effect of autoclave-based autogenous-pressure vs. ambient pressure conditions on the synthesis and properties of carbon-supported Pt–Rh–Sn nanoparticle electrocatalysts. The Pt–Rh–Sn nanoparticles were characterized by X-ray spectroscopy, electron microscopy and mass spectroscopy and deployed as catalysts for the electrocatalytic ethanol oxidation reaction. Pt–Rh–Sn catalysts precipitated with carbon already present showed narrow particle size distribution around 7 nm, while catalysts supported on carbon after particle formation showed broader size distribution ranging from 8 to 16 nm, similar metal loadings between 40 and 48 wt.% and similar atomic ratios of Pt:Rh:Sn of 30:10:60. The highest ethanol oxidation activity at low overpotentials associated with exceptionally early ethanol oxidation onset potential was observed for ambient-pressure catalysts with the active ternary alloy phase formed in presence of the carbon supports. In contrast, catalysts prepared under ambient pressure in a two-step approach, involving alloy particle formation followed by particle separation and subsequent deposition on the carbon support, yielded the highest overall mass activities. Based on the observed synthesis–activity correlations, a comparative assessment is provided of the synthetic techniques at high vs. low pressures, and in presence and absence of carbon support. Plausible hypotheses in

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terms of particle dispersion and interparticle distance accounting for these observed differences are discussed.

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1. Introduction

Platinum is a commonly used anodic material in acidic low temperature fuel cells. Since alcohol oxidation on pure platinum doesn't reach the desired activities, research in the field of Direct Ethanol Fuel Cells (DEFC) has focused widely on the development of binary and ternary Pt-based alloys [1–3]. The introduction of ternary electrocatalytical systems for the ethanol oxidation reaction (EOR) in recent research efforts has brought the development of DEFC as alternate power sources a big step forward [4,5]. Ethanol is of a particular interest for mobile applications such as electric vehicles, due to high energy density 8 kWh kg^{-1} , low toxicity, biocompatibility and abundant availability. It is, however, not easily oxidized completely to CO_2 and water. This is due to difficulties in the C–C bond cleavage in ethanol and the reaction may involve several different mechanism pathways with the formation of a high number of reaction intermediates such as CH_x species or acetaldehyde and, to some extent, to the formation of CO-intermediates leading to poisoning of the active sites on Pt catalysts [3,6–11]. Efforts to develop highly active and selective EOR electrocatalysts have therefore concentrated on the addition of co-catalysts to platinum [12–16,34–38].

Our previous research focused on the promising family of EOR nanocatalysts based on mixtures of Pt, Rh and Sn [3,5,17–23]. In a recent comprehensive study on a set of Pt–Rh–SnO₂ nanoparticle catalysts an optimal Pt–Rh–Sn atomic ratio of 3:1:4 has been proposed [5]. In our previous work we addressed the optimal structural arrangement of the atoms of the three components in the surface and bulk of the final active catalyst. On its surface, metallic Pt and Rh are atomically mixed with Sn, giving rise to active-surface-site ensembles. Our aim was to maximize activity and selectivity and find a single-phase Rh-doped Pt–Sn Nigglite structure as the preferred and catalytically most active nanocrystalline phase [22]. Synthesis routes to nanoparticle EOR catalysts containing Platinum, Rhodium and Sn range from impregnation-reductions methods [24] to deposition of metal atoms on oxide surfaces followed by galvanic displacement [3]. We implemented in our work a modified polyol method in diethylene glycol solvent [25], controlling the temperature during the reaction with a heating mantle. This approach yields ternary single phased catalyst with SnO_x next to metallic Pt and Rh on the surface in close proximity. Recent reports also claim improved electrocatalytic stability and elevated activities for ternary electrocatalysts by microwave-assisted selective deposition of nanoparticles onto carbon [26] and ternary PtSn@Rh/C systems by a two-step microwave-assisted polyol method as a promising catalyst preparation method for optimizing the Pt–Sn–Rh ternary system for EOR application [27].

In order to compare the two synthesis approaches and clearly establish a preferable synthetic approach towards PtRhSn catalysts, we first compared a one-pot reduction of metal precursors at ambient pressures both in the presence and absence of carbon support (referred to as “*ap-PtRhSn+C*” and “*ap-PtRhSn/C*”; *ap materials*). Synthesis conditions followed our previously used polyol method under a temperature control using a standard laboratory heating mantle device. Thereafter, we compared two variations of the two synthesis routes involving microwave-assisted temperature control in an autoclave associated with

autogenous overpressure conditions (referred to as “*op-PtRhSn+C*” and “*op-PtRhSn/C*”; *op materials*).

2. Experimental section

2.1. Catalyst preparation

All electrocatalysts (40 wt.% of metal loadings, Pt:Rh:Sn atomic ratios of 3:1:4) were prepared using Pt(acac)₂, Rh₂(OAc)₄, and Sn(acac)₂ as metal precursors, 1,2-tetradecandiol, oleic acid and oleylamine in diethylene glycol as reducing and capping agents, and Ketjen Black as support. All precursors were mixed together, including carbon for the direct supported electrocatalysts, heated up to 260 °C and stirred under reflux at that temperature for 30 min. For the heating mantle temperature controlled process the reaction mixture was under ambient pressure conditions, resulting in the “*ap-PtRhSn+C*” and the “*ap-PtRhSn/C*” materials. In the microwave-assisted temperature-controlled process autogenous pressures up to 30 bar and could build up inside the reaction mixture, resulting in the “*op-PtRhSn+C*” and the “*op-PtRhSn/C*” materials. Ketjen black carbon was sonicated for 1 h on ice. Then, the unsupported alloy particles (i.e. “*ap-PtRhSn/C*” and “*op-PtRhSn/C*”) were precipitated with isopropanol, redispersed in n-hexane and added to the Ketjen black carbon dispersion, sonicated for another hour on ice, and stirred overnight at RT. All particles were finally separated by centrifugation, freeze-dried, and the residue dried in a furnace under N₂, oxidized under O₂/N₂, and calcinated by heating under H₂/Ar atmosphere (see detailed information in previous publication [22]).

2.2. Catalyst characterization

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used for compositional analysis; performed using a 715-ES-inductively coupled plasma analysis system (Varian). Transmission Electron Microscopy (TEM) and Energy dispersive x-ray spectroscopy (EDX) were carried out using a FEI TECNAI G² 20 S-TWIN microscope operated at 200 kV, equipped with a GATAN MS794 P CCD-detector to study morphology and composition. The mean particle size was determined from TEM images by counting of at least 50 particles. Cu K α X-ray diffraction patterns were collected using a D8 Advance diffractometer (Bruker) equipped with a Lynx Eye Detector and KFL Cu 2K X-ray tube. The diffraction patterns were collected in a 2 θ –80° 2 θ range with a step size of 0.00142° dwelling for 30 s at every step. The XRD patterns were analyzed using the MDI Jade 8 software package. Bragg peak positions were compared with the reference XRD patterns (PDF data files, National Institute of Science and Technology).

2.3. Electrochemical measurements

All electrochemical measurements were carried out in a three-compartment electrochemical glass cell at room temperature using a Biologic SP 150 potentiostat. All potentials reported here are given in respect to a reversible hydrogen electrode (RHE). The 0.5 M C₂H₅OH + 0.1 M HClO₄ electrolyte was deaerated with high-purity N₂ before every measurement. During the experiments N₂ was

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