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Pt-rich_{core}/Sn-rich_{subsurface}/Pt_{skin} nanocubes as highly active and stable electrocatalysts for the ethanol oxidation reaction

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Abstract

Direct ethanol fuel cells (DEFC) are one of the most promising electrochemical energy conversion devices for portable, mobile and stationary power applications. However, more efficient and stable and less expensive electrocatalysts are still required. Interestingly, the electrochemical performance of the electrocatalysts towards the ethanol oxidation reaction (EOR) can be remarkably enhanced by exploiting the benefits of structural and compositional sensitivity and control. Here we describe the synthesis, characterization and electrochemical behaviour of cubic Pt-Sn nanoparticles. The electrochemical activity of the cubic Pt-Sn nanoparticles was found to be about three times higher than that obtained with unshaped Pt-Sn nanoparticles and six times higher than that of Pt nanocubes. In addition, stability tests indicated the electrocatalyst preserves its morphology and remains well-dispersed on the carbon support after 5,000 potential cycles, while a cubic (pure) Pt catalyst exhibited severe agglomeration of the

nanoparticles after a similar stability testing protocol. A detailed analysis of the elemental distribution in the nanoparticles by STEM-EELS indicated that Sn dissolves from the outer part of the shell after potential cycling, forming a ~0.5 nm Pt skin. This particular atomic composition profile having a Pt-rich core, a Sn-rich subsurface layer and a Pt-skin surface structure is responsible of the high activity and stability.

Keywords: *Pt-Sn nanocubes, core-shells, EELS-mapping, ethanol oxidation reaction, stability test*

Introduction

Electrochemical energy conversion and storage play essential roles in addressing the global energy challenge. In particular, direct ethanol fuel cells (DEFC) represent an attractive alternative to resources based on fossil fuel combustion for portable power generation. Ethanol is an eco-friendly and renewable fuel (naturally available in large quantities from biomass), and its complete oxidation to CO₂ and H₂O (with 12e⁻ exchanged in the desired electrocatalytic process) would lead to high energy densities. In addition, the easy handling, storage and transportation of a liquid fuel, such as ethanol, avoids some of the problems associated with gaseous fuel (e.g. H₂) systems^{1,2}. Over the past decades, platinum (Pt) has been shown to be the most active pure metal catalyst for the ethanol oxidation reaction (EOR). However, Pt is prone to deactivation by the adsorption of some intermediates (such as CO) and reaction by-products during the different pathways of the reaction³⁻⁵. This fact, in combination with the high cost of Pt, has fueled the search for more active and stable EOR electrocatalysts. To achieve this objective, the synthesis of nanoparticle catalysts (with high surface area to volume ratios), the combination of Pt with other metals such as Ru^{6,7}, Sn⁸⁻¹¹, Rh^{11,12}, Ni^{12,13} or Au^{14,15}, and the control of the exposed Pt surface structure¹⁶⁻²², have been

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3 extensively studied individually. However, the deliberate and integrated combination of these
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5 three approaches is clearly complex.
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10 Over the past years, while shape-controlled Pt-M (M = Ni, Co, Fe, Cu, Sn, Ir) nanoparticles²³⁻
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12 ³⁸ have been extensively studied for the oxygen reduction reaction (ORR)^{24,25,28-31,33,35-37} and
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14 the methanol oxidation reaction (MOR)^{27,33,38}, studies dealing with the EOR on shape-
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16 controlled Pt and Pt-based catalysts are rather scarce³⁹⁻⁴². Although Pt-Sn is the most active
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18 bimetallic electrocatalyst investigated so far for the EOR^{8-11,20,22} and shows highly facet-
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20 sensitive activity, the study of shaped controlled Pt-Sn nanoparticles towards the EOR has not
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22 yet been reported. Herein we report the first synthesis of Pt-Sn cubic core-shell nanoparticles,
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24 using a previously described method²³, with greatly enhanced activity towards the EOR.
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26 These nanoparticles not only exhibit higher EOR catalytic performance than current
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28 polyoriented Pt-Sn nanocatalysts⁸, but also enhanced durability under potential cycling,
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30 making them promising candidates for next generation DEFCs.
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38 **Experimental**

39 **Reagents**

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42 Platinum(II) acetylacetonate (Pt(acac)₂, 97%), tin(II) chloride pentahydrate (SnCl₂ · 5H₂O,
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44 95 %), oleylamine (OAm, 70 %), oleic acid (OA, 90 %) and tungsten hexacarbonyl (W(CO)₆,
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46 99.99 %) were purchased from Sigma-Aldrich. Acetic acid (HOAc, 96 %) was obtained from
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48 Merck. Ethanol and acetone (Reag. Ph. Eur) were purchased from Panreac, and n-hexane
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50 (96 %) from Scharlau.
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Catalyst preparation

Pt-Sn cubic nanoparticles were prepared by using a method similar to that described by Zhang et al.²³. 0.032 mmol of Pt(acac)₂, 8.0 mL of OAm and 2.0 mL of OA were added to a three-neck flask equipped with a condenser. The solution was heated to 130 °C with mild stirring under an Ar atmosphere. At this temperature, W(CO)₆ (0.108 mmol) was rapidly added to the reaction mixture, and the Ar flow was turned off at the same time. Subsequently, a solution of the Sn precursor, prepared by dissolving 0.032 mmol of SnCl₂ · 5H₂O in 4.0 mL of OAm and 1.0 mL of OA, was slowly injected into the flask, and the temperature raised to 230 °C and kept at this value for 30 min. Once the reaction was allowed to cool down, the resulting Pt-Sn nanocubes were washed twice with a mixture of hexane/ethanol (2:1) and finally dispersed in hexane. The suspension of Pt-Sn nanocubes in hexane was added to a solution containing the appropriate amount of carbon Vulcan XC-72R (to obtain a metal loading of 20 wt. %), in hexane using a simple impregnation method, which consisted of intermittent stirring and ultrasonication of the mixture for 3 h, and ageing overnight. The suspended Pt-Sn/C catalyst in hexane was precipitated by adding ethanol and further centrifugation. The resulting solid was dispersed in acetic acid and heated to 60 °C for 6 h under stirring. Finally, the catalyst was washed with ethanol several times, filtered and dried in an oven at 70 °C overnight.

Cubic Pt/C and unshaped Pt-Sn/C catalysts were prepared following procedures previously described^{8,43}. The total metal loading was 22.4 wt. % for cubic Pt/C, 18.1 wt. % for Pt-Sn nanocubes and 19.1 wt. % for unshaped Pt-Sn/C.

Physicochemical characterization

The cubic Pt-Sn/C nanocatalyst was characterized by powder XRD using a Panalytical X'Pert diffractometer with Cu-K α radiation. Diffraction patterns were collected at 3 ° min⁻¹ for 2 θ values between 20 ° and 100 °. For XPS analysis, a VG-Microtech Mutilab 3000 spectrometer with a hemispherical electron analyzer and a MgAl α X-ray source was employed. Sample charging was corrected by referencing the energies to the C1s peak at 284.6 eV. The total metal loading was evaluated from thermogravimetric analyses (TGA, Mettler-Toledo TGA/SDTA851 thermobalance). The TEM image presented in Figure S1 was obtained on a JEOL JEM-1400 Plus microscope working at 120 kV. STEM images presented in Figures 1, S3, S5 and S6 and EDX analysis were performed using a Tecnai F20 with a Shottky field emission gun operated at 200 kV and equipped with an Oxford X-Max 80mm² X-ray detector. The STEM-EELS images were acquired on a FEI Titan Themis S/TEM operated at 300kV equipped with a Gatan GIF Tridiem spectrometer. Composition maps for Sn and Pt were obtained by integrating the signal from the Sn M_{4,5} and Pt M_{4,5} edges, respectively after background subtraction using a linear combination of power laws background fit with 1.5 pixel oversampling.

Electrochemical characterization

Electrochemical experiments were carried out in a de-aerated 0.5 M H₂SO₄ (98%, Merck) aqueous solution at room temperature (RT) employing a Solartron model 1280 B electrochemistry station. A high surface area carbon rod was used as counter electrode and a reversible hydrogen electrode (RHE), against which all potentials are referred to, as reference electrode. Catalyst inks were prepared by ultrasonically dispersing 2 mg of the catalyst in

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3 0.5 mL of ultrapure water (Millipore) and 15 μL of Nafion (5 wt %). The working electrode
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5 was prepared by dropping a 10 μL aliquot of the prepared ink for Pt cubes and 5 μL for Pt-Sn
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7 nanocubes onto a freshly polished glassy carbon disk electrode and drying under N_2
8
9 atmosphere. For EOR experiments, ethanol (Merck p.a.) was added to the de-aerated
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11 electrolyte to reach a final concentration of 1.0 M.
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17 Cyclic voltammetry (CV) was employed over a potential range from 0.05 to 0.90 V at a scan
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19 rate of 50 and 20 mV s^{-1} for ECSA and EOR studies, respectively. The area under the curves
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21 between 0.05 and 0.45 V from the CVs of Figure 5 were integrated to calculate the ECSA by
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23 using a conversion factor of $210 \mu\text{C cm}^{-2}$.⁴⁴
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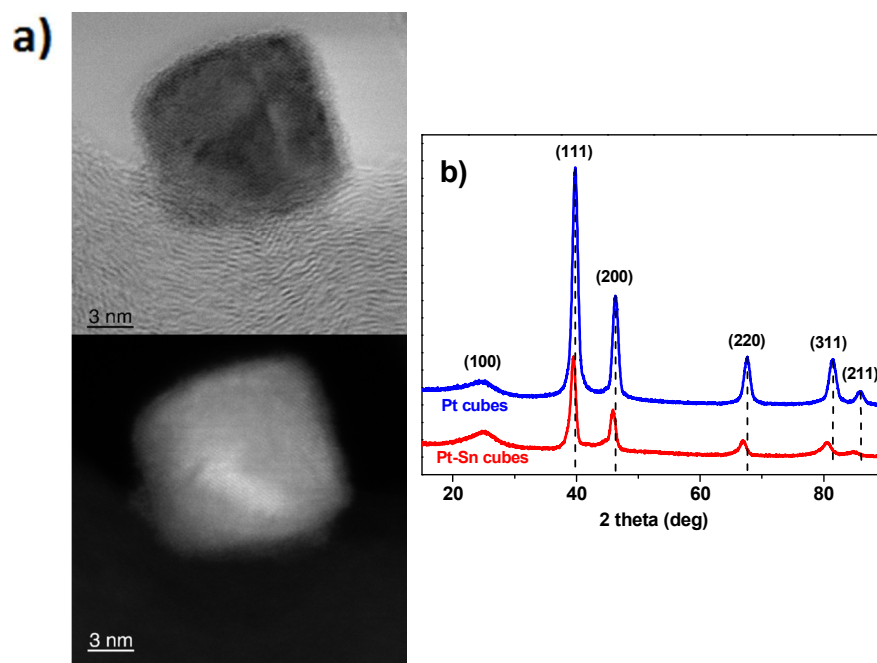
28 Chronoamperometry experiments at constant potential (0.50 V) were carried out to estimate
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30 the steady-state activity of the catalysts for the EOR for 600 s.
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35 **Results and discussion**

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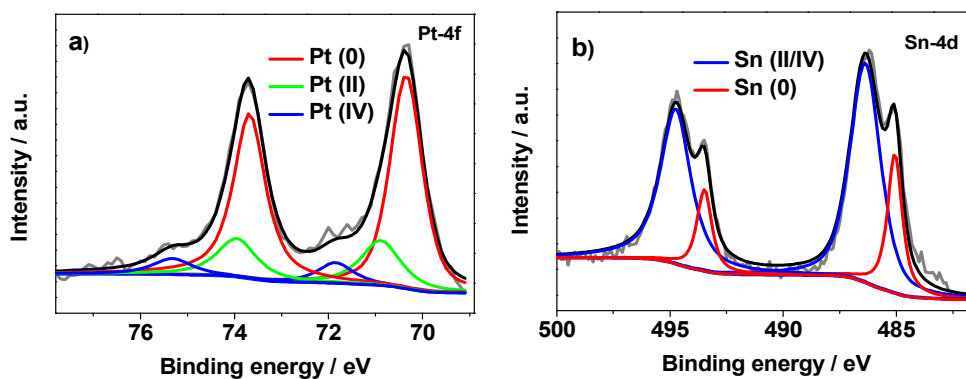
38 A cubic morphology of Pt-Sn nanoparticles was achieved by the simultaneous use of
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40 oleylamine (OLA) and oleic acid (OA) as solvent and capping agents, and $\text{W}(\text{CO})_6$ as a
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42 reducing agent²³, respectively. Figure S1 shows some representative transmission electron
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44 microscopy (TEM) images of the as-prepared, unsupported Pt-Sn nanoparticles, which show a
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46 predominantly cubic morphology with a homogeneous size distribution and a mean edge
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48 length of 10.6 nm with a standard deviation of 0.4 nm (Figure S2). While spherical
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50 nanoparticles were occasionally observed, they represented fewer than 10% of the total. The
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52 synthesized Pt-Sn nanocubes were supported on carbon (Vulcan XC72R) and were washed
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3 following an acid treatment protocol described elsewhere^{29,36}. Bright-field (BF) and annular
4 dark-field (ADF) scanning electron microscopy (STEM) images of the carbon-supported Pt-
5 Sn nanoparticles (henceforth referred to as Pt-Sn/C) displayed a good dispersion of the
6 catalyst on the carbon support following the cleaning protocol (Figure S3). The cubic
7 morphology was further confirmed by higher magnification BF-STEM and ADF-STEM
8 images (Figure 1a). These images further show that the crystalline Pt-Sn cubes (with visible
9 lattice planes) are covered by a thin, low density, amorphous layer. The X-ray diffraction
10 (XRD) pattern, shown in Figure 1b, displayed the typical face-centered cubic (fcc) peaks of
11 Pt, namely (111), (200), (220), (311) and (222), and the graphitic reflection plane of the
12 carbon black support (002) at $2\theta = 24.5^\circ$. The peak positions in the XRD pattern were shifted
13 to lower angles when compared with Pt/C, consistent with the size difference between Pt and
14 Sn and indicative of the fact that the Sn atoms have been incorporated into the fcc Pt structure
15 to form an alloy. The surface chemical composition of the nanoparticles was also investigated
16 by X-ray photoelectron spectroscopy (XPS).



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6 Figure 1. a) BF-STEM (top) and ADF-STEM (bottom) images of a carbon-supported Pt-Sn
7 nanocube. b) XRD patterns of Pt and Pt-Sn nanocubes.
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12 Figure 2 shows XPS spectra of Pt 4f (Figure 2a), deconvoluted into three peaks attributed to
13 Pt (0), Pt (II) and Pt (IV) species located at 70.4, 71.1 and 71.9 eV, respectively, and the Sn
14 3d (Figure 2b) spectra, deconvoluted into two different peaks assigned to Sn (0) at 485.0 eV
15 and Sn (II/IV) at 486.4 eV. As can be seen, Pt is predominantly in its reduced state (71 wt.%
16 as Pt (0)) whereas only 20 wt.% and 9 wt.% of Pt (II) and Pt (IV) were found, respectively. In
17 stark contrast, Sn is mostly oxidized on the surface of the catalyst (79 wt.% Sn (II/IV)) with
18 only a 21 wt.% of Sn (0) having been observed. Finally, a Pt-Sn atomic ratio of 24:76 was
19 calculated by XPS, indicating that the amount of Sn is three times higher than the amount of
20 Pt on the surface of the Pt-Sn nanocubes. This suggests that the thin, low density layer visible
21 on the exterior of the Pt-Sn cube in Figure 1a is primarily composed of Sn oxide.
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51 Figure 2. a) Pt_{4f} and b) Sn_{3d} deconvoluted XPS spectra of carbon supported Pt-Sn nanocubes.
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3 In order to determine the distribution of Pt and Sn within the cubic nanoparticles, we
4 performed STEM electron energy loss spectroscopy (EELS) to generate elemental
5 composition maps. Figure 3 shows Pt and Sn EELS composition maps with a simultaneous
6 ADF image of three Pt-Sn nanoparticles, including two cubic nanoparticles and a spherical
7 one. The composition maps indicate that each cubic Pt-Sn nanoparticle contains a Pt-rich core
8 surrounded by a Sn-rich shell that is approximately 2-3 nm thick. The spherical nanoparticles
9 are Sn-rich and uniform in composition. This observation of a Sn-rich shell on the cubes is in
10 agreement with XPS analysis, where a higher content of Sn was found at the surface of the
11 particles. EELS maps of Pt-Sn nanoparticles oriented near the (111) direction (Figure S4) also
12 show that the Sn-rich shell appears to be uniform across the cube, with no preference for
13 edges, corners or faces. Energy dispersive X-ray (EDX) analysis was also employed to
14 quantify the atomic composition of the Pt-Sn particles. The overall average composition of
15 the catalyst was determined to be approximately 56 at.% Pt and 44 at.% Sn. Composition
16 measurements on several individual particles indicated that cubic particles were 60 at.% Pt
17 and 40 at.% Sn on average, while the less-common spherical particles were 36 at.% Pt and
18 64 at.% Sn. Line-scan measurements on cubic particles indicated that their Sn-rich shells had
19 a typical composition of 44 at.% Pt and 56 at.% Sn near the particle surfaces, while their cores
20 were enriched in platinum.
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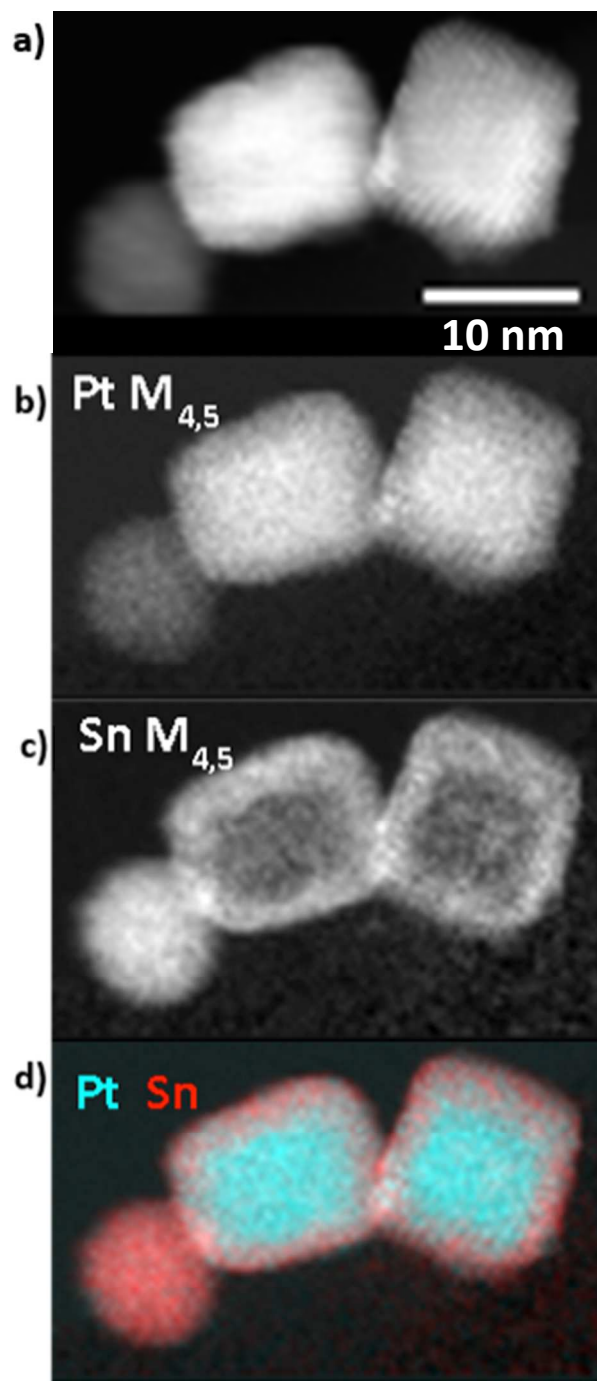


Figure 3. a) ADF-STEM image of Pt-Sn nanoparticles, b) EELS maps of Pt, c) Sn, (d) and the composite Pt-Sn map with Sn in red and Pt in cyan.

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3 It is generally accepted that for bimetallic Pt-based catalysts, the onset of EOR usually takes
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5 place at electrode potentials where the less noble metal is leached from the surface of the
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7 bimetallic alloy. In addition, it has been previously shown that potential cycling, especially to
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9 high potentials, can give rise to severe changes in the surface structure of shape-controlled Pt
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11 nanocatalysts⁴⁴. For those reasons, the chemical microstructural stability and durability of the
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13 Pt-Sn cubes were evaluated by STEM imaging and EELS elemental mapping after potential
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15 cycling. The cycling protocol consisted of sweeping the electrode potential between 0.05 and
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17 0.90 V vs RHE for 5,000 cycles in an Ar-saturated 0.5 M H₂SO₄ solution at a scan rate of a
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19 100 mV s⁻¹. The same protocol was applied to carbon supported Pt nanocubes (Pt/C) with a
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21 mean particle edge length of about 8.2 nm and a standard deviation of 1.6 nm, obtained using
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23 the same synthetic procedure^{43,45}. An ADF-STEM image of a collection of such particles
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25 prior to potential cycling is shown in Figure S5. STEM images of both samples were
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27 acquired before and after cycling to identify changes in the morphology and dispersion of the
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29 nanoparticles after the removal of the nanoparticles by dipping the electrode into a vial
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31 containing a high purity isopropanol solution without any sonicate process. Imaging of the Pt-
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33 Sn cubes (Figure S6a) showed that, after 5,000 cycles, the particles maintained their cubic
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35 morphology as well as good dispersion on the carbon support, while the Pt cubes (Figure
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37 S6b), although they preserved their cubic morphology, suffered severe agglomeration after the
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39 cycling test. The improved stability of the Pt-Sn nanoparticle dispersion may be attributed, at
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41 least in part, to a higher affinity of Sn for the carbon support relative to Pt, which leads to the
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43 preservation of the good dispersion of the PtSn nanoparticles after potential cycling. EELS
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45 elemental mapping (Figure 4a) and line-scans compositions, extracted from the Pt and Sn
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47 maps across the region indicated by the yellow arrow (Figure 4b), of cubic Pt-Sn
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nanoparticles, before and after potential cycling, show that Sn is leached from the catalyst surface, forming a Pt skin layer approximately 0.5 nm thick, as has been observed for other Pt alloy catalysts in acidic media. The resulting structure formed is Pt-rich_{core}/Sn-rich_{subsurface}/Pt_{skin} which is schematically depicted by models in Figure 4c.

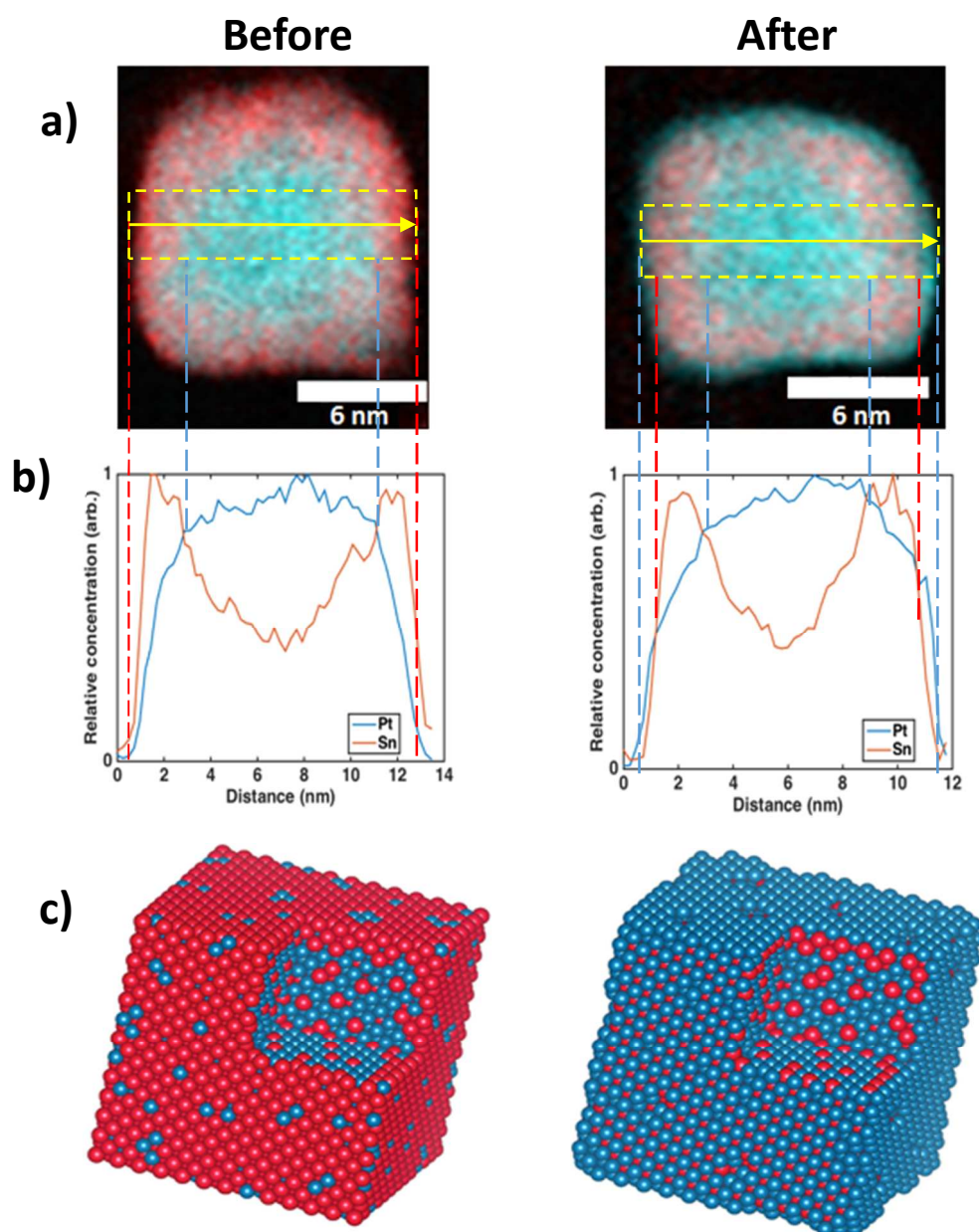


Figure 4. a) STEM-EELS composite images with Sn in red and Pt in cyan. b) Cross-sectional composition line profiles from EELS maps for Pt and Sn recorded across the region indicated

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3 by the yellow arrow in (a). c) Schematic 3D representation of a Pt-Sn cubic nanoparticle
4 before and after subjecting the sample to potential cycling between 0.05 V and 0.90 V in 0.5
5 M H₂SO₄ electrolyte at 100 mV s⁻¹.
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14 Cyclic voltammetry was also employed to monitor surface structure changes induced by the
15 potential cycling. The voltammetric profiles of Pt-Sn cubic nanoparticles in sulfuric acid after
16 1, 1,000, 2,000, 3,000, 4,000 and 5,000 cycles are shown in Figure 5a. As can be seen, no
17 reversible nor well-defined Pt hydrogen adsorption/desorption peaks can be observed in the
18 first cycle since the Sn-rich shell and oxide layer cover the Pt active sites. However, the initial
19 voltammetric profile evolved to the characteristic response of pure Pt/C, with clearly observed
20 peaks at 0.14 V and 0.26 V emerging with continued potential cycling. On the other hand, at
21 potentials above 0.5 V (where OH adsorption/desorption and oxide formation occurs) the
22 current density drops with increasing number of cycles. These results are in good agreement
23 with dissolution of the non-noble metal (Sn) from the surface of the nanoparticles to form a Pt
24 skin, as observed by STEM-EELS (Figure 4). It is worth noting that even after 5,000 potential
25 cycles, the Pt-Sn/C displayed the characteristic voltammetric response of cubic nanoparticles,
26 namely a peak at 0.27 V and a feature centered at 0.37 V, associated with hydrogen
27 adsorption/desorption on (100) steps and terrace borders sites, and long (100) domains,
28 respectively⁴⁶. This suggests that the Pt-Sn nanoparticles not only maintain their cubic
29 morphology, but also their preferential (100) surface structure after the potential cycling
30 stability test. For comparison, the stability of cubic Pt/C nanoparticles was also tested by
31 cyclic voltammetry (Figure 5b). The voltammetric profile shows well-defined hydrogen
32 adsorption-desorption peaks from the initial cycle, with a profile characteristic of Pt surfaces
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with predominantly (100) facets, as described above. The Pt/C maintains a characteristic cubic profile after extended cycling, although the peaks at +0.26 and +0.37 diminish in amplitude more rapidly than the peak at +0.14V, and the corresponding features for PtSn/C, suggesting a loss of (100) surface area on the Pt/C cubes. Such a loss could be caused by reshaping of the particles (possibly/likely as a result of the incipient surface oxidation at potentials near 0.9V) or by aggregation of the Pt cubes in such a way that the cubes stick “face-to-face” blocking the (100) surfaces, thus lowering their (100) surface area.

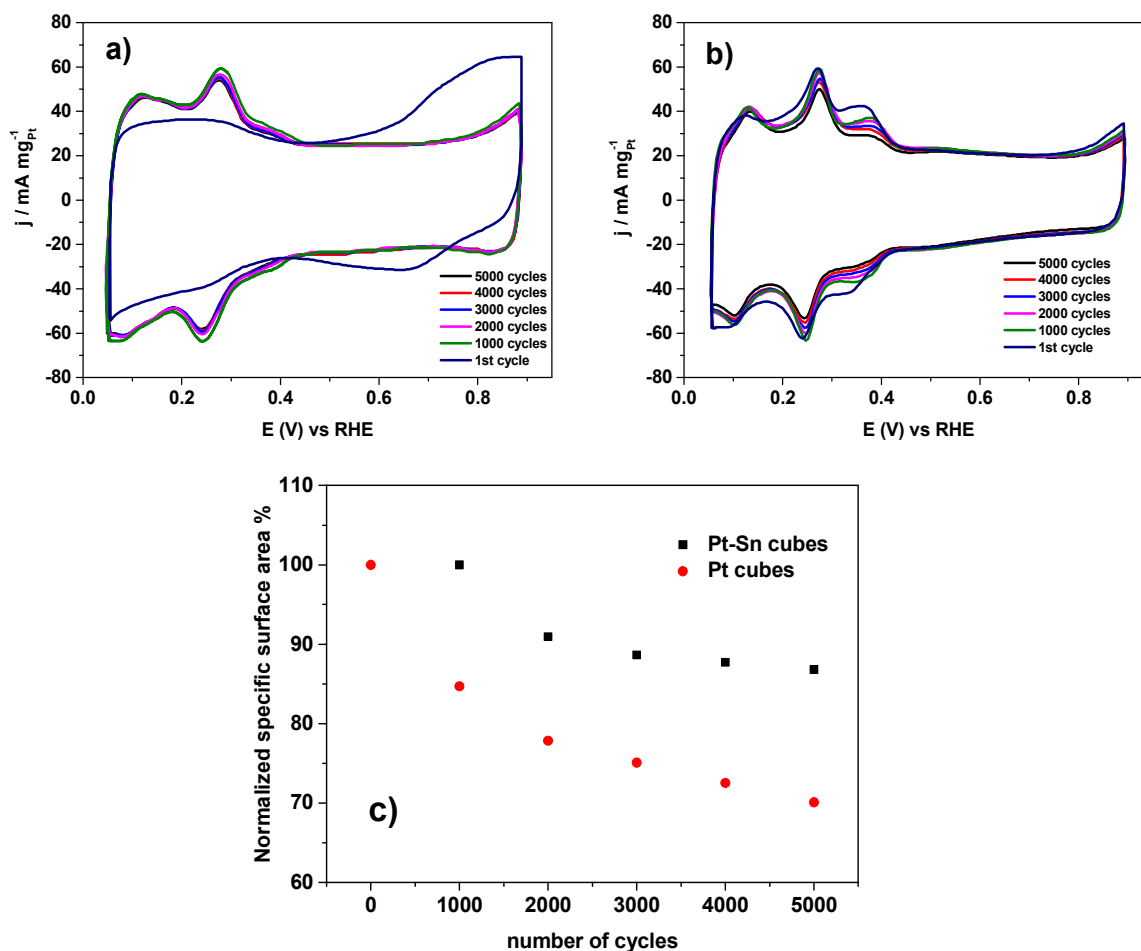


Figure 5. Voltammetric profiles of a) Pt-Sn cubes and b) Pt cubes nanoparticles in an Ar-purged 0.5 M H₂SO₄ solution after various numbers of potential cycles, as indicated, at a scan

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3 rate of 100 mV s⁻¹. c) % Normalized specific surface area as a function of the number of
4 voltammetric cycles for Pt-Sn (■) and Pt (●) catalysts.
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9 Figure 5c shows the specific surface area, after a given number of potential cycles, for cubic
10 Pt-Sn/C and Pt/C samples, calculated from the charge involved in the adsorption of hydrogen
11 (after double-layer subtraction) between 0.05 and 0.45 V⁴³ and normalized by the maximum
12 Pt specific surface area values (31 m² g_{Pt}⁻¹ for Pt cubes after 1 cycle and 32 m² g_{Pt}⁻¹ for Pt-Sn
13 cubes after 1000 cycles). It can be seen that the specific surface area for Pt nanocubes
14 decreased more rapidly, with potential cycling, than for the Pt-Sn nanocubes, with losses of
15 30 % (21.7 m² g_{Pt}⁻¹) and 15 % (27.2 m² g_{Pt}⁻¹) after 5,000 cycles, respectively.
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27 The electrocatalytic activity of the cubic Pt-Sn/C catalyst, towards ethanol electrooxidation,
28 was evaluated in acidic electrolyte and compared to that of the cubic Pt/C sample as well as
29 with that of an unshaped Pt-Sn/C nanocatalyst, with a mean diameter of about 3.1 nm, with a
30 Pt:Sn atomic ratio of 1:1, used in previous work^{8,9}. Figure 6a shows the EOR profiles for the
31 cubic Pt-Sn/C nanocatalyst, before and after a pretreatment in 0.5 M H₂SO₄ solution during
32 5,000 potential cycles. The initial current is low, suggesting that under these conditions, the
33 significant amount of Sn in the Sn-rich shell hinders the oxidation of ethanol on Pt atoms
34 (which are known to be the active sites). In addition, the dissolution of the Sn shell after 5,000
35 cycles in acid media leads to more exposed Pt atoms with low coordination number available
36 to react with ethanol. In addition, the EOR profile on the unmodified glassy carbon was also
37 included in the supporting information for comparison (Figure S7), where can be observed
38 that the bare glassy carbon is inactive for the EOR. The electrocatalytic activity of the cycled
39 Pt-Sn nanocubes was compared to that exhibited by the cubic Pt/C and unshaped Pt-Sn/C^{8,9}
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3 catalysts. The EOR voltammetric profiles for the three samples are shown in Figure 6b. The
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5 voltammetric profiles and electrocatalytic activity towards the EOR of cubic Pt/C and
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7 unshaped Pt-Sn/C catalysts after 5,000 cycles were not obtained due to the lower initial
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9 activity (in the first cycle) of these catalysts, compared with the activity of Pt-Sn nanocubes
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11 after the stability test. Current densities (j) were normalized to the electroactive surface area
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13 (ECSA) to obtain the specific activities (current densities in mA cm^{-2}) of the different
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15 catalysts, and as can be observed, the cubic Pt-Sn/C sample exhibited the highest
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17 electrocatalytic activity among the three catalysts studied. The superior EOR catalytic
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19 performance and catalyst stability of the Pt-Sn nanocubes was further confirmed by
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21 potentiostatic chronoamperometry experiments at a potential of +0.50 V (Figure 6c).
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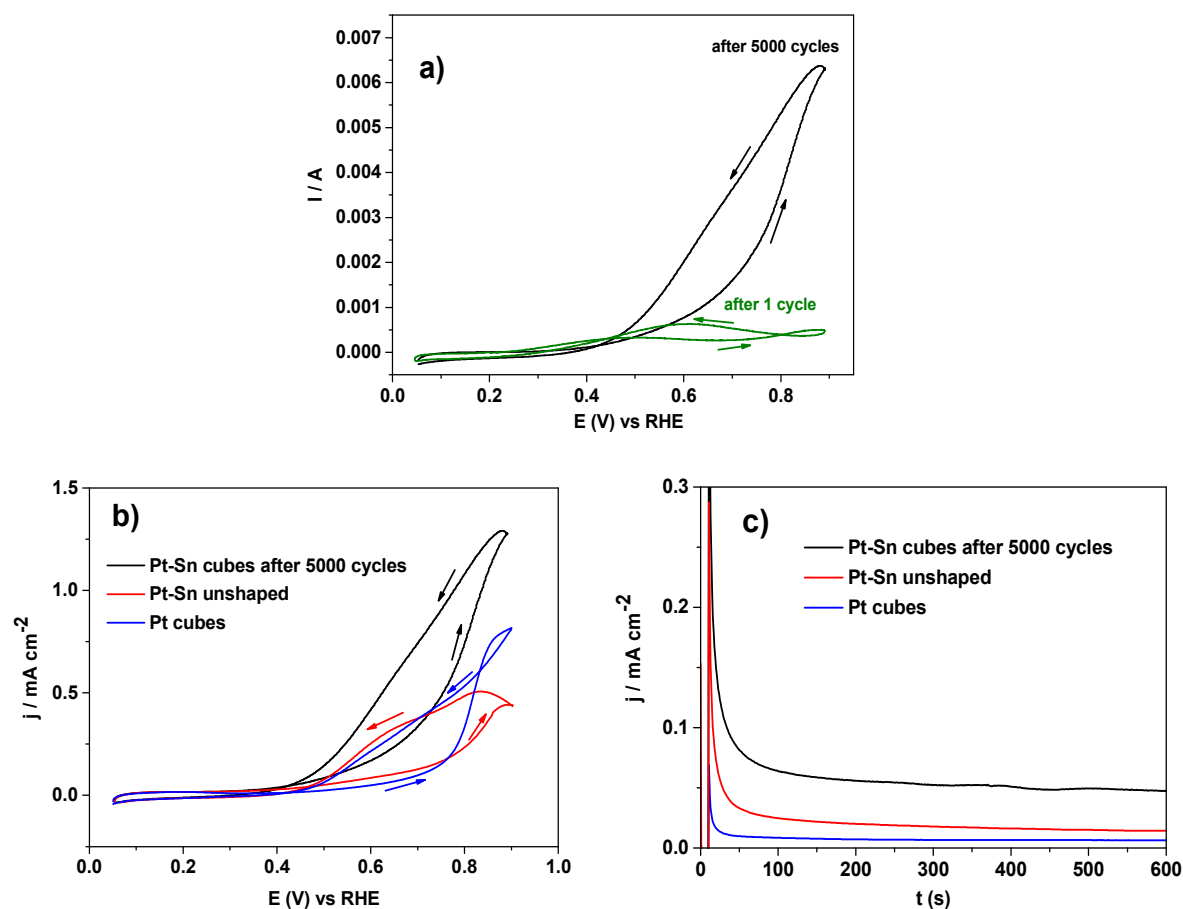


Figure 6. a) Cyclic voltammetric profiles for the EOR on Pt-Sn nano cubes after 1 and 5,000 cycles at a scan rate of 20 mV s^{-1} . b) Comparison of EOR curves at a scan rate of 20 mVs^{-1} and c) current transients at 0.50 V (from an initial potential of $+0.05 \text{ V}$) of the activated Pt-Sn nanocubes (black), unshaped Pt-Sn nanoparticles (red) and Pt-cubic nanoparticles (blue) in Ar-purged $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M EtOH}$ solution.

The transients were carried out by stepping the potential from a value where ethanol oxidation was negligible ($E_i = 0.05 \text{ V vs RHE}$), to 0.50 V (typical potential for fuel cell operation), and holding the potential at this latter value for 600 s . The behavior typical for Pt-based electrodes was found in all cases, namely, a sharp current decay at short times, subsequently attaining a stationary value. The current decay depends on the adsorption, on Pt, of strongly adsorbed CO

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3 (CO_{ad}) and CH_{x,ad} formed during the oxidation of ethanol, and which require high potentials
4 to be oxidized and, thus, removed from the surface^{4,5}. The cycled cubic Pt-Sn/C nanoparticles
5 exhibited outstanding durability towards ethanol oxidation, with steady-state currents about
6 three times higher than those exhibited by unshaped Pt-Sn nanoparticles and six times higher
7 than Pt nanocubes.
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17 We ascribe the exceptional activity of the cycled Pt-Sn nanocubes to two main factors. On the
18 one hand, the catalyst has a high density of Pt(100) surface sites, which favor the cleavage of
19 the C-C bond of the ethanol molecule¹⁷. In addition, the PtSn interior of the nanocubes can
20 exert both an electronic effect as well as a lattice strain effect, both of which are well known
21 to enhance electrocatalytic activity. It is also possible that the presence of Sn enhances the
22 oxidation of strongly adsorbed intermediate species such as CO and other reaction
23 intermediates. In fact, a significant catalytic enhancement effect for the EOR was recently
24 observed by the modification of Pt nanocubes with Sn adatoms⁴⁷. In that case, the
25 enhancement was ascribed to a faster removal of CO from the surface of Pt during the
26 reaction. While that is possible in our case, the EELS elemental mapping after potential
27 cycling indicated that the outermost layer of the nanocubes was essentially pure platinum,
28 which would argue against such an effect in the present case.
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47 **Conclusions**

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49 In summary, in this work we present a novel nanostructured electrocatalyst for the EOR
50 consisting of Pt-Sn nanocubes having a Pt-rich core, a Sn-rich subsurface layer and a Pt-skin
51 surface structure (Pt-rich_{core}/Sn-rich_{subsurface}/Pt_{skin}). After activation (removal of outer Sn layer)
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3 this material exhibits exceptional electrocatalytic performance, with activities three times
4 higher than unshaped Pt-Sn catalysts and six times higher than cubic Pt nanoparticles.
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6 Moreover, this electrocatalyst not only shows superior EOR catalytic performance, but also
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8 greater durability with lower specific surface area loss after 5,000 cycles. Our study provides
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10 a promising electrocatalyst for DEFCs, in particular, and alcohol based fuel cells, in general.
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Pt-richcore/Sn-richsubsurface/Ptskin nanocubes as highly active and stable electrocatalysts for the ethanol oxidation reaction

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