

Synthesis of PdSn intermetallic compounds as anode catalysts for hydrogen evolution reactions in fuel cells.

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Introduction/ background:

Fuel cells use electrochemical reactions to generate energy, which is a sustainable and clean method. Fuel cell adoption and successful commercialization depend on overcoming a number of obstacles, including the creation of effective and long-lasting HER catalysts. Given their exceptional activity for the HER, noble metals like Pt have been used extensively as catalysts. The scalability and affordability of fuel cell technology are, however, constrained by their high price and scarce availability. Intermetallic compounds have emerged as promising substitutes for noble metal catalysts, offering a distinctive combination of properties that can improve the efficiency of fuel cells [1]. These substances have improved stability, optimized electronic structures, and tailored reactivity that can greatly improve the HER's catalytic activity and efficiency. A few work has been reported on PdSn for various electrochemical applications which includes oxygen reduction [2-6], glucose oxidation [7], ethanol oxidation [8], glycerol oxidation [9,10], formic acid oxidation [11,12]. And recently on PdSn alloy for HER reaction [13]. But no study is found for the use of PdSn intermetallic for HER reaction. HER kinetics can be improved by the unique electrochemical properties by the combination of Pd and Sn elements in a particular crystal structure [13]. To fully explore PdSn intermetallics' potential as effective anode catalysts for fuel cells, it is crucial to comprehend the synthesis processes, characterize the crystal structures, and assess their electrochemical performance. The importance of this project lies in its contribution to the creation of substitute catalyst materials for the HER in fuel cells. It is possible to gain important knowledge about PdSn intermetallic compounds' suitability as inexpensive and effective catalysts by examining their synthesis and electrochemical characteristics. Fuel cell technology's scalability, affordability, and sustainability can be significantly impacted by the successful development of PdSn intermetallics as anode catalysts, encouraging broader adoption and easing the transition to a clean energy future.

Objectives:

The objective of this research is the synthesis of ordered intermetallic PdSn compounds for electrochemical HER with activity on par or better than the state-of-the-art Pt on carbon. We focus on PdSn intermetallic, as Pd is having the same electronic structure as Pt and alloying with Sn will reduced the cost of the catalyst. These materials were synthesized in nanostructured form, which are expected to show enhanced activity due to the increase in surface area. The main objective of the proposal can be summarized as below.

1. Synthesis of known PdSn ordered intermetallics by solvothermal method.
2. Physico- Chemical Characterisation of the compound by pXRD, XPS, ICP and HRTEM
3. Perform the catalytic activity of the PdSn intermetallic compounds for the electrochemical hydrogen evolution reaction using CV and LSV.

Promising works will be published in high profile international journals.

Methodology

Synthesis: To equimolar solution mixture of 18.7mg (0.1mM) of SnCl_2 and 30.4mg (0.1mM) of $\text{Pd}(\text{acac})_2$ in 18mL of Tetraethylene glycol added 15.1mg (0.4 mM) of NaBH_4 . It is then transferred to a Teflon lined autoclave kept in a pre-heated muffle furnace at 180°C for 48 h. The product thus formed was collected by centrifugation at 10000 rpm, washed with ethanol, and dried in vacuum oven for 24 h at 60°C .



Characterisation:

Powder XRD: pXRD measurement was done on a Rigaku Miniflex X-ray diffractometer with a $\text{Cu-K}\alpha$ X-ray source ($\lambda = 1.5406 \text{ \AA}$). The scanning was done in 2 theta range of 10° to 80° with the step size 0.02° and a scan rate of 0.5 s/step. The experimental patterns obtained were compared to the simulated patterns available in Pearson Crystal Database.

XPS: XPS measurements were carried out using Thermo K-alpha+ spectrometer using Al K α radiation with energy 1486.6 eV. The individual core-level spectra were corrected using C1s at 284.6 eV as standard. The experimental peaks were fitted using CasaXPS software.

TEM: Transmission electron microscopy (TEM)

TEM and high-resolution TEM (HRTEM) images, patterns were collected using a JEOL 200 TEM instrument. Samples for these measurements were prepared by dropping a small volume of sonicated nanocrystalline powders in ethanol onto a carbon-coated copper grid. The obtained data was analysed using imagej software.

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES was performed using a Perkin Elmer Optima 7000 DV instrument. In a typical experiment, 2mg of the sample was digested in 1 ml aqua regia then diluted to 10 ml volume with deionized water. The solid particles were separated by thorough centrifugation before measurements.

Electrochemical HER studies:

The catalytic activity of the materials for HER is performed in Origaly's electrochemical workstation. In order to prepare the working electrode, 5mg of PdSn intermetallic was mixed with 0.1mg of Vulcan. Followed by the addition of 500 microlitre of 1:1 isopropyl water mixture and 10microlitre of naffion. This mixture was sonicated for about 2 hours. 20 microlitre of the above mixture is coated on glassy carbon electrode and left for drying overnight. 0.5M of sulphuric acid is purged by passing nitrogen gas for about 30 minutes which is used as the electrolyte. The working unit consists of calomel electrode as reference electrode, graphite rod as auxiliary electrode and catalyst coated glass carbon electrode as working electrode. The HER activity of the catalyst is measured while the potential between the working electrode and reference electrode is swept linearly in time. The LSV plot is observed between the range of -100mV and -500Mv at a scan rate of 5mV/sec. Subsequently 100 cycles of ACT was performed in the range between -100mV to 800mV. Following to this LSV plot was obtained. For comparison, Pt/C coated on GCE prepared the same way.

Results and discussion:

- From XRD, figure 1a, it is observed that, all the peaks of synthesized compound were found to be matching with that of the simulated pattern, indicating that the compound crystallized in orthorhombic crystal system having space group of *Pnma*.
- In XPS spectra, the Pd $3d_{5/2}$ peaks resolved into two peaks at the position of 335.6 and 337.2 indicating the presence of Pd in two different oxidation states (figure 1b). The major peaks at 335.6 eV can be attributed to intermetallic Pd, where as the small peak at 337.2 eV can be attributed to Pd $^{2+}$ due to the formation of oxide on the surface. Similarly, Sn $3d_{5/2}$ spectra resolved in to three peaks at 484.9, 486.7 and 488.58 which represents the Sn(0) in metallic state and Sn $^{\delta+}$ oxidation state and Sn $^{\delta+}$ oxidation state (figure 1c).
- The HRTEM images of the sample are shown in figures 1d and e. the sample appears as spherical agglomerates of nano particles which are interconnected by diffusion. The d spacing was calculated as 0.227nm, 0.229 nm, corresponding to (211), (112), planes of PdSn respectively.
- HER activity recorded as LSV are plotted in figure 1f. it is observed that the onset potential is around -0.25V.

Table 1. XPS measurements of PdSn intermetallics

Sample		3d $_{5/2}$ Peak Parameters			Reference
			Binding energy (eV)	Oxidation State of metal	
PdSn	As synthesized	Pd	335.6486	Pd $^{\delta+}$	[14,15]
			337.2110	Pd $^{2+}$	
		Sn	484.9331	Sn	
			486.7037	Sn $^{\delta+}$	
			488.5838	Sn $_x$ O $_y$	

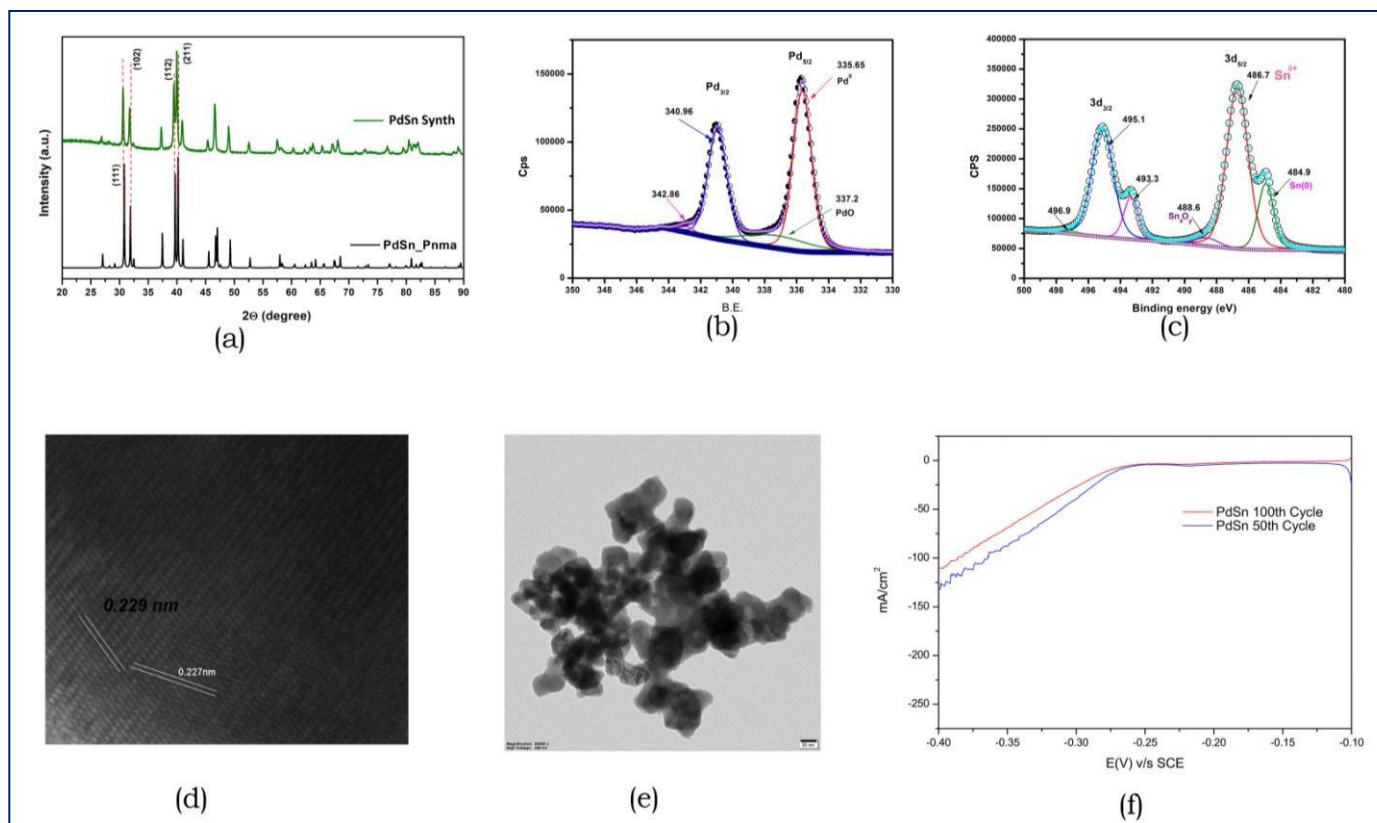


Figure 1. a) The pXRD pattern of PdSn synthesised compared with the the simulated pattern, b) The XPS analysis of Pd and C) Sn 3d orbitals d) HRTEM images showing d-spacing e) HRTEM image of PdSn f) LSV reordered for the PdSn catalyst after 50th and 100th activation cycle.

Scope of Future:

Compared to platinum-based anodes, PdSn intermetallic is more affordable. PdSn is a desirable alternative for large-scale HER applications because of its lower cost, which makes hydrogen production more feasible.

It is a promising for accelerating the hydrogen evolution process due to its effective electrocatalytic performance, lower onset potential, and higher current density. Even higher efficiency levels might be unlocked with more refinement of the PdSn composition and structure.

Throughout extensive electrochemical testing, PdSn intermetallic has demonstrated exceptional stability and toughness. Long-term HER applications can benefit from its resistance to deterioration and catalyst poisoning.

PdSn is a good candidate for mass production due to the abundance and affordability of its component elements. PdSn's intermetallic composition makes its synthesis and production processes simple. PdSn anodes can be easily integrated into hydrogen production systems with further optimization and scaling up, facilitating the switch to sustainable energy sources.

Future development of PdSn as an anode material may benefit from ongoing developments in materials science, catalysis, and electrochemistry. The properties of PdSn can be modified for optimum HER performance using methods like nanostructuring, surface modifications, and advanced characterization techniques.

Integration of PdSn anodes with different renewable energy systems is essential as the demand for renewable energy sources increases. To effectively transform renewable energy sources into hydrogen fuel, PdSn can be used in conjunction with devices like electrolyzers or photoelectrochemical cells. The creation of sustainable energy ecosystems would benefit from this integration.

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