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REGULAR ARTICLE

Nanoscale Electronic and Surface Property Engineering of Pt Nanomaterials by Rare-Earth Praseodymium for Energy Application

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Rare-Earth (RE) elements offer unique opportunities for nanoscale property modulation in electrocatalysis due to their distinctive electronic structures and strong oxophilic nature. This work investigates nanoscale electronic and surface property engineering of Pt nanomaterials through RE praseodymium incorporation for energy electrocatalytic applications, focusing on the ethanol oxidation reaction (EOR). Praseodymium incorporation alters the electronic structure, surface chemistry, and metal-support interactions of Pt nanocatalysts, resulting in improved CO tolerance and enhanced reaction kinetics. The effects of composition, nanostructure, morphology, and interfacial bonding on electrocatalytic performance were systematically examined. Structural and surface characteristics were analyzed using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Electrochemical behavior and charge-transfer kinetics were evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). The results demonstrate that Pt-Pr nanocomposites exhibit enhanced charge-transfer efficiency and stability, highlighting rare-earth-driven nanoscale property engineering as an effective strategy for advanced energy conversion systems.

Keywords: Nanomaterial, Synergistic effect, Structure-function correlation, Energy electrocatalysis.

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1. INTRODUCTION

Conventional thermal power generation poses substantial environmental challenges due to the emission of greenhouse gases and harmful air pollutants, including carbon dioxide, sulfur oxides, nitrogen oxides, and fine particulate matter. These harmful emissions perturb the Earth's radiative energy balance, thereby intensifying global warming and accelerating climate change. Coal-fired power plants are the dominant contributors, releasing large quantities of carbon dioxide and sulfur oxides that deteriorate ambient air quality and promote acid rain formation, leading to adverse respiratory and cardiovascular health outcomes. Conventional thermal power plants also require extensive use of water for steam generation and cooling processes, which generate thermal and chemical contaminated effluents that compromise water quality and disrupt the aquatic life [1-6].

In contrast, electrochemical energy conversion systems represent a sustainable alternative to conventional combustion-based power generation. Among these, Direct Alcohol Fuel Cells (DAFCs) utilize liquid fuels such as methanol and ethanol, which offer distinct advantages, including high volumetric energy density, facile storage and transportation and enhanced operational safety relative to hydrogen-based systems. Despite these benefits, the practical deployment of DAFCs remains constrained by sluggish reaction kinetics, catalyst degradation and limited control over product selectivity. Fuel cells convert chemical energy directly into electrical energy through electrochemical reactions, which avoids combustion and achieves efficiencies with less pollutant emissions, making them attractive for portable energy applications [7-12].

In this aspect, the ethanol oxidation reaction (EOR) is a crucial anodic process that significantly influences the power density and overall efficiency of direct ethanol fuel cells (DEFCs). Achieving high performance requires the development of a stable and highly active electrocatalyst that is capable of facilitating efficient electron transfer and the activation of reactants at the electrode-electrolyte interface. Furthermore, both structural characteristics and compositional design of the catalyst play a critical role in governing reaction pathways, intermediate adsorption behaviour, and long-term resistance to catalyst deactivation [13-15].

Platinum based catalyst our widely employed for ethanol oxidation due to their low onset potential and favourable reaction kinetics. However, their white spread application is hindered by costly material, limited durability, and susceptibility to poisoning by strongly adsorbed carbonaceous species such as CO and CH_x species. To overcome these limitations, bimetallic and multimetallic catalyst systems – including PtRh, PtSn, and PtRu have been

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extensively studied. These systems reduce the platinum usage and increase the activity and stability through synergistic effects. Nevertheless, incomplete C-C bond cleavage and inherently slow EOR kinetics remain the primary rate-limiting challenges in the development of high-performance direct ethanol fuel cells.

In recent years, Rare Elements (RE), when alloyed with platinum, have emerged as an effective strategy for enhancing electrocatalytic performance. The low alloying energy of RE metals promotes better atomic mixing and structural stability. Lanthanides, with their unique 4f orbital properties, strengthen metal interactions, stabilize reaction intermediates, and optimize charge transfer in electrooxidation. Their relative abundance and the lanthanide contraction enable tailored physicochemical properties. Such rare alloy catalysts significantly improve selectivity, activity, and durability in advanced fuel cell electrocatalysts by modifying electronic characteristics and enhancing reaction processes [16-25].

Previous studies indicate that rare earth metals improve the ethanol electrooxidation activity of platinum-based catalysts. Neto et al. were the first to show that incorporating these elements enhances performance via a bifunctional mechanism, where rare earth species supply oxygen-containing groups that aid in the oxidation of carbonaceous intermediates adsorbed on platinum sites.

Among the rare elements, the one most extensively investigated is Cerium oxide (CeO_2), a rare element significant for low-temperature fuel cell applications, characterized by its fluorite crystal structure, high oxygen vacancy concentration, and reversible Ce redox couple, which allows it to enhance the oxidation process at the interface effectively. Eu_2O_3 also helps ethanol oxidation. However, these catalysts show limiting current density. To address these issues, this study investigated MWCNT-supported bimetallic PtPr electrocatalysts with various molar ratios that were synthesized via an impregnation-reduction approach. Pr is used to show how the electronic or ligand effect enhances catalytic activity. Pr_2O_3 alters the Pr 5d band structure, leading to improved catalytic activity and resistance to poisoning effects. Multi-walled carbon nanotubes (MWCNTs) enhance ethanol electrooxidation (EEO) by acting as efficient catalytic supports due to their high surface area and brilliant electrical conductivity, which promotes uniform metal dispersion, strong metal support interaction, as well as improved CO-tolerance. Detailed structural, composition and electrochemical characterization were conducted to coordinate the catalyst morphology and the bonding with ethanol oxidation reaction kinetics.

2. MATERIALS AND METHODS

2.1 Materials

Praseodymium (III) nitrate hexahydrate $Pr(NO_3)_3 \cdot 6H_2O$ (Sisco Research Laboratories Pvt. Ltd.), Chloroplatinic acid ($H_2PtCl_6.6H_2O$) (Arora Matthey Ltd.), $NaBH_4$ (Merck), H_2SO_4, Ethanol (Merck) were the chemicals used.

2.2 Synthesis Procedure

The electrocatalysts C/PtPr (50:50, 84:16, 91:9) were synthesized by the metal impregnation and followed by reduction, Filtration, and drying method. For the synthesis procedure, the required amount of MWCNT was dispersed in 200 ml of double distilled water and sonicated for approximately 15 minutes using a digital sonicator. Thereafter, appropriate amounts of metal salts solution were added to the suspension, and the resulting mixture was kept in a magnetic stirrer for 2 hours to ensure uniform dispersion of the metal precursors. Lastly, an appropriate amount of sodium borohydride was added in drop-wise fashion under continuous stirring to achieve complete reduction of the metal ions to their metallic States. The resulting catalyst was then filtered, thoroughly washed and dried overnight in a vacuum oven at 80 °C.

2.3 Physical and Electrochemical Characterization of Catalyst

XRD were recorded in BRUKER AXS with Model D8, where Cu Kα radiation ($\lambda = 1.5405$ Å) and the 2θ were in range of 10°-90°. 2θ step size is 0.02°. Fourier Transform Infrared (FTIR) spectroscopy analysis was carried out on a PerkinElmer FT-IR/FIR spectrophotometer. To make the working electrode, the catalyst was sonicated in ethanol for 180 seconds, creating a uniform electrocatalyst ink that was drop-cast onto a Teflon-wrapped carbon block, resulting in a catalyst loading of about 1.5 mg cm^{-2}. In the three-electrode system, the carbon block served as the working electrode, with Ag/AgCl as the reference and a Pt wire as the counter electrode. Electrochemical measurements, like cyclic voltammetry (CV), linear sweep voltammetry (LSV), EIS, and chronoamperometry (CA), were performed using a 0.5 M H_2SO_4 and 1 M ethanol solution in a 20 mL electrolyte with an EmStat4 potentiostat. CA data were collected over 640 seconds, while CV and LSV were evaluated across multiple scan rates within a potential range of – 0.5 V to +1.5 V. CA was recorded at 0.6 V. EIS analysis were carried out at 0.55 V in the frequency range of 0.1 Hz-35000 Hz.

3. RESULT AND DISCUSSION

3.1 X-ray Diffraction (XRD) Analysis

The bulk structural information of the catalysts is determined by XRD analysis. The XRD patterns of the C/PtPr (50:50, 84:16) and C/Pt catalysts are illustrated in Fig. 1. In all the catalysts, the (002) plane shown for the Carbon phase, and (111), (200), and (220) planes shown for Pt phase. Incorporation of Pr in PtPr, displacement of peaks is observed. Both show a typical face-centered cubic (fcc) pattern. The peaks at 39.62, 46.24, and 67.45 can be assigned to the (111), (200), and (220) planes of the crystal structure of Pt. The 2θ value corresponds to the (111) plan for Pt and C/$Pt_{50}Pr_{50}$ C/$Pt_{84}Pr_{16}$ are exhibited at 39·829, 39.99, and 40·17, respectively. The shift of 2θ values in Pt, compared to those PtPr, caused the right sides to shift, which indicates lattice contraction in binary catalysts. This lattice contraction weakens the binding energy of adsorbed poisoning species and improves the anti-poisoning competence during the EOR.

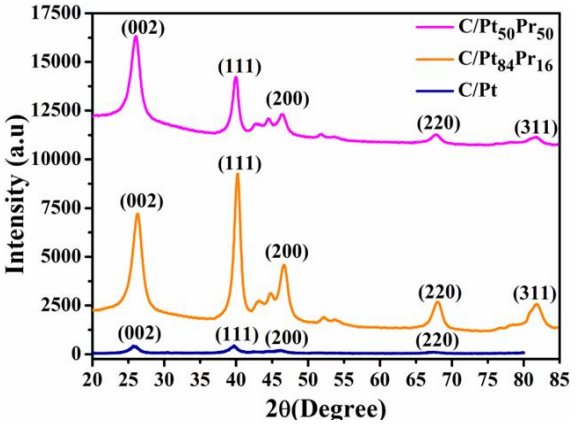


Fig. 1 – XRD patterns of the C/Pt, and C/PtPr binary electrocatalysts

3.2 FTIR Analysis

Fig 2 shows the FTIR spectra of C/PtPr catalysts. Two metal oxide bonds are found at 559 cm^{-1} and at 1963 cm^{-1} for Pr-O and Pt-O bonds in electrocatalysts. Also, a peak is assigned to the vibration of O-H stretching at 3678 cm^{-1}. Decrease of Pr content, peak intensities are broader, which indicates an increase in metal support interaction (MSI) in the catalyst. These bonds formation and MSI in catalysts are crucial for EOR.

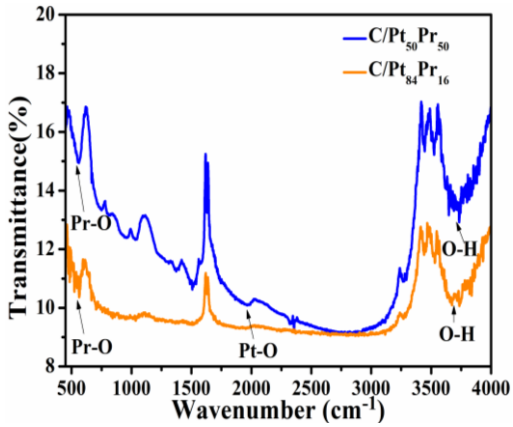


Fig. 2 – FTIR spectra of C/PtPr binary electrocatalysts

3.3 Cyclic Voltammetry (CV) Analysis

Fig. 3 displays the cyclic voltammograms of C/PtPr electrocatalyst at 0.02 V/s. Onset potential is the important variable, which evaluates the kinetics of EOR. It was observed that the onset potential of 16 % Pr containing electrocatalyst is very low compared to other catalysts. The onset potential of $C/Pt_{84}Pr_{16}$ is 0.496 V. 50 % and 91 % Pt containing surface is poisoned by carbonaceous species, which hinders oxidation, and the onset potential is much higher than $C/Pt_{84}Pr_{16}$. The enhanced ethanol oxidation activity of the $C/Pt_{84}Pr_{16}$ catalyst is attributed to a bifunctional mechanism, wherein after adsorption on 84 % content Pt surface, Ethanol is oxidized to CO. 16 % content Pr oxidatively splitting water and adsorbed OH on the Pr surface which provides oxygenated species (OH_{ads}) at very low potential and removes adsorbed CO from Pt surface and enhances oxidation kinetics, and following reaction occurred:

$$Pr + H_2O \rightarrow Pr–OH_{ad} + H^+ + e^-, \quad (1)$$

$$Pt–CO_{ad} + Pr–OH_{ad} \rightarrow CO_2 + H^+ + e^- \quad (2)$$

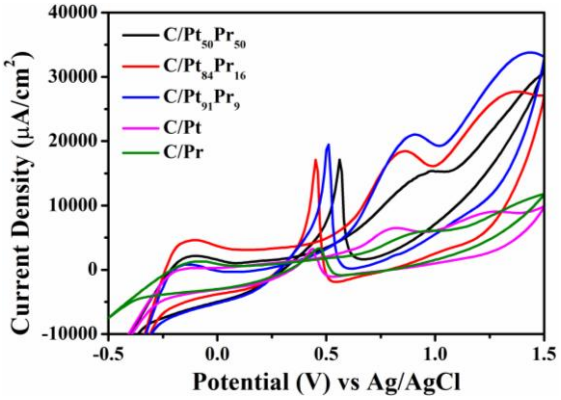


Fig. 3 – Cyclic voltammograms of C/PtPr catalysts in 1 M EtOH and 0.5 M H_2SO_4 at optimum scan rate

3.4 Linear Sweep Voltammetry

Evaluating potentiodynamic polarization behaviour and kinetics of the reaction, LSV techniques were used in this study, where Tafel slope values were calculated. Fig. 4 displays the LSV plots of electrocatalysts. The optimal Tafel slope values correspond to the 84:16 ratio of PtPr, which shows the highest catalytic activity with ethanol adsorption on surface.

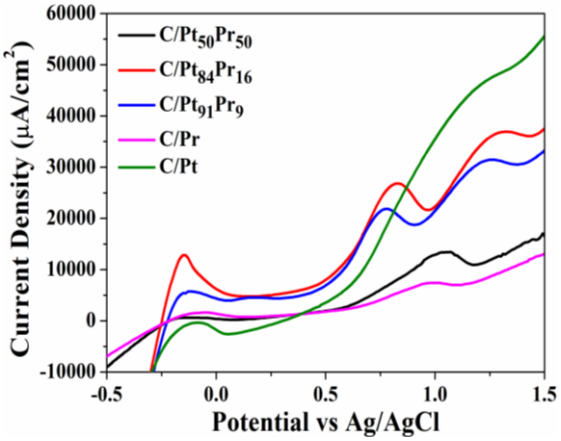


Fig. 4 – LSV curves of C/PtPr catalysts in 1 M EtOH and 0.5 M H_2SO_4 at optimum scan rate

3.5 Chronoamperometry Analysis

To investigate surface deactivation in acid environment, chronoamperometric technique was carried out, which is shown in Fig 5. A starting current density is dropped sharply in accordance with a gradual decline. As seen, the Time vs current density plot for the $C/Pt_{84}Pr_{16}$ generates the highest oxidation current than other binary and single metal catalysts. It is observed that 16 % of Pr enhanced charge transfer, which contributes to higher current retention capacity throughout the analysis. Also, it ($C/Pt_{84}Pr_{16}$) shows maximum stability and minimum poisoning. C/Pr catalyst shows the lowest stability due to high solution resistance and high CO poisoning on the electrode surface.

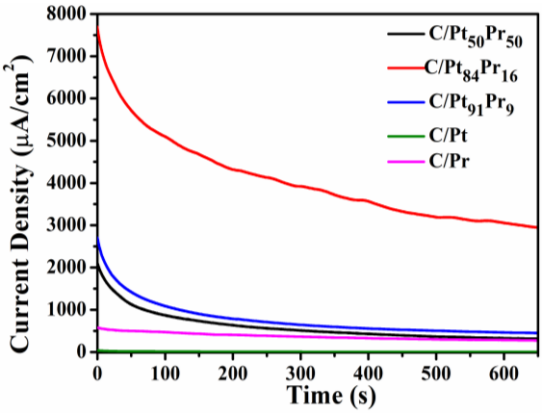


Fig. 5 – Chronoamperograms of C/PtPr, C/Pt and C/Pr electrocatalysts at 0.6 V

3.6 Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots of C/PtPr, C/Pt, and C/Pr have been shown in Fig. 6a. The arc in the complex-plane plots explained the presence of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) which reveal the reaction dynamics of electrocatalysts in acidic medium for EOR. A prominent small semicircular arc is shown for (84:16) ratio for C/PtPr catalyst, which indicates the lowest charge transfer resistance with high efficiency of the catalyst.

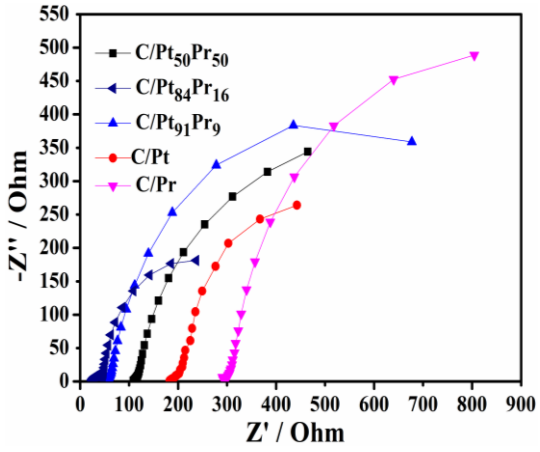


Fig. 6a – Impedance spectroscopy of C/PtPr catalysts in 1 M EtOH and 0.5 M H_2SO_4 at 0.55 V

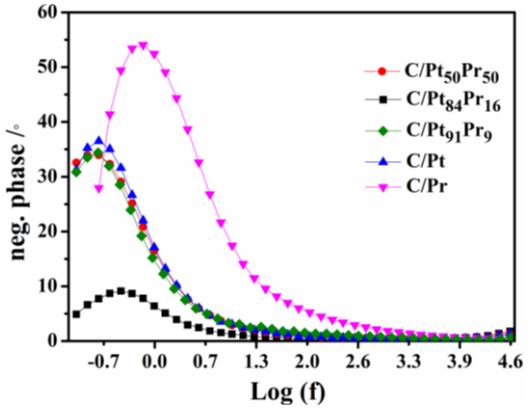


Fig. 6b – Bode plot-frequency vs phase angle of electrocatalysts of C/PtPr, C/Pt, and C/Pr

The shift of charge transfer resistance is descending order: C/Pr > C/Pt > $C/Pt_{50}Pr_{50}$ > $C/Pt_{91}Pr_9$ > $C/Pt_{84}Pr_{16}$.

From the Bode plot of the negative phase angle versus log(*f*) (Fig. 6b), shows the phase shifts with frequency during EOR, which reveals pseudocapacitive behaviour and inductive behaviour representing the charge transfer and intermediates adsorption of catalysts.

4. CONCLUSION

In brief, the findings demonstrated the role of Pr with Pt in electrocatalysts for the EOR. All the analyses confirmed that PtPr(84:16) is a highly promising and durable candidate for direct ethanol fuel cell (DEFC) applications with the highest peak current density and a favorable negative shift in the potential, indicative of superior reaction kinetics.

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DECLARATION OF INTEREST STATEMENT

There is no conflict of interest in this manuscript.

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Інженерія електронних властивостей і властивостей поверхні платинових наноматеріалів на нанорівні за допомогою рідкісноземельного елемента празеодиму для застосування в енергетиці

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Рідкісноземельні (РЗ) елементи відкривають унікальні можливості для модифікації властивостей нанорозмірних матеріалів в електрокаталізі завдяки своїй специфічній електронній структурі та вираженій оксифільності. У цій роботі досліджується керування електронними та поверхневими властивостями наноматеріалів на основі платини (Pt) шляхом введення рідкісноземельного елемента – празеодиму (Pr) – для застосування в енергетичних електрокаталітичних системах, зокрема в реакції окиснення етанолу (EOR). Введення празеодиму змінює електронну структуру, хімію поверхні та взаємодію між металом і носієм у нанокаталізаторах на основі Pt, що призводить до підвищення стійкості до отруєння чадним газом (CO) та покращення кінетики реакції. Було проведено систематичний аналіз впливу складу, наноструктури, морфології та міжфазних зв'язків на електрокаталітичні характеристики. Структурні характеристики та властивості поверхні досліджували методами рентгенівської дифракції (XRD) та інфрачервоної спектроскопії з перетворенням Фур'є (FTIR). Електрохімічну поведінку та кінетику перенесення заряду оцінювали за допомогою циклічної вольтамперометрії (CV), лінійної вольтамперометрії (LSV), електрохімічної імпедансної спектроскопії (EIS) та хроноамперометрії (CA). Отримані результати демонструють, що нанокомпозити Pt-Pr характеризуються підвищеною ефективністю перенесення заряду та стабільністю. Це підтверджує, що модифікація властивостей наноматеріалів за допомогою рідкісноземельних елементів є ефективною стратегією для створення передових систем перетворення енергії.

Ключові слова: Наноматеріал, Синергічний ефект, Кореляція «структура – функція», Енергетичний електрокаталіз.