



# Plasma-induced alloying as a green technology for synthesizing ternary nanoparticles with an early transition metal



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## ABSTRACT

The strategy of employing Pt alloys with other transition metals (TMs) is advantageous owing to the enhancement of the oxygen reduction reaction (ORR) activity and the reduction of Pt usage. The ternary alloy system with early TMs can overcome stability issues and even enhance the intrinsic activity of the catalysts owing to rearrangement of electronic structures between three metal elements. Herein, efficient catalysts with V—an early TM—were successfully obtained via a plasma-induced alloying strategy. The effect of V in the PtCoV/C catalyst, which exhibits the highest ORR activity among the synthesized Pt–TM–V (TM = Co, Ni, Cu) catalysts, was determined. The addition of V induces electron rearrangement in PtCoV, inhibiting the oxidation of Co and V and optimizing the oxygen-binding energy of Pt. Thus, incorporation of V into PtCoV nanoparticles enhances the electrochemical ORR activity and stability. The catalytic performance of PtCoV achieved 966 mV of half-wave potential, 3.05 A/mg<sub>PGM</sub> of mass activity, and 8.58 mA/cm<sub>2</sub> of specific activity. This systemic strategy not only proposes a novel and facile approach for the synthesis of ternary alloy catalysts but also reveals the intricacies of the catalytic activity, allowing the application of ternary alloy electrocatalysts.

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## Introduction

Hydrogen is regarded as the most promising energy source to meet the growing demand for eco-friendly energy, in which electricity is generated via a pollutant-free reaction. Proton exchange membrane fuel cells (PEMFCs), a type of hydrogen fuel cell, have

been successfully commercialized for applications in the automotive market owing to their high-power density and potential [1,2]. However, the oxygen reduction reaction (ORR) activity, which is indicative of PEMFC performance, remains insufficient. Furthermore, an improvement in the long-term stability, a major challenge facing PEMFCs, is needed [3–6].

Pt is widely used as a cathode electrocatalyst for oxygen reduction owing to its excellent intrinsic properties [7,8]. Although its use in commercial fuel cells is increasing, some of the issues encountered include limited natural Pt resources and high cost. To overcome these problems, the alloying of Pt with other metals has been explored to decrease the usage of Pt and improve its catalytic activity [9–11]. Alloying with TMs not only decreases the amount of Pt used but also increases its intrinsic catalytic activity [12–15]. If the electronegativity of the TM is lower than that of Pt, the electronic structure of Pt can be modified, which can transfer some electrons from TM to Pt, leading to a downshift of the d-band center [11,16–18]. According to the d-band theory, the binding between Pt

**Abbreviations:** ADT, Accelerated degradation test; CV, Cyclic voltammograms; DFT, Density functional theory; ECSA, Electrochemical surface area; EDS, Energy dispersive spectroscopy; FCC, Face-centered cubic; KIST, Korea Institute of Science and Technology; ORR, Oxygen reduction reaction; PEMFC, Proton exchange membrane fuel cells; PVD, Physical vapor deposition; STEM, Scanning transmission electron microscope; TEM, Transmission electron microscopy; TGA, Thermogravimetric analysis; TM, Transition metals; UST, University of Science and Technology; XANES, X-ray absorption near edge structure; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

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