

Palladium-copper bimetallic nanocatalyst for electrochemical ethanol oxidation and oxygen reduction in alkaline media

Maja D. Obradović, Vuk V. Radmilović*, Velimir R. Radmilović#, Snežana Lj. Gojković*

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia

*University of Belgrade - Faculty of Technology and Metallurgy, Belgrade, Serbia

#Serbian Academy of Sciences and Arts, Belgrade, Serbia



INTRODUCTION

- Ethanol is non-toxic and its crossover through a membrane is lower than methanol due to its larger molecule size. However, the splitting of C–C bond in ethanol is energetically difficult and much effort in electrocatalysts' improvement is still needed to take the advantage of the high mass energy density of ethanol [1,2].
- Electrochemical oxidation of alcohols requires a noble metal, Pt or Pd, to adsorb the molecule, but also some other oxophilic metal to facilitate further reaction of the adsorbed intermediates [3,4,5]. Copper is inactive for alcohol oxidation but its addition to palladium enhances the ethanol oxidation reaction (EOR) rate [3,4,6].
- Various forms of Pd-Cu electrocatalysts exhibited improved mass activity for the EOR and oxygen reduction reaction (ORR) [7], but the effect of Cu addition on the specific activity is not so clear.
- Aim of the present study:** to establish the influence of the of Cu addition to carbon-supported Pd nanoparticles as a catalyst for EOR and ORR in the alkaline solution.

EXPERIMENTAL

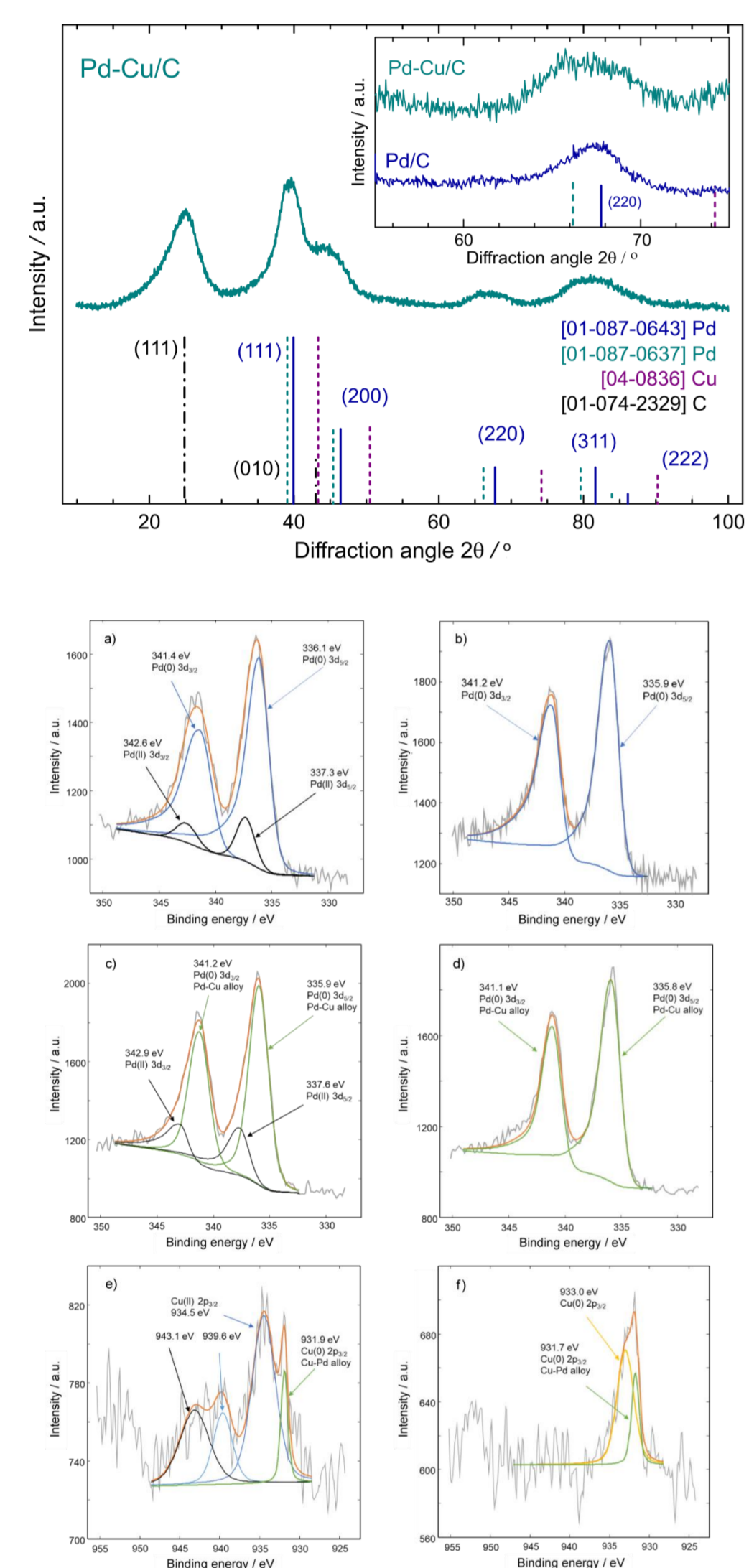
- Pd/C and Pd-Cu/C catalysts were synthesized by borohydride reduction method with no surfactants or capping agents [4]. Commercial Pt/C (E-TEK®) and synthesized powders were applied in the form of a thin-film on a glassy carbon (GC) substrate of rotating disc-electrode;
- Electrochemically active surface area (EASA) of all the catalysts was calculated from the charge of CO_{ads} stripping voltamogram ($\nu = 20 \text{ mV s}^{-1}$) in alkaline solution [6]:

$$EASA = \frac{Q_{\text{exp}}(\text{CO}_{\text{ads}})}{Q^*(\text{CO}_{\text{ads}}) \cdot m} \quad Q^*_{\text{Pt}}(\text{CO}_{\text{ads}}) = 330 \mu\text{C cm}^{-2}, Q^*_{\text{Pd}}(\text{CO}_{\text{ads}}) = 320 \mu\text{C cm}^{-2}$$

- EOR was examined under potentiodynamic ($\nu = 50 \text{ mV s}^{-1}$) and potentiostatic ($E = 0.55 \text{ V}$) conditions in deaerated 0.1 M NaOH containing 0.5 M CH₃CH₂OH at 25 °C;
- ORR was examined under potentiodynamic ($\nu = 20 \text{ mV s}^{-1}$) conditions in aerated 0.1 M NaOH;
- All potentials are expressed on the scale of the reversible hydrogen electrode (RHE);
- The electrochemical cell was thermostated at $298 \pm 0.5 \text{ K}$; A Gamry Interface 1010E potentiostat was employed for all measurements.

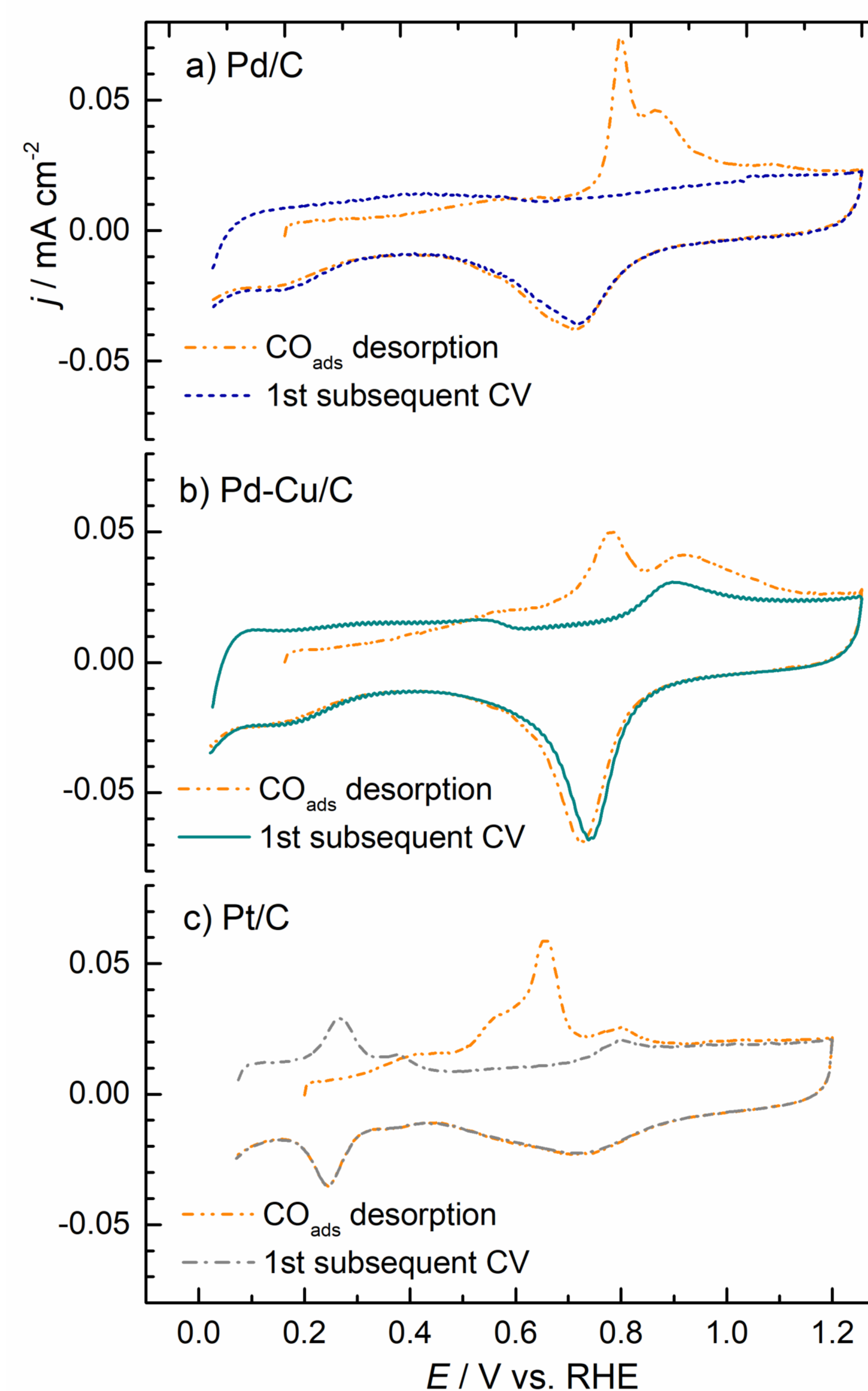
RESULTS

Pd/C and Pd-Cu/C nanocatalyst were characterized by TGA, XRD analysis, STEM images and EDS elemental mapping, as well as XPS analysis [6]

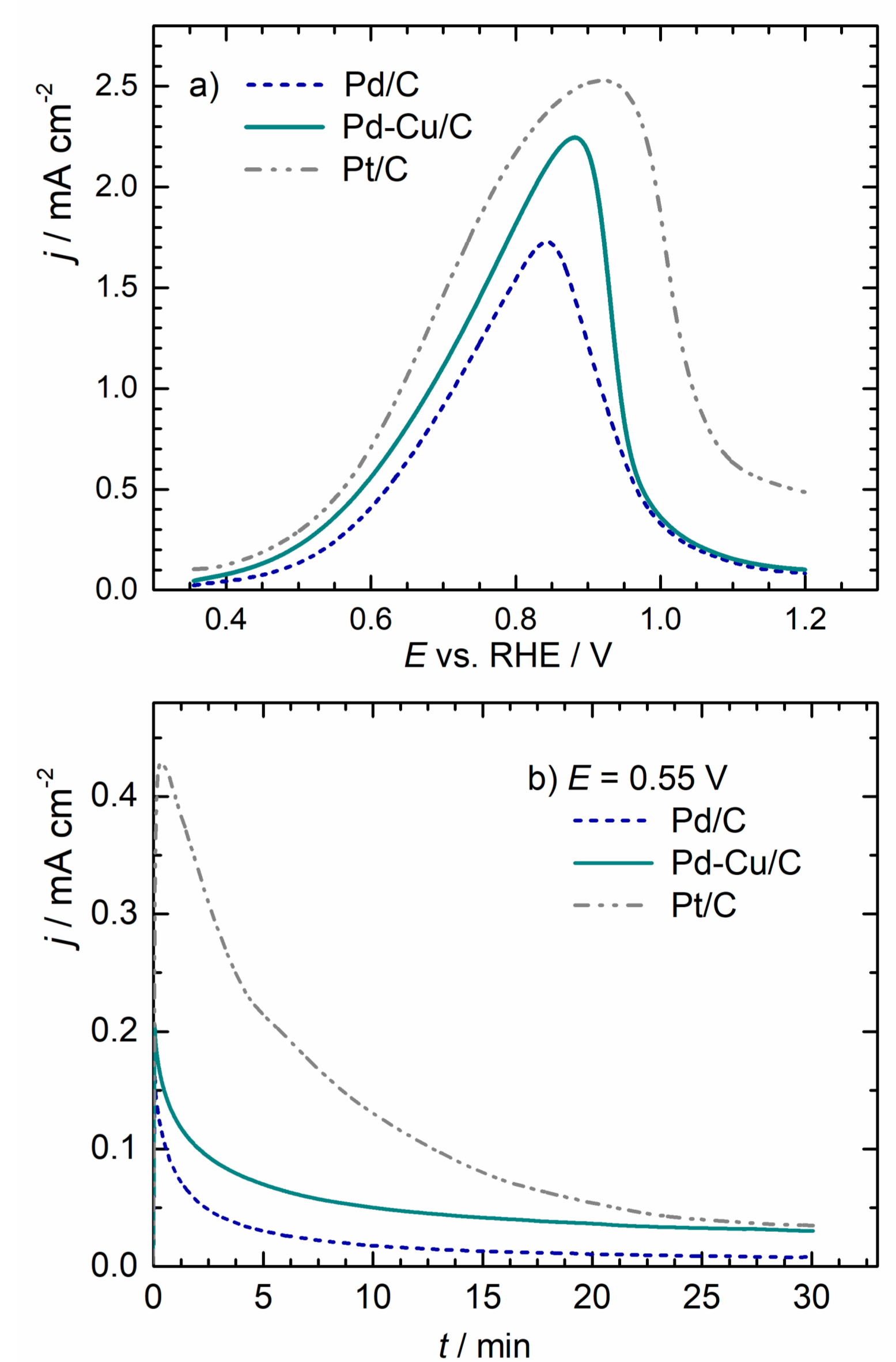


- XRD analysis and TEM characterization suggested that Pd/C and Pd-Cu/C powders synthesized with nanosized structure, with particle size of $4 \pm 1 \text{ nm}$ and $2.34 \pm 0.50 \text{ nm}$, respectively;
- Based on TGA measurement, total metal loadings of the Pd-Cu/C and Pd/C catalysts were found to be 16.1 mass% and 17.6 mass%, respectively;
- The average atomic ratio Pd:Cu in the Pd-Cu/C catalyst was determined from EDS analysis, EDS maps and XPS analysis to be between 5 : 1 to 4:1;
- XRD, STEM and high-energy resolution XPS analysis of Pd/C and Pd-Cu/C suggest the alloying between Pd and Cu.

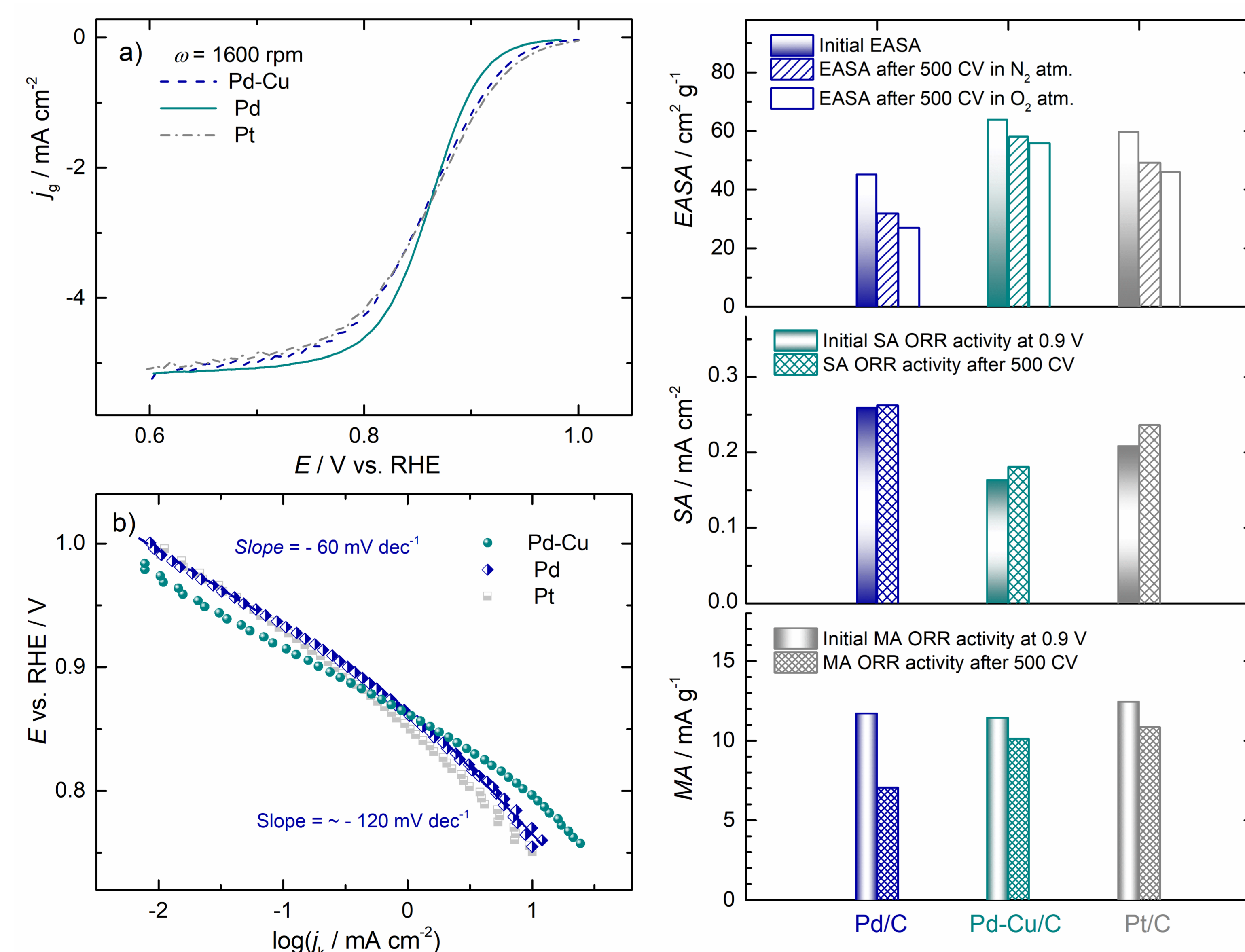
CO_{ads} stripping on Pd/C, Pd-Cu/C and Pt/C nanocatalyst in alkaline solution



EOR on Pd/C, Pd-Cu/C and Pt/C nanocatalyst in alkaline solution



ORR on Pd/C, Pd-Cu/C and Pt/C nanocatalyst in alkaline solution



CONCLUSIONS

- The onset potential and the peak potential of CO_{ads} stripping on Pd-Cu/C were more negative than this for Pd/C, indicating that Cu atoms provide oxygen-containing species at adjacent Pd sites at a lower potential than that achieved on pure metal.
- Adding Cu to Pd enhances the intrinsic activity of Pd for the EOR. Bimetallic catalysts surpassed Pd/C by mass activity, as well.
- The activity of Pt/C for EOR was higher compared with Pd-based catalysts, both as specific and as mass activity, but with a significant decline over 30 min potentiostatic stability test. Therefore, the bifunctional and electronic effect contributed to the good performance of the Pd-Cu nanoalloy for EOR.
- The onset potential of ORR on Pd/C and Pt/C was the same and ~ 18 mV more positive than that of the Pd-Cu/C nanoalloy. The Tafel plots for all nanocatalysts have a linear region with slopes of -60 mV dec^{-1} at low overpotentials, and $\sim -120 \text{ mV dec}^{-1}$ at high overpotentials. However, it was found that the SA ORR activity of Pd-Cu/C were higher than the SA of Pt/C and Pd/C at high current densities.
- Over the durability test, the EASA of all the catalysts decreased, but the effect was the most pronounced for Pd/C. SA of ORR for all the catalysts did not change significantly during the durability test, but the MA of Pd-Cu/C was evidently higher compared to Pd/C.
- Influence of Cu on the Pd stability makes Pd-Cu nanoalloy a promising catalyst for ORR in alkaline media.

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