

Effect of Pd NPs Loading onto ZrO₂/Carbon Printex L6 as an Hybrid Catalyst on O₂ Reduction Reaction for Efficient Production of H₂O₂

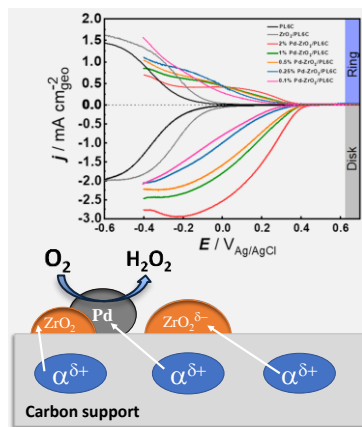
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An obstacle faced when using electrochemical H₂O₂ production in advanced oxidative processes (EAOP) lies in the low catalytic activity of non-noble materials. In this way, carbon-based catalysts containing low loading of Pd nanoparticles (NPs) was explored as an interesting strategy to increase the selectivity of this reaction (S_{H₂O₂}). To evaluate the effect of the matrix on the growing Pd NPs and the activity in terms of H₂O₂ production, Pd-based catalysts (from 0.1 to 2.0 wt.%) were synthesized on a hybrid matrix made of ZrO₂ supported on amorphous Printex L6 carbon (PL6C). The cyclic voltammetry results suggested the effective presence of Pd in the materials, and the decrease in the charge of the redox Pd-H peak could be related to the decrease in metal loading. As expected, the catalytic activity was dependent on the amount of Pd. However, when the loading of Pd was reduced from 2.0% to 0.1%, the selectivity for H₂O₂ production increased from 28% to 83%. We thus conclude that the catalyst composed of 0.1%Pd-ZrO₂/PL6C is promising for saving costs in the production of H₂O₂, which can be applied to the treatment of polluted effluents.

Introduction

The electro-Fenton (EF) process is one of the most advanced oxidation strategies applied to the degradation of organic pollutants contained in wastewater. Both environmental and viability benefits are obtained from EF process thanks to the electrochemical production of H₂O₂ (O₂ + 2e⁻ + 2H⁺ → H₂O₂) and the regeneration of Fe²⁺ (Fe³⁺ + e⁻ → Fe²⁺) [1]. However, a challenge being faced for the electrochemical production of H₂O₂ lies behind the design of low-overpotential catalysts that selectively convert O₂ to H₂O₂. To develop carbon-based catalysts with high electrochemical activity for the oxygen reduction reaction (ORR), many authors have reported that the use of noble metals becomes indispensable [2,3]. However, the challenge of producing noble metal nanoparticles lies on the difficulty in producing small and widely distributed particles on the substrate, in order to maximize the use of the metal loading, and also to avoid the formation of oversized particles or large metal agglomerates. For this reason, a hybrid substrate made of ZrO₂ on Printex carbon was used as a support for the growth of Pd nanoparticles. The ZrO₂ centers can facilitate the interaction between the Pd nanoparticles and the carbonaceous substrate. Therefore, the proposed approach here is to evaluate the viability of ZrO₂/PL6C material as a support for anchoring low amounts of Pd NPs, and then assess the electrochemical ORR towards H₂O₂ production in acidic medium.

Material and Methods

Pd particles onto the substrate were produced from

the reduction of Pd²⁺ ions by ascorbic acid, which is typically used in synthesis routes as a reducing agent [4]. Briefly, an ink was made using 160 mg of ZrO₂/PCL6 containing 3 mg of PdCl₂ in 20 mL in ultrapure water. Next, the mixture was heated to boiling point on a hot plate under magnetic stirring. In order to produce the metal nanoparticles, 78 mg of ascorbic acid were added to the ink and the mixture was heated for 5 min.

The selectivity for H₂O₂ production (S_{H₂O₂}) was analyzed on a rotating ring disk electrode (RRDE), containing a disk of glass carbon and a platinum ring, by using the Paulus (Eq. 1) [5].

$$S_{H_2O_2} = \frac{2i_r/N}{i_{d^+} + i_r/N} \times 100 \quad (\text{Eq. 1})$$

where i_r indicates the ring electrode current (in amperes (A)), i_{d^+} is the current measured in the disk (also in amperes (A)), and N refers to the collection coefficient of the RRDE tip (PINE, $N = 0.37$).

Results and Discussion

The synthesized catalysts were electrochemically characterized by cyclic voltammetry. Fig 1a shows the profiles for bare PL6C and ZrO₂/PL6C, only appearing the reversible peak at -0.3 V vs Ag/AgCl that is related to quinone redox groups present in the carbon material [6-8]. The increase in capacitive current observed on the curve of the hybrid substrate (ZrO₂/PL6C) is due to the increase of electrochemical surface area (ECSA) of carbon, which results from the modification with ZrO₂NPs [6]. On other hand, when Pd NPs were incorporated onto

the catalyst (Fig. 1b), a decline in the capacitive current was observed, attributed to the conductive effect of the noble metal on the material. Furthermore, it was also possible to detect the reduction of the Pd-O species at 0.3 $V_{Ag/AgCl}$, as well as the reversible hydrogenations of Pd-H and Pd-HH in the regions of -0.2 and -0.4 $V_{Ag/AgCl}$, respectively [3]. As expected, the charge of the peaks associated with the redox reaction of Pd decreases at lower loading of the metal, thus confirming the lower ratio of the Pd metal on the substrate. In fact, Fig. 1c shows that the Pd loading decrease affected the ORR onset potential, which had a slight shift of 100 mV toward more negative values, from 0.4 $V_{Ag/AgCl}$ for 2%Pd-ZrO₂/PL6C to 0.26 $V_{Ag/AgCl}$ for 0.1%Pd-ZrO₂/PL6C. Significantly, even using only 0.1% Pd in the composition of the catalyst, a 260 mV gain was obtained for more positive values at the onset of the ORR as compared to ZrO₂/PL6C (0.0 $V_{Ag/AgCl}$). Despite the very low Pd concentrations employed, the high activity of the Pd-based catalyst may be associated with the synergism found among the nanoparticles and the ZrO₂/PL6C hybrid support. Fig. 1d displays the most linear regime for the $S_{H_2O_2}$ values, obtained within the limiting current range for the synthesized catalysts. Interestingly, by reducing the Pd loading onto the surface of the hybrid catalyst, a significant increase in the $S_{H_2O_2}$ was also observed. We can notice an improvement of the $S_{H_2O_2}$ values ranging from 28% for the 2.0%_Pd-ZrO₂/PL6C catalyst to 82% for the 0.1% Pd-ZrO₂/PL6C. This

latter value is similar to those obtained with PL6C (84%) or ZrO₂/PL6C (88%) substrates. Therefore, the 0.1%Pd-ZrO₂/PL6C electrocatalyst has shown to be very promising for saving energy costs related to the electrochemical production of H₂O₂, which is valuable towards the application of advanced oxidation processes.

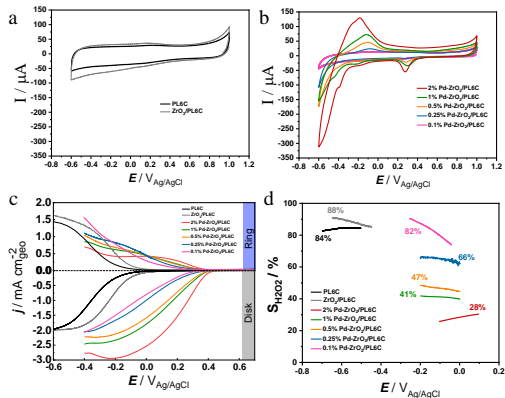


Figure 1. (a,b) Cyclic voltammograms with the carbon-based catalysts obtained on 150 mL N₂-saturated solution of 0.1 mol L⁻¹ K₂SO₄ at pH 3 at a scan rate of 50 mV s⁻¹. (c) Linear sweep voltammetry obtained with an RRDE at a scan rate of 5 mV s⁻¹ and rotation rate of 900 rpm, using O₂-saturated electrolyte. (d) Selectivity toward H₂O₂ production ($S_{H_2O_2}$) for each catalyst.

Table 1. Detailed composition of the catalysts and electrochemical results obtained towards H₂O₂ production.

Catalyst	Material composition ^a	E_{onset} (V vs Ag/AgCl)	$S_{H_2O_2}$ (%)
PL6C	C: 100%/ ZrO ₂ : 0% /Pd: 0%	-0.12	88
ZrO ₂ /PL6C	C: 95% /ZrO ₂ : 5% /Pd: 0%	0.00	84
0.1% Pd-PL6C	C: 99.9% /ZrO ₂ : 0% /Pd: 0.1%	0.06	82
2.0% Pd-PL6C	C: 98% /ZrO ₂ : 0% /Pd: 2.0%	0.30	84
0.1% Pd-ZrO ₂ /PL6C	C: 94.5% : /ZrO ₂ : 5% /Pd:0.1%	0.26	83
2.0% Pd-ZrO ₂ /PL6C	C: 93.1% /ZrO ₂ : 4.9% /Pd: 2.0%	0.40	28

^a Mass percentage used in the synthesis of materials.

Conclusions

The use of a hybrid substrate containing ZrO₂ on amorphous carbon allowed synthesizing a material that produced H₂O₂ with high selectivity (83%) when containing 0.1_{wt}% palladium. Also, the 0.1%Pd-ZrO₂/PL6C catalyst was more catalytic (E_{onset} up to 300 mV more positive) than the ZrO₂/PL6C hybrid matrix. Thus, we have found a catalyst with promising results for saving energy costs referred to the oxygen reduction reaction for H₂O₂ production.

Acknowledgments

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