Effective upcycling of Pd(II) waste into an atomically precise Pd(II)-based catalyst for alkaline fuel cells applications

Francesco Montanari[*1], Marco Bonechi[1,2], Carlotta Cappanni[1], Pietro Gentilesca[1], Matteo Savastano[2,3], Mirko Severi[1], Antonio Bianchi[1,2], Massimo Innocenti[1,2]

[1]*University of Florence, Department of Chemistry "Ugo Schiff", Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy.*

[2] *National Interuniversity Consortium of Material Science and Technology (INSTM), via G.Giusti 9, 50121, Italy.*

[3]*University San Raffaele Roma, Department of Human Sciences for the Promotion of Quality of Life, Via di Val Cannuta 247, 00166 Rome, Italy.*

** francesco.montanari@unifi.it*

Significance and Relevance

This work presents a novel approach toward the development of an efficient Pd(II)-based catalyst for the ORR in alkaline media. Selective extraction of Pd(II) from wastewater by functionalized multi-walled carbon nanotubes leads to excellent performance of the catalyst, reaching 90% H_2O production with comparable onset and half-wave potentials to bulk platinum electrodes while using only 1.94% of Pd(II). The assembly of the catalyst can be carried out under environmentally friendly conditions, at room temperature, in water and without a protected atmosphere. This approach couples waste management with sustainable energy production and furthers the circular economy approach for clean energy technologies.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport and circular economy

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Complementing recent acts such as the European Green Deal, much emphasis has been directed toward the adaptation of renewable energy sources for clean energy production[1]. In this respect, resource-efficient waste management through upcycling metal waste into active electrocatalysts toward hydrogen-related reactions holds quite a central position in the concept of a circular economy[2]. The oxygen reduction reaction (ORR) is of prime importance to the efficiency of fuel cells, which may enable the use of chemical energy in electrical form with only water as a byproduct[3]. However, due to the intrinsically slow kinetics of the ORR, highly active electrocatalysts are still required for improving fuel cell performance. It is well known that the best catalysts, from an elemental composition point of view, are certainly the ones derived from platinum group metals (PGMs). Accordingly, with the limited availability and high cost of PGMs, efforts have been made to minimize their use in ORR electrocatalysts and recover them from wastewater as one of the important directions[4]. In this respect, atomically precise electrocatalysts are of peculiar interest due of their high atomic utilization efficiency, special electronic structure, and homogeneous distribution of active centers[5].

Results and Discussion

In the present study, we report the preparation of an atomically precise heterogeneous catalyst containing Pd(II) ions anchored on multi-walled carbon nanotubes and the results of its application in accelerating the ORR. The catalyst was prepared by selective and quantitative extraction of Pd(II) from the mixture of metal ions that usually accompany Pd(II) in wastewater from the processing of this metal. This approach enables the in situ transformation of Pd(II) waste into a valuable ORR catalyst. The process relies on the strategic selection of a ligand to functionalize the multi-walled carbon nanotubes MWCNT surface. The ligand consist in an unit which ensure stable coordination of the catalytic metal centre (Pd(II)) and in a unit capable of anchoring the complex on MNWCT. Notably, the entire assembly of the catalyst (MWCNT-LPd) is environmentally sustainable, proceeding spontaneously in water, at room temperature, without requiring a controlled atmosphere, and with minimal energy intake.

The successful extraction of Pd(II) was verified using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), confirming the highly selective and quantitative recovery of the metal. The

resulting catalyst (MWCNT-LPd) was thoroughly characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS), which confirmed the uniform distribution of Pd, the absence of competing metals, and the oxidation state of the coordinated Pd(II). Prior to electrochemical evaluations, the catalyst was treated with a Nafion polymeric dispersion to enhance its performance during rotating ring-disk electrode (RRDE) experiments. These studies explored the ORR catalytic mechanism and determined the number of electrons transferred per oxygen molecule. Electrochemical testing revealed a nearly complete 4-electron ORR pathway (90% H_2O production), with an onset potential of -0.118 V and a half-wave potential of -0.307 V. This performance is comparable to that of bulk platinum electrodes, demonstrating the catalyst's efficiency and cost-effectiveness as an alternative to platinum for fuel cells. Additionally, extended electrochemical testing confirmed the stability of MWCNT-LPd, showing no structural degradation or palladium loss.

The study successfully integrated waste management with sustainable energy production, transforming Pd(II)-containing waste into a robust and efficient ORR catalyst under environmentally benign conditions. This advance highlights a cost-effective alternative to platinum electrodes for fuel cells, placing emphasis on resource recovery and clean energy within a circular economy framework.

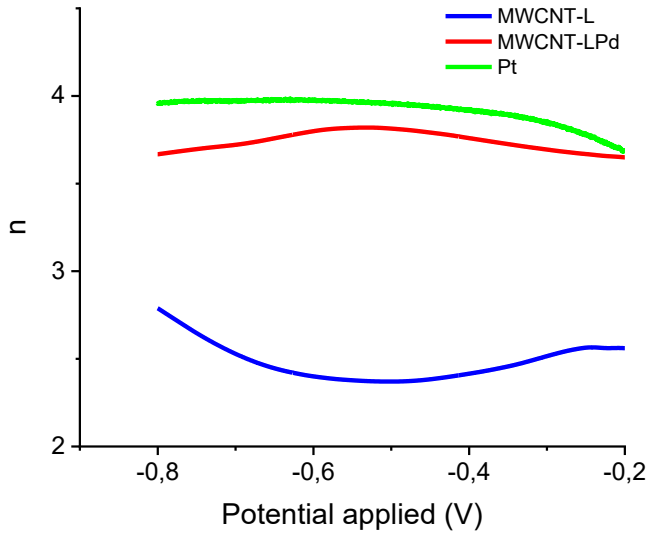

Figure 1: ORR electrocatalytic performance, KOH 0.1 M O_2 saturated solution, 1600 rpm rotation rate, 10 $mV \cdot s^{-1}$ scan rate. RRDE number of exchanged electrons per O_2 molecule (n) as function of the potential applied at the RRDE working electrode.

References

1. Montiel, M. A. *et al., Appl. Catal. B Environ.*, **2023**, *327, 122414.*
2. Chen, Z. *et al., Nano-Micro Lett.* **2022**, *15, 4.*
3. Bonechi, M. *et al., Catalysts,* **2021**, *11, 764.*
4. Monini, V. *et al., Dalton Trans.*, **2024**, *53, 2487-2500.*
5. Yan, L. *et al., Chem*, **2023**, 9, 280-342.

Acknowledgements

The authors acknowledge the support offered by Project 2022NW4P2T CUP B53D23013890006 "From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production" PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by Italian Ministry of University and Research and NextGenerationEU.