Impact of Polymorphism of Metal-Organic Frameworks on Electrocatalytic Properties of CeO_2 in the Oxygen Evolution Reaction

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Hydrogen (H_2) has emerged as a promising energy source, due to the environmental problems caused by the extensive use of fossil fuels [1]. Although water splitting is the best method for obtaining this gas, high-performance electrocatalysts are necessary to make the process viable. CeO2 has stood out among all materials due to its outstanding electrocatalytic activity and natural abundance [1,2]. Thus, this work reported two different cerium oxides (CeO_2), obtained using two cerium-based Metal-Organic Frameworks (MOFs) polymorphs as templates. The MOFs-Ce were synthesized using succinate and cerium (III) nitrate ligand ($[Ce_2(Succ)_3(H_2O)_2]$, Succ = succinate) via the hydrothermal method (MOF-Ce (H), with monoclinic structure and block-like morphology) and crystallization at room temperature (MOF-Ce (RT), with triclinic structure and rod-like morphology). Both MOFs were heat treated at 350°C to produce the cerium oxides (named CeO_2(H) and CeO_2(RT), respectively). All materials were characterized by XRD, FT-IR, Raman, UV-VIS, XPS, and SEM-EDS. Rietveld refinement confirmed the formation of CeO_2 with fluorite structure, and crystallite size of 8.3 nm and 6.2 nm, for CeO_2(H) and CeO_2(RT), respectively. XPS data confirm the presence of Ce^{3+} and Ce^{4+} on the oxide´s surfaces, and the high content of oxygen vacancies in the oxide structures, agreeing with the Raman results. SEM images show the total preservation of the morphologies in the cerium oxides, compared to the respective MOF-precursor. Electrochemical data (Table 1) indicated overpotentials (η) and Tafel slopes of 326 mV and 58.92 mV dec^{-1} for CeO_2 (H), and 319 mV and 62.25 mV dec^{-1} for the CeO_2 (RT) sample, at $j = 10$ mA cm^{-2}, in 1.0 mol L^{-1} KOH electrolyte. The electrochemically active areas obtained from cyclic voltammetry were ECSA = 307 cm^2 (CeO_2 (H)) and ECSA = 423 cm^2 (CeO_2 (RT)). Chronopotentiometry indicated high stability for up to 24 hours for both electrocatalysts. The EIS measurements show lower ohmic resistance for the CeO_2(RT) sample. All results indicate excellent electrocatalytic performance, especially for CeO_2 (RT), compared to other materials in the literature.

Table 1 – Electrocatalytic parameters for the CeO_2(H) and CeO_2(RT) electrocatalysts

Electrocatalyst	η (mV)	Tafel slope (mV dec^{-1})	ECSA (cm^2)	R_s (Ω)
CeO_2 (H)	**326**	**58.92**	**307**	**0.53**
CeO_2 (RT)	**319**	**62.25**	**423**	**0.47**

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References

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