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Doctoral Dissertation
Doctoral Program in Metrology (38th Cycle)

Electrochemical measurements to support energy transition: water electrolyzers characterization

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Politecnico di Torino
28th January 2026

Abstract

Water electrolysis represents a key technology for energy transition, and among the different technologies, alkaline water electrolysis is the most developed, thanks to relatively low cost, compared to others, and the possibility of working without critical raw materials or noble electrodes. A crucial aspect of water electrolysis is the anodic process: oxygen evolution reaction (OER) is characterized by a sluggish kinetics, high overpotential, and severe stability issues in alkaline environments. For this reason, the design of active and stable catalysts is essential. However, despite the extensive research efforts in recent years, the lack of standardized protocols for catalyst testing make it difficult to compare results among different laboratories.

To address this gap, this research proposes to develop and apply standardized measurement methodologies for the characterization of electrodes used in water electrolysis, combining electrochemical techniques, to extract key performance indicators, with physicochemical characterization methods to correlate morphological and structural properties with electrochemical performance.

In particular, I defined two complementary experimental protocols, tailored to the specific nature of the investigated materials and integrating both DC and AC electrochemical techniques. In particular, DC methods provide quantitative insights on electrocatalytic activity and stability, while AC techniques, such as electrochemical impedance spectroscopy, represent a powerful diagnostic tool for resolving the individual contributions of charge transfer, double-layer capacitance, diffusion, and interfacial phenomena over a wide frequency range, by the usage of an electrical circuit, modeling the electrochemical behaviour of the system. The combination of AC and DC measurements allows obtaining a more comprehensive assessment of electrocatalysts performance, enabling the identification of degradation pathways and enhancing the comparability of results. Experimental activity focused on functionalized Porous Transport Layers (PTLs) in stainless steel, which can be used in new generation anion exchange membrane water electrolyzers (AEMWEs), and on perovskite-based electrodes, explored for their catalytic activity and stability toward the OER. These materials were selected to represent both technologically relevant and scientifically challenging systems, where surface modification, microstructural control, and compositional tuning play decisive roles in determining electrochemical behaviour.

A *Protocol for functionalized PTLs* was applied to Ni-based and NiFe-based metal-organic framework (MOF) nanostructures. NiFe MOF-based electrodes, in particular, have been integrated as anodes in anion-exchange membrane electrolyzers (AEMWE). In both cases, the measurement approach allowed a reliable correlation among structural features, electrocatalytic activity, and degradation mechanisms, highlighting the advantages of a reproducible measurement framework.

A *Thin-Film Electrode Protocol* was instead applied to perovskite catalysts, i.e. Ti-doped $\text{SrCoO}_{3-\delta}$. The application of a specific protocol, integrating electrochemical and spectroscopic techniques, confirmed the role of structural doping in achieving durable performance.

Overall, this dissertation demonstrates how measurement science can play an important role in electrocatalysis research providing a metrological framework for electrochemical measurements in hydrogen-related energy research, aiming to enhance the reliability and comparability of electrochemical testing across research institutions and industrial laboratories.

