Electrodeposited Ni@NiO$_x$/C Cathodes for High-Performing Precious Metal-Free Anion Exchange Membrane Water Electrolyzers

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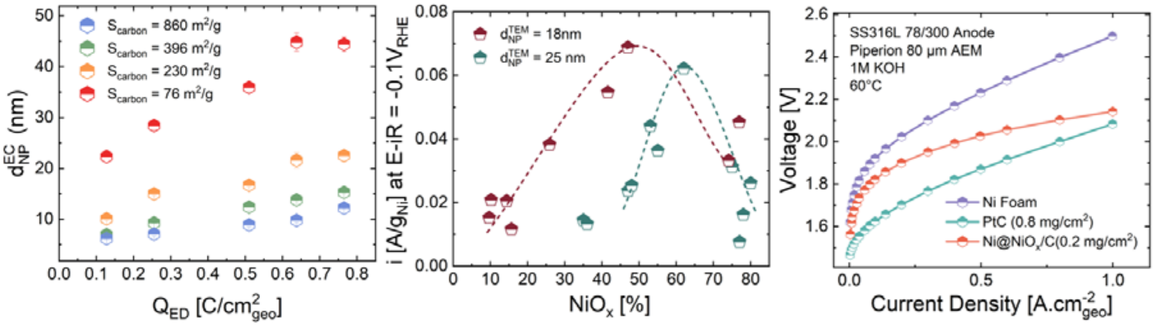
Anion Exchange Membrane Water Electrolysis (AEMWE) is a promising technology for the large-scale production of green hydrogen. However, its deployment largely depends on the development of high-performing, precious metal-free electrocatalysts for the alkaline hydrogen evolution reaction (HER), with Ni/NiO$_x$ heterostructured materials being among the most promising candidates[1]. Indeed, while metallic Ni has rather poor intrinsic HER activity (as Ni strongly adsorbs hydrogen), its performance substantially improves when combined with (hydr)oxide NiO$_x$ sites[2]. Moreover, nanoparticulated structures are crucial for high activity (*i.e.*, a high density of HER active sites). However, the development of Ni-based catalysts with a high specific surface area and high mass activity remains a challenge. To this end, the effect of NiO$_x$ coverage on nanoparticle (NP) surfaces on their HER activity needs to be better understood.

The objective of this work consists in unveiling correlations between (i) the nickel nanoparticle size, (ii) the optimal Ni/NiO$_x$ ratio for the HER, and (iii) their performance at the cathode of a single-cell AEMWE.

For this purpose, a library of Ni NPs supported on carbon black was prepared via electrodeposition with the size controlled by the specific surface area of carbon and the deposition charge (**Fig.1A**). The particle size was estimated from electrochemical measurements (d_{NP}^{EC}, based on the electrochemical surface area and mass of Ni NPs) and TEM images (d_{NP}^{TEM}), with both methods showing consistent results. Using electrodeposition as a synthetic approach allows a convenient access to a wide range of NiO$_x$ coverages, from a fully metallic (as prepared) Ni surface to a partially oxidized (after electrochemical oxidation/reduction treatment) Ni/NiO$_x$ surface. Then, the electrocatalytic activity of these Ni NPs was studied in a model three-electrode cell, showing that the optimal Ni/NiO$_x$ ratio for HER performance depends on the particle size (**Fig.1B**). Subsequently, the optimal structures were scaled up to 25 cm² electrodes to evaluate their performance in a single-cell AEMWE. The results showed that our carbon-supported Ni@NiO$_x$ cathode outperforms a commercial nickel foam electrode and even shows competitive performance to a commercial Pt/C electrode at high current density despite a 4 times lower metal loading (**Fig.1C**).



<u>Figure 1.</u> **A.** Ni NPs size as a function of the electrodeposition charge for various carbon blacks (0.1 mg/cm$^2_{geo}$). **B.** HER performances as a function of the NiO$_x$ surface coverage for Ni NPs of 15 and 25 nm. **C.** Polarization curves acquired in a single AEMEC at 60°C with different cathodes: commercial Ni foam, commercial Pt/C NPs on GDL, and 25 nm Ni@NiO$_x$/C NPs on GDL.

[1] A. G. Oshchepkov, et al. *ACS Catal*. **2019**, 9, 9, 8520–8528.
[2] M. Gong, et al. *Nat Commun*. **2014**, 5, 4695.

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