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## O-46 | FE,NI,N-DOPED CNT AS BIFUNCTIONAL OXYGEN ELECTROCATALYST

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### Introduction

Considering the harmful effects of fossil fuels on the environment, the increase in the global energy demand, and the need to achieve a sustainable green future, there is currently an intense research effort focused on renewable energy sources. In this context, hydrogen appears as an excellent energy vector to achieve climate neutrality. Hydrogen can be used in a unitized regenerative fuel cell (URFC), which operates in fuel cell (FC) or electrolyzer (EL) mode. In the former, H<sub>2</sub>O and energy are generated whereas water splitting takes place in the latter to produce the necessary reactants for the FC. Accordingly, no environmentally unfriendly products are formed during URFC's operation. Nonetheless, it requires bifunctional oxygen catalysts (BOCs) for the oxygen reduction (ORR) and evolution (OER) reactions due to its compartmentalization and the reactions' sluggish kinetics. Nowadays, the main benchmark catalysts are noble metals, which are scarce and very expensive. Therefore, tailoring widely available and low-cost carbon materials is an interesting alternative to replace those catalysts. Moreover, nickel has been broadly reported as one of the most promising OER electrocatalysts, whereas the synergy between iron and nitrogen can lead to interesting ORR performances. Accordingly, this work aims to design highly electroactive Fe,Ni,N-doped CNT BOCs.

### Materials and Methods

Highly electroactive BOCs were prepared by modifying CNTs. An ethanol solution containing nickel nitrate was added dropwise by incipient wetness impregnation (IWI) under sonication to the CNT and then dried overnight. Then, the resulting material underwent a thermal treatment at different temperatures (160-325 °C) and under different atmospheres (N<sub>2</sub> and H<sub>2</sub>), resulting in several catalysts (CNT<sub>Ni\_XY</sub>, where X represents the treatment temperature and Y represents the atmosphere used) with different nickel species. Additionally, one sample (CNT<sub>Fe</sub>) was prepared by adding iron(II) phthalocyanine by IWI to the CNT under sonication and then drying it overnight. This material was then treated under N<sub>2</sub> atmosphere at 500 °C for 2 h. Furthermore, another sample (CNT<sub>Ni\_260H2</sub>/CNT<sub>Fe</sub>) was prepared by physically mixing the Ni-doped sample with the highest OER electroactivity (CNT<sub>Ni\_260H2</sub>) with the monometallic Fe-doped CNT catalyst (CNT<sub>Fe</sub>).

### Results and Discussion

The prepared monometallic Ni-doped materials were directly used as electrocatalysts in the OER using a three-electrode cell configuration with a rotating disk electrode. The linear sweep voltammetry (LSV) curves obtained showed that using a thermal treatment temperature of 260 °C and a H<sub>2</sub> atmosphere led to the catalyst with the highest OER electroactivity of all monometallic samples prepared (CNT<sub>Ni\_260H2</sub>). Furthermore, its mixture with CNT<sub>Fe</sub> further enhanced the performance of the electrocatalyst achieving the lowest OER overpotential (340 mV).

Regarding the ORR, the incorporation of iron(II) phthalocyanine (FePc) on the CNT surface had already displayed remarkable ORR activity, even better than Pt on carbon black (Pt/C), the ORR benchmark [1].

Both Fe-containing samples ( $\text{CNT}_{\text{Fe}}$  and  $\text{CNT}_{\text{Ni}_{260\text{H}_2}}/\text{CNT}_{\text{Fe}}$ ) displayed similar ORR electroactivities, which were slightly higher than that of Pt/C and much higher than the monometallic Ni-doped sample. Moreover, these samples presented short-term stabilities similar to or higher than Pt/C.

### Conclusions

The incorporation of two different metal precursors (nickel nitrate and iron phthalocyanine) on the CNT structure was performed to prepare bifunctional oxygen electrocatalysts. The results suggested that using a medium temperature (260 °C) and a  $\text{H}_2$  atmosphere favored the OER electrocatalysis. This sample was then further mixed with a sample of CNT-supported iron phthalocyanine and tested towards both ORR and OER. The bimetallic sample presented similar electrocatalytic performance and higher short-term stability than the commercial Pt/C electrocatalyst towards the ORR, and higher OER activity than the monometallic samples. Overall, nickel displayed high electroactivity towards the OER, whereas the  $\text{FeN}_4$  macrocycle excelled towards the ORR. Nonetheless, both monometallic catalysts exhibited poor performances towards the opposite reaction, hence a low oxygen bifunctionality. However, their combination by physical mixing led to an enhanced OER electroactivity without compromising the ORR performance. The bimetallic sample showed one of the lowest ever reported potential gaps between OER and ORR (0.67 V) for carbon-based electrocatalysts and largely surpassed the performance of the noble metal catalysts. Hence, the carbon material herein prepared is a perfect candidate for upscale testing in more industrially relevant applications.

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### References

- [1] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira, Optimization of cobalt on CNT towards the oxygen evolution reaction and its synergy with iron (II) phthalocyanine as bifunctional oxygen electrocatalyst, *Catalysis Today*, (2023) 114057.