

## The effect of alkaline cations on nitrate electro-reduction reaction at Fe-N-C nanostructures

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Eco-friendly electrocatalytic strategies have recently been highlighted to convert environmental pollutants into value-added products, such as nitrate from agricultural activities into ammonia. Materials based on non-noble metals such as Fe-N-C, have been reported as promising electrocatalysts depicting both high activity and durability. Herein, we explored the effect of alkaline cations in the electrolyte during the nitrate reduction reaction (NO<sub>3</sub>RR) catalyzed by Fe-N-C. The synthesis consisted of pyrolysis of the component precursors; and can be found in detail elsewhere. [1] Characterization by transmission electron microscopy coupled to energy-dispersive X-ray spectroscopy (TEM/EDX) revealed 50-100 nm FeO particles dispersed onto larger carbon-nitrogen structures. Catalytic activity was evaluated in a three-electrode cell setup with 0.5 mol L<sup>-1</sup> MOH + 0.1 mol L<sup>-1</sup> MNO<sub>3</sub> (M = Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup>). A Catalyst ink was prepared and deposited *via* drop-casting onto a glassy carbon rotating disk electrode (RDE). Then, with the system set at 1000 rpm, cyclic voltammetry and chronoamperometry techniques were performed. In the presence of nitrate in the solution, the reduction current at -0.4 V<sub>RHE</sub> showed an increase of *ca.* 250x, with consequent detection of ammonia in the electrolyte, indicating that the catalyst is selective for NO<sub>3</sub>RR. The activity also depends on the cation, following the current order at -0.4 V: -6.4 mA (Li<sup>+</sup>); -5.0 mA (Na<sup>+</sup>); and -5.0 mA (K<sup>+</sup>). These results can be explained by the strong interaction between hydrated Li<sup>+</sup> (Li-(H<sub>2</sub>O)<sub>x</sub>) and polarized surfaces, activating water to deliver protons to nitrate or its reaction intermediates reduction steps. Overall, the Fe-N-C catalyst can convert nitrate to ammonia and the activity can be modified by electrolyte cations.

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### References:

[1] C. B. Gozzo, et al., Journal of Electroanalytical Chem, v. 963, p,118300, 2024