

Why the quantitative isotope tests were not conducted for nitrate detection in “Electrochemical Oxidation of Nitrogen towards Direct Nitrate Production on Spinel Oxides”

The electrochemical nitrogen fixation in recent years mainly focuses on the ammonia synthesis from the nitrogen reduction reaction (NRR). Despite the progress achieved, this method typically suffers from low ammonia conversion: the ammonia produced is generally so small (usually no higher than 5 ppm) that the ammonia detected cannot be firmly attributed to electrochemical NRR rather than potential contamination^{1,2}. To overcome this challenge, the quantitative isotope experiment, which uses isotopically labelled ¹⁵N₂ gas and detects yielded ¹⁵NH₃ with an isotope-sensitive method, is considered qualified to measure the ammonia produced from electrochemical nitrogen fixation.

In addition to the NRR, the electrochemical nitrogen fixation by nitrogen oxidation reaction (NOR) to synthesize nitrate/nitric acid has been reported since last year³⁻⁷. In these papers, the detected nitrate concentrations from NOR are mostly obviously larger than ammonia concentrations measured from NRR. Particularly, the highest nitrate concentration detected preliminarily by IC in our work is around 100 ppm. These results topple the necessity of the isotope test for nitrate concentration measurement, as it is only obligatory when the product concentration is not significantly larger than the potential contamination. To further prove this statement, a series of control experiments have been conducted to measure and exclude the influence from possible contamination. In details, control electrolysis experiment under Ar at same applied potential has been performed to measure the potential-dependent contamination from carbon paper, leaching/decomposition of catalyst/support, impurities in the electrolyte chemicals, etc; control experiments by purging N₂/Ar without electrolysis for same duration has also been performed to measure the leakage from atmosphere, impurities adsorbed on electrodes/reactors and in electrolyte chemicals, etc. These control experiments have been performed for every test parameter, and the nitrate yield concentration is calculated based on the Equation 1 in the paper.

$$[\text{NO}_3^-]_{\text{yield}} = ([\text{NO}_3^-]_{\text{yield,N}_2,\text{CA}} - [\text{NO}_3^-]_{\text{yield,N}_2,\text{OCP}}) - ([\text{NO}_3^-]_{\text{yield,Ar,CA}} - [\text{NO}_3^-]_{\text{yield,Ar,OCP}}) \quad (1)$$

where $[\text{NO}_3^-]_{\text{yield}}$ is the nitrate concentration produced through NOR used for FE and yield rate calculation; $[\text{NO}_3^-]_{\text{yield,N}_2,\text{CA}}$ and $[\text{NO}_3^-]_{\text{yield,N}_2,\text{OCP}}$ are the nitrate concentrations produced in N₂-saturated 1 M KOH throughout CA and under OCP, respectively; $[\text{NO}_3^-]_{\text{yield,Ar,CA}}$ and $[\text{NO}_3^-]_{\text{yield,Ar,OCP}}$ are the nitrate concentrations produced in Ar-saturated 1 M KOH throughout CA and under OCP, respectively.

The concentrations of nitrate, after extracting the contamination obtained by those control experiments, are still at a relatively high level (as shown in the Figure 3c in the paper). As a matter of fact, the quantitative isotope tests in some of the most recent papers^{5,7} on electrochemical nitrogen oxidation reaction (NOR) also show that the influence of impurity is limited when the nitrate concentration is at a high level. Therefore, the obtained nitrate concentrations of NOR in our paper are reliable even without the isotope tests.

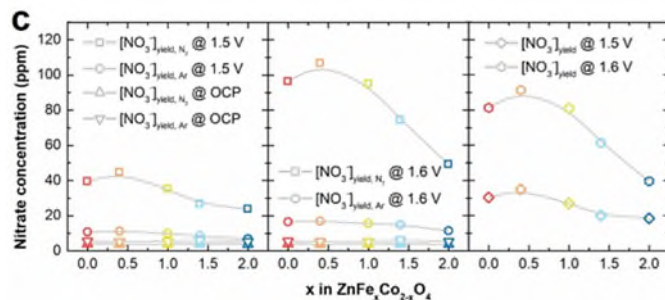


Figure 3c. Comparison of the nitrate concentrations yielded in N₂-saturated and Ar-saturated 1 M KOH throughout chronoamperometry at 1.5 V and 1.6 V vs. RHE and under OCP

References

- (1) Andersen, S. Z.; Čolić, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Nørskov, J. K.; Chorkendorff, I. *Nature* **2019**, *57*, 504.
- (2) Tang, C.; Qiao, S.-Z. *Chem. Soc. Rev.* **2019**, *48*, 3166.
- (3) Wang, Y.; Yu, Y.; Jia, R.; Zhang, C.; Zhang, B. *Natl. Sci. Rev.* **2019**, *6*, 730.
- (4) Dai, C.; Sun, Y.; Chen, G.; Fisher, A. C.; Xu, Z. *J. Angew. Chem. Int. Ed.* **2020**, *59*, 9418.
- (5) Fang, W.; Du, C.; Kuang, M.; Chen, M.; Huang, W.; Ren, H.; Xu, J.; Feldhoff, A.; Yan, Q. *Chemical Communications* **2020**, *56*, 5779.
- (6) Zhang, L.; Cong, M.; Ding, X.; Jin, Y.; Xu, F.; Wang, Y.; Chen, L.; Zhang, L. *Angew. Chem. Int. Ed.* **2020**, *59*, 10888.
- (7) Kuang, M.; Wang, Y.; Fang, W.; Tan, H.; Chen, M.; Yao, J.; Liu, C.; Xu, J.; Zhou, K.; Yan, Q. *Adv. Mater.* **2020**, *32*, 2002189.

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