# Cation effect on electrocatalytic nitrate reduction to ammonia

J. Forner[1], Y. Wang[1], A. Dutta[1], P. Broekmann[1]*

[1]Department of Chemistry, Biochemistry and Pharmaceutical Science, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

The electrochemical reduction of nitrate to ammonia ($NO_3$-RR) is a sustainable approach to mitigate nitrate pollution. Previous studies have shown that alkali metal cations play a significant role in electrochemical reduction processes. The influence of alkali metal cations on the activity, selectivity, and mass transport during $NO_3$-RR was investigated in this work.

In previous research [1][2], it was observed that the electric field induced by solvated cations can modulate the activity and selectivity in the electrochemical reduction of $CO_2$ by affecting the electrochemical double layer, particularly the outer Helmholtz plane. As the cation size increases, the hydration sphere radius decreases, resulting in a decrease in hydration energy and an increase in mobility ($Li^+ < Na^+ < K^+ < Cs^+$) [3]. This trend allows for tuning of activity, selectivity, and mass transport by selecting the appropriate supporting cation.

In this study, a porous Cu-foam catalyst deposited onto a copper mesh support using the dynamic hydrogen bubble template method was employed to examine the influence of alkali metal cations ($Li^+ < Na^+ < K^+ < Cs^+$) on $NO_3$-RR. By adjusting the composition and concentration of the supporting electrolyte, the effects of different alkali cations were investigated.

The results revealed that the partial current density, and consequently the nitrate removal rate, increased following the order $Li^+ < Na^+ < K^+ < Cs^+$. These consistent trends in $NO_3$-RR emphasize the pivotal role played by the electrostatic effect, which stabilizes negatively charged species at the electrode interface. The experimental surface coverages of alkali metal cations align with their free energies of hydration, following the order $Li^+ > Na^+ > K^+ > Cs^+$. The conversion rate of nitrate to ammonia increases according to the coverage of specifically absorbed alkali metal cations that exhibit lower degrees of hydration. These findings suggest that the extent of dehydration of alkali metal cations at the electrode-electrolyte interface significantly influences their ability to facilitate nitrate reduction.

[1] Resasco, J., Chen, L. D., Clark, E., Tsai, C., Hahn, C., Jaramillo, T. F., Chan, K., & Bell, A. T. *Journal of the American Chemical Society*, **2017**, *139*(32), 11277–11287.
[2] Chen, L. D., Urushihara, M., Chan, K., & Nørskov, J. K. *ACS Catalysis*, **2016**, *6*(10), 7133–7139. https://doi.org/10.1021/acscatal.6b02299
[3] Hayamizu, K., Chiba, Y., & Haishi, T. *RSC Advances*, **2021**, *11*(33), 20252–20257.
[4] Bender, J. T., Petersen, A. S., Østergaard, F. C., Wood, M. A., Heffernan, S. M. J., Milliron, D. J., Rossmeisl, J., & Resasco, J. *ACS Energy Letters*, **2023**, *8*(1), 657–665.