Liquid product quantification *via* NMR in CO_2 electrocatalytic reduction over phosphate-derived nickel catalysts

P. Preikschas[1], A. J. Martín[1], J. Pérez-Ramírez[1]*

[1]Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich

The emergence of Ni-based catalysts that enable the production of diverse multicarbon products necessitates the development of highly sensitive and flexible quantification techniques for accurate catalyst evaluations.[1] In response to this need, we have developed robust ^{1}H NMR protocols that possess the desired characteristics. These protocols include optimized water suppression using an adapted WATERGATE method[2] and a significant reduction in NMR experiment time achieved by incorporating a relaxation agent (**Fig. 1a**). By combining these protocols with an Automated Product Analysis Routine (APAR) developed in Python and accessible to all catalysis practitioners (**Fig. 1b**), we have established a comprehensive approach for samples containing up to twelve liquid products. Faradaic efficiencies can be obtained within a time frame of 15 min, including NMR analysis and data processing. This approach exhibits low quantification limits ranging from 0.3-3.2 µM, enabling the determination of Faradaic efficiencies as low as 0.1%.

Employing these powerful tools on phosphate-derived Ni (PD-Ni) catalysts, we have made notable discoveries. Specifically, we have identified four previously unreported eCO_2RR products, namely acetate, ethylene glycol, hydroxyacetone, and *i*-propanol. Furthermore, we have uncovered performance trends associated with varying potential, electrolyte buffer capability, and bulk pH (**Fig. 1c**). For example, long-chain products exhibit a positive response to lower overpotentials and near-neutral pH. Additionally, we have observed that low bicarbonate concentrations promote the concurrent formation of methane along with other carbon products while favoring oxygenates over hydrocarbons. This work establishes a solid foundation for the advancement of this new class of materials by providing sensitive and flexible tools for quantifying liquid products. Furthermore, these tools can be directly applied to evaluate other catalysts that generate complex liquid mixtures, including copper-based catalysts.

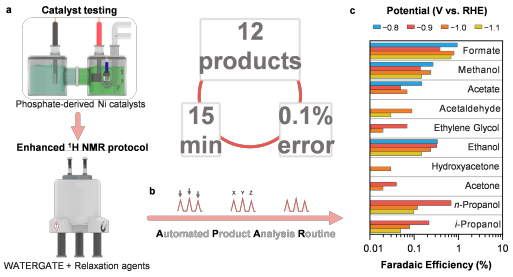

Fig. 1a Complex liquid mixtures generated by CO_2 electroreduction over phosphate-derived Ni catalysts can be accurately quantified by ^{1}H NMR using water suppression *via* WATERGATE and relaxation agents. **b** Raw NMR data is automatically processed by a developed routine (APAR) to provide **c** Faradaic efficiencies for a set of 12 products revealing performance trends. 15 min are required from the start of NMR analysis until Faradaic efficiencies are available with errors below 0.1%.

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[2] R. W. Adams, C.M., Holroyd, J.A. Aguilar, M. Nilsson, G.A. Morris, *Chem. Commun*. **2013**, *49*, 358.