

Electrocatalytic hydrogenation: Strategies for energy storage

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Electrocatalytic hydrogenation:

Strategies for energy storage

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In this lecture, I'll describe our efforts to enable the storage of intermittent but renewable electricity from solar and wind in liquid fuels. We are developing new homogeneous catalyst design concepts for the electrocatalytic oxidation of alcohols and reduction of ketones in an effort to establish the feasibility of electrochemical energy conversion strategies employing versatile ketone/alcohol redox couples. We describe the reactivity of highly active transfer-hydrogenation catalysts as electrocatalysts.¹⁻⁴ These systems provide energy-efficient pathways for reversible electro-hydrogenation of ketones or dehydrogenation reactions of alcohols. We have developed new tandem catalytic strategies for the electrocatalytic reduction of acetone to isopropanol,⁴ an attractive liquid organic hydrogen carrier. The selective electrocatalytic reduction of acetone was enabled by two advances: the development and electrochemical characterization of modestly hydridic and acid-stable metal hydrides derived from Ir and Fe cyclopentadienone complexes, and the discovery that cobaltocenium can function as an electrochemical mediator that selectively generates that metal hydride under electroreductive conditions in tandem electrocatalytic cycles. The role of cobaltocenium is critical, as the reductive protonation of cobaltocenium with mild acids generates $(C_5H_5)Co^I(C_5H_6)$, which functions as an electrocatalytic hydride mediator analogous to that of NADH cofactors.

References.

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3. Galvin, C. M.; Waymouth, R. M., Electron-Rich Phenoxyl Mediators Improve Thermodynamic Performance of Electrocatalytic Alcohol Oxidation with an Iridium Pincer Complex. *J. Am. Chem. Soc.* **2020**, *142* (45), 19368-19378.
4. Marron, D. P.; Galvin, C. M.; Dressel, J. M.; Waymouth, R. M., Cobaltocene-Mediated Catalytic Hydride Transfer: Strategies for Electrocatalytic Hydrogenation. *J. Am. Chem. Soc.* **2024**, *146* (25), 17075-17083.



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Bob is the Robert Eckles Swain Professor of Chemistry at Stanford University. He received B.S. in Mathematics and B.A. in Chemistry from Washington and Lee University and his Ph.D. in Chemistry at the Caltech in 1987 with Professor R.H. Grubbs. He was a postdoctoral fellow with the late Professor Piero Pino at the ETH in Zurich in 1987 and joined the faculty at Stanford as an Assistant Professor in 1988. He received the Alan T. Waterman Award from the NSF in 1996, EPA's Presidential Green Chemistry Challenge Award in 2012, the ACS Polymer Chemistry Award in 2022, and the Herman F Mark Award in 2023. He was inducted as a fellow of AAAS in 2024 and as a member of the National Academy of Sciences in 2026. He has won several university teaching awards, including the Walter J. Gores Award, the Phi Beta Kappa Teaching Award, and is currently a Bass Fellow in Undergraduate Education. His research interests are at the interface of Inorganic, Organic and Polymer Chemistry, in particular the development of new concepts in catalysis for the selective synthesis of both macromolecules and fine chemicals. Particular areas of interest include electrocatalysis for energy storage, catalytic strategies to renewable polyesters and polycarbonates, and catalytic methods for the synthesis of functional degradable polymers for gene delivery.