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Research Seminar

When: April 6, 2023

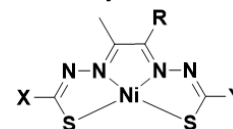
Time: 12:00 p.m.

Location: CBL-16

Hydrogen Evolution Reaction (HER): From Homogenous to Heterogenous Approach

Abstract:

Hydrogen is an important energy storage alternative to fossil fuels. Its very high energy density makes its use in fuel cells an attractive approach to facilitating the net reduction of carbon emissions. The majority of H_2 is currently produced through steam reformation cracking of petroleum feedstocks. A more environmentally friendly way of producing green H_2 is by electrolytic splitting of water.¹ The most efficient catalysts for the hydrogen evolution reaction (HER) are platinum group metals that possess low overpotentials, but they are both rare and expensive, and not practical for use in industrial processes.² There is considerable interest in the development of solid-state and molecular HER electrocatalysts containing earth abundant metals with low overpotentials for use in water electrolysis. This study explores six different Ni(II) complexes that are derivatives of diacetyl-bis(4-methyl-3-thiosemicarbazone ligand, ATSM, which contain systematic changes in ligand structure to evaluate its effect on HER activity in both aqueous and non-aqueous solutions. The ligands were modified by replacing an electron donating methyl group (R) with a less donating phenyl group in the backbone or by replacing $NHCH_3$ (X and/or Y) groups with electron withdrawing OEt groups in the sidearm positions. All of the Ni(II) complexes display two reversible reduction processes. The first event is associated with a ligand-centered reduction, which shifts by 500 mV across the series. The second event is associated with the reduction of Ni(II) to Ni(I), and it shifts 400 mV across the series. A thorough evaluation of the homogeneous HER activity of the six Ni(II) complexes revealed three of the complexes follow a ligand-assisted metal-centered process during catalysis, while other three complexes follow a ligand-centered process. This observation is supported by differences in the kinetic isotope effect between the two groups of complexes. All complexes had turn over frequencies exceeding $42,000\text{ s}^{-1}$, and the Faradaic efficiencies ranged from 75-95% over 2 hours of controlled potential coulometry. Reducing the basicity of the ligand makes it less favorable to protonation and lowers the HER activity of the complex. The heterogeneous HER activity the Ni(II) complexes were evaluated on three different supports. First the complexes were drop cast on a glassy carbon electrode to make thin films and their HER activity evaluated at a current density of 10 mA/cm^2 in $0.5\text{ M H}_2\text{SO}_4$. The catalyst with at least one $NHCH_3$ group in sidearm position displayed lower overpotentials (400 mV for methyl backbone and 520 mV for phenyl backbone) than the ligands containing OEt groups in both sidearm positions.³ Finally, we evaluated the HER activity of the best catalyst, NiATSM (R= CH_3 and X=Y= $NHCH_3$), on two additional carbon supports, carbon paste and pencil. We found that NiATSM displays a higher overpotential on carbon paste ($\eta = 500\text{ mV}$) compared to glassy carbon. Whereas the overpotential on cheap disposable pencils ($\eta = 400\text{ mV}$) is compared to the more expensive glassy carbon electrode ($\eta = 400\text{ mV}$). Etching of the pencil surface by an acetone soak further reduces the overpotential of NiATSM by 50 mV.⁴



References:

1. Zhu, J.; Hu, L.; Zhao, P.; Lee, L. Y. S.; Wong, K.-Y., Recent advances in electrocatalytic hydrogen evolution using nanoparticles. *Chemical Reviews* **2019**, *120* (2), 851-918.
2. Cheng, N.; Stambula, S.; Wang, D.; Banis, M. N.; Liu, J.; Riese, A.; Xiao, B.; Li, R.; Sham, T.-K.; Liu, L.-M.; Botton, G. A.; Sun, X., Platinum single-atom and cluster catalysis of the hydrogen evolution reaction. *Nature Communications* **2016**, *7* (1), 13638.
3. Paudel, M., Manuscript under preparation.
4. Paudel, M.; Daniels, B.; Arts, A. M.; Gupta, A.; Kalbfleisch, T.; Hofsommer, D. T.; Grapperhaus, C. A.; Buchanan, R. M.; Gupta, G., Unravelling the potential of disposable and modifiable pencils as catalyst supports for hydrogen evolution reaction. *New Journal of Chemistry* **2022**.