

Le Coq de Boisbaudran award

SOLVOMETALLURGY FOR RARE EARTHS

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Solvometallurgy is the extraction of metals from ores, extractive waste, industrial process residues, production scrap and urban waste using non-aqueous solutions.¹ Solvometallurgy differs from hydrometallurgy by the absence of a discrete water phase. In this lecture, the principles of solvometallurgy and its application to the extractive metallurgy of rare earths are presented.

An excellent example for illustrating the potential of solvometallurgical processes is the use of the functionalised ionic liquid betainium bistriflimide, [Hbet][Tf₂N], to recover rare earths from fluorescent lamp phosphor waste and end-of-life permanent magnets. [Hbet][Tf₂N] can selectively dissolve the red phosphor Y₂O₃:Eu³⁺ (YOX) without affecting the other components in the waste fraction.² Of particular interest is the possibility to dissolve Y₂O₃:Eu³⁺ (YOX) without bringing the halophosphate phosphor in solution. The YOX phosphor is rich in the critical elements yttrium and europium and represents more than 70% of the intrinsic value of the lamp phosphor waste. After dissolution, europium and yttrium can be recovered from the ionic liquid phase by precipitation of a mixed yttrium-europium oxalate. At the same time, the ionic liquid is regenerated. By calcination, the oxalate can be transformed into Y₂O₃:Eu³⁺ with the same luminescence properties as a new batch of the lamp phosphor. Oxalic acid is the only chemical that is consumed in this cyclic process. A process based on the leaching of (microwave) roasted NdFeB magnets in [Hbet][Tf₂N] was developed.³ The special thermomorphic properties of the [Hbet][Tf₂N]–H₂O system cause the mixture to be homogeneous during leaching at 80 °C (temperature above the cloud point temperature) and biphasic when cooling back down to room temperature. The formation of a biphasic system induces metal separation where iron(III) goes to the ionic liquid phase and the rare-earth ions and cobalt(II) ions to the water phase with high separation factors.

Non-aqueous solvent extraction with two immiscible organic phases can offer some advantages compared to extraction from aqueous solutions. For instance, the distribution coefficients are often different from those for extraction from water, and this can lead to enhanced selectivities for separation of mixtures of metals ions. Several examples of non-aqueous solvent extraction processes have been developed, both for intragroup separations of rare earths and for separation of rare earths from transition metals.⁴⁻⁶ The most promising systems are based on the use of ethylene glycol as the more polar phase. In several cases, the separation efficiencies are much better than for the corresponding aqueous systems.

References

- 1 K. Binnemans and P.T. Jones, *J. Sust. Metall.* **3**, 570–600 (2017).
- 2 D. Dupont and K. Binnemans, *Green Chem.* **17**, 856–868 (2015).
- 3 D. Dupont, K. Binnemans, *Green Chem.* **17**, 2150–2163 (2015).
- 4 N.K. Batchu et al., *Sep. Purif. Technol.* **174**, 544–553 (2017).
- 5 N.K. Batchu et al., *RSC Adv.* **7**, 45351–45362 (2017).
- 6 Z. Li, X.H. Li, S. Raiguel, K. Binnemans, *Sep. Purif. Technol.* **201**, 318–326 (2018).

Plenary lectures

THE EVOLVING LOW OXIDATION STATE CHEMISTRY OF THE RARE-EARTH AND ACTINIDE METALS

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One of the fundamental aspects of the chemistry of any element is the number of oxidation states that are available to do productive chemistry in molecular complexes. This feature is so critical to the chemistry of each element that the limits of oxidation states have been probed extensively for decades. The redox tables of textbooks summarize the well-established results. Surprisingly, in the past few years, the redox chemistry for the rare-earth metals and the actinides has changed substantially. Molecular complexes containing new oxidation states have been discovered which appear to have a new type of electron configuration. By 2016, studies of these unexpected new oxidation states led to a coherent set of generalizations that explained the synthetic and structural bases of their discovery [1,2]. This talk will describe the latest results in the new oxidation state chemistry which show that the 2016 generalizations need to be modified as the redox chemistry of these metals continues to evolve.

References

1. W. J. Evans, Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States, *Organometallics* 35 (2016) 3088-3100.
2. D. H. Woen, W. J. Evans, Expanding the +2 Oxidation State of the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes, in: Bünzli, J.-C. G. and Pecharsky, V. K., *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier Science, B.V., Amsterdam, 2016, Vol. 50, Ch. 293, pp. 337-394.

UPCONVERSION SUPER DOTS FOR BIOPHOTONICS AND NANOPHOTONICS APPLICATIONS

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Doping is the key to the new design of materials towards achieving enhanced performance and untapped properties. The restraint of ‘concentration quenching’, where having too many emitters too close to each other leads to a quenching of the overall luminescence, has been long challenging the field of optical luminescent materials.

In my talk, I will illustrate the mechanism, and showcase new strategies that bypass the concentration quenching effect in highly doped luminescent nanoparticles, which now starts to advance the field of luminescence nanomaterials. A broad range of new design strategies and controlled synthesis to enable high doping concentrations will be discussed. We call this new library of highly doped luminescent nanoparticles “Super Dots”. The particular emphasis of my talk will be on the new optical properties and their superior performance in a wide range of emerging applications, including single molecule sensing, colour tuning, optical multiplexing, lasing, and super resolution nanoscopy.

I will then showcase our studies around time-resolved photonics devices and ultra-bright Super Dots [1,7], which has further enabled time-domain multiplexing technology of τ -Dots [2,3], controlled synthesis of Hyper Dots [5], low-power high-contrast super resolution microscopy [6,11], and discovery of surface phonon assisted enhancement of Thermal Dots [8]. To know more about the many exciting opportunities in nanophotonics and biophotonics, raised by upconversion nanoparticles, please choose a topic of interest and read one of our review papers [4, 9, 10, 12, 13].

References

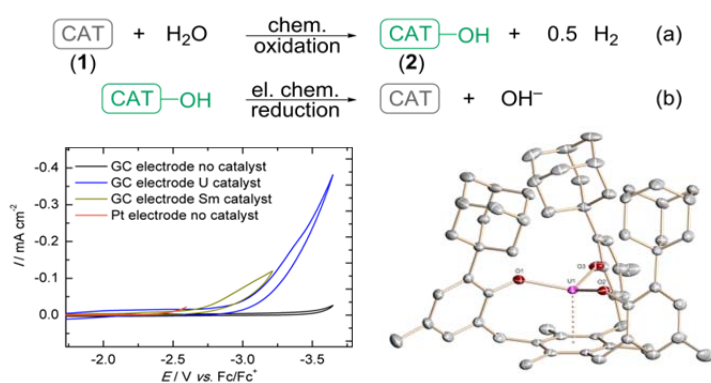
- [1] Zhao J, et al, Nature Nanotechnology, 8, 729-734 (2013),
- [2] Lu Y, et al, Nature Communications, 5, 3741 (2014),
- [3] Lu Y, et al, Nature Photonics, 8, 32-36 (2014),
- [4] Zhou B, et al, Nature Nanotechnology, 10 (11), 924-936 (2015)
- [5] Liu D, et al, Nature Communications, doi: 10.1038/ncomms10254 (2016),
- [6] Liu Y, et al, Nature, doi: 10.1038/nature21366 (2017)
- [7] Wang F, et al, Light: Science & Applications, doi: 10.1038/lsa.2018.7 (2018)
- [8] Zhou J, et al, Nature Photonics, doi: 10.1038/s41566-018-0108-5 (2018)
- [9] Jin D, et al, Nature Methods, doi: 10.1038/s41592-018-0012-4 (2018)
- [10] Wen S, et al, Nature Communications, doi: 10.1038/s41467-018-04813-5 (2018)
- [11] Chen C, et al, Nature Communications, just accepted (2018)
- [12] Lin G, et al. Chem, doi: 10.1016/j.chempr.2018.01.009 (2018)
- [13] Zhou J, et al. Small, doi: 10.1002/sml.201801882 (2018)

Electrocatalytic Production of H₂ from Water With f-Element-Based Molecular Catalysts

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Research on renewable energies and energy storage, such as H₂ production from H₂O, has become a key challenge for our society. The low efficiency of conventional H₂O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium (²³⁸U, DU), uranium complexes are widely discussed as effective and economic catalysts for stable substrates.



In our previous studies of the uranium-monoarene complex [(^{Ad,Me}ArO)₃mes]U (**1**), unique electrochemical and well defined synthetic behavior were found, rendering trivalent **1** a perfect candidate for electrocatalysis.

Indeed, the mesitylene-anchored tris(aryloxy) uranium coordination complex **1** (see figure above) was found to be the first molecular uranium catalyst for electrocatalytic H₂ production.^[1] Utilization of **1** during H₂O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance of the reaction by three orders of magnitude. Isolation of key intermediates, such as the rare U(IV) hydroxide and the U(V) oxide as well as *in situ* EPR experiments allowed to determine the reaction mechanism of H₂O reduction with low valent U(III).^[2] In collaboration with the Evans' group, this reactivity also has been studied in a series of lanthanide complexes [(^{Ad,Me}ArO)₃mes)Ln] (**2-Ln**), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the lanthanide ion. The results suggest a distinctively different reaction mechanism that involves divalent Ln species.^[3]

References

1. D. P. Halter, F. W. Heinemann, J. Bachmann, K. Meyer, "Uranium-mediated electrocatalytic production of H₂ from water", *Nature*, **530**, 317-321 (2016).
2. D. P. Halter, F. W. Heinemann, L. Maron, K. Meyer, "The role of uranium-arene bonding in H₂O catalysis", *Nature Chem.*, **10**, 259-267 (2018).
3. D. P. Halter, F. W. Heinemann, L. Maron, K. Meyer, "Electrocatalytic H₂O reduction with f-elements: Mechanistic Insight and overpotential tuning in a series of lanthanide complexes", *J. Am. Chem. Soc.*, **140**, 2587-2594 (2018).

Clean thermal energy to electricity conversion thanks to rare earth Zintl phases

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Thermoelectric devices for power generation convert thermal energy directly into electrical energy, require minimal maintenance, and can be operated over a large temperature range (room temperature to greater than 1000 °C). These devices are reliable and scalable power sources. There are a wide range of waste heat recovery applications, including automotive, solar renewable energy, and industrial processes. Zintl phases have been identified as a classification of compounds that provide efficient thermoelectric properties with the discovery of a high figure of merit, zT , at high temperatures for $\text{Yb}_{14}\text{MnSb}_{11}$ [1]. While the 2+ rare earths are expected to substitute into existing Zintl structures, the 3+ rare earths add additional complexity and allow for fine tuning and optimization of properties [2]. The crystal chemistry and structure-property relations of these new compounds will be highlighted along with a vision towards further optimization and other relevant applications [3].

References

- [1] S. M. Kauzlarich, S. Brown, G. J. Snyder, “Zintl phases for thermoelectric devices”, *Dalton Transactions* (2007) 2099-2107.
- [2] N. Kazem, S.M. Kauzlarich “Thermoelectric Properties of Zintl Antimonides” in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 50, Ch. 288, J.-C. G. Bünzli, V. K. Pechardky, Eds, Elsevier B.V., Amsterdam: (2016), p. 177-208.
- [3] Y. Hu, C.-W. Chen, H. Cao, F. Makhmudov, J. H. Grebenkemper, M. N. Abdusalyamova, E. Morosan, S. M. Kauzlarich, “Tuning Magnetism of $[\text{MnSb}_4]^{9-}$ Cluster in $\text{Yb}_{14}\text{MnSb}_{11}$ through Chemical Substitutions on Yb Sites: Appearance and Disappearance of Spin Reorientation”, *Journal of the American Chemical Society* 138 (2016) 12422-12431.