

The contribution of coordination chemistry to electrochemical energy storage: some failures and successes

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Porous coordination polymers (also quoted Metal-Organic Frameworks, MOFs) were primarily investigated for their sorption/desorption properties, and found to be promising candidates for various applications including gas storage and capture (e.g. H₂ and CO₂, respectively), fluid separation, controlled drug release, and so on. More recently, this class of materials, together with non-porous coordination polymers, were also considered in the field of electrochemical energy storage, notably in secondary batteries such as Li-ion batteries. Electrodes of Li-ion batteries are complex, multiscale composite systems. Apart from the redox active material that stores and releases charges, other components of the electrodes which are present in a lower amount (conducting additive, binder, possibly coating) are also critical to achieve high performance. In the last years, we get interest in taking advantage of the characteristics of the coordination bonds (moderate strength, reversibility) and coordination networks (versatile composition, porosity, flexibility) to integrate such solids in electrodes for Li (or other alkali)-ion batteries.

Two approaches will be discussed:

(i) The use of coordination compounds as redox-active materials. We are particularly interested in the combination of both organic and inorganic redox active units in the same solid (typically ketone/phenolate and Fe³⁺/Fe²⁺, respectively), in order to achieve suitable charge storage performance and potentially good electron transport properties. The synthesis of such materials will be presented, using either direct synthesis routes¹ or post-lithiation.² Through a combination of characterization tools, including X-ray diffraction (XRD) and ⁵⁷Fe Mössbauer spectroscopy, we will first describe the as-synthesized state of these solids, especially focusing on the accurate determination of the oxidation state of each component, and then study their evolution upon electrochemical driven redox processes.

(ii) The use of coordination compounds as coating and binding materials for silicon electrodes. Silicon is indeed considered as a very promising negative electrode material for next generation Li-ion batteries, as its full reduction to Li₁₅Si₄ offers a ~10 times higher electrochemical storage capacity than standard graphite. Nevertheless, its practical use is hampered by the huge volume change associated with the redox reaction, which leads to electrodes damage and ultimately very rapid capacity fading.³ We attempted to address this issue by developing a MOF coating on Si electrodes, which can potentially act as artificial passivation layer,⁴ as well as through the development of new amorphous coordinatively reticulated binders, which are made of hydrophilic organic polymers and metallic salts.⁵ By combining various experimental techniques (infrared spectroscopy, powder XRD, solid state NMR, scratch tests, SEM- and STEM-EDX analyses, solid state electrochemistry,...) we will show how the formation of coordination networks, either between the Si particles or at their surfaces, impacts on the mechanical properties of the electrodes, on their resilience toward electrochemical cycling and ultimately on their electrochemical energy storage performance.

¹ a) H. Mkhadder et al., *Dalton Trans.* **2021**, 50, 13399; b) M. Denis et al., *Inorg. Chem.* **2022**, 61, 9308; c) N. Gedikoglu et al., *J. Mater. Chem. A.* **2023**, 11, 23909; d) S. De et al., *J. Mater. Chem. A* **2023**, 11, 25465.

² M. Denis et al., *Mol. Systems Des. Engin.* **2023**, 8, 1030.

³ T. Devic et al., *ACS Energy Lett.* **2019**, 4, 550.

⁴ N. Kana et al., *ACS Applied Energy Mater.* **2023**, 6, 9218.

⁵ a) D. Mazouzi et al., *Electrochem. Acta.* **2019**, 304, 495; b) L. Huet et al., *Small Methods* **2022**, 2200827; c) L. Huet et al., *ACS Applied Mater. Interfaces* **2023**, 15, 15509; d) L. Huet et al., *Energy Techno.* **2023**, 2201483.