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Previews

Precision intercalation chemistry: The next step for battery development?

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Just because an intercalated atom can squeeze into a host material doesn't mean the resulting properties are as anticipated or desired—strain and distortion of the host material during intercalation complicates prediction. Here, a recent study by Banerjee and colleagues at Texas A&M University is highlighted, introducing protecting groups that enable specific site-selection for precision intercalation chemistry.

It has long been known that lithium (Li) ion insertion into host materials can be leveraged for energy storage. Nowadays, ubiquitous use of portable electronics relies on rechargeable battery function. With ever-increasing demand for electrification of the entire transportation infrastructure, efforts are constantly underway to develop high-performance, cost-effective, and environmentally friendly battery electrode materials. Achieving high degrees of Li insertion into an electrode material would seem a logical way to increase battery capacity and performance. However, higher degrees of Li ion storage invariably induce large amounts of disorder into a host structure, which complicates analysis, destabilizes material integrity, and makes it challenging to pin down the sites being filled by Li ions at high depths of discharge. A key question in this area is how to analyze specific ion host sites independently and to thereby implement materials design, taking into account the entire range of Li occupancies within the structure.

Notwithstanding the impressive body of work in the realm of intercalation chemistry, selective intercalation into specific ion sites remains scarcely realized. Though it is well known that many structures exhibit multiple host locations, deconvolution of these sites and associated ion pathways is a daunting task. Multi-electron or multi-ion intercalation reactions into a single lattice pose a critical problem: strain and distortion of the host material during intercalation complicates analysis.[1] At high degrees of lithiation (deep discharge), precise structural analysis becomes difficult in compounds with multiple potential host sites.

A solution to this problem may lie in implementing a strategy that has long been in play for organic chemists: introducing protecting groups. Protecting groups in organic chemistry are used to isolate a specific functional group on a molecule from reaction conditions that affect other regions of the structure. Recently, the Banerjee group at Texas A&M University has implemented an analogous technique for insertion chemistry.[2] The protecting groups utilized are transition metal atoms that selectively occupy specific crystallographic sites. Li ions, having less affinity than the transition metal species, find alternate pathways and sites inside an existing structure.

Of the many materials available for studying insertion chemistry, V_2O_5 is a particularly intriguing option. Multi-electron redox processes at the V centers, as well as an ability to reversibly host ions with good stability in a variety of interstitial sites, make this structure a logical candidate for probing the effect of intercalant ordering. Simply put, there are enough sites in the structure for multiple guest ions to occupy unique crystallographic locations. Full intercalation of Li into V_2O_5 will produce $Li_2V_2O_5$; however, structural distortion in this composition makes detailed analysis of Li ion locations difficult.[3] This disorder is a primary motivator for protecting group development.

Choosing the appropriate atoms to use as crystallographic site protecting groups requires careful consideration of a variety of properties. Ionic radius and hardness of the intercalated species; size, coordination, and accessibility of available sites; anion lattice polarizability and transition metal redox capabilities; all these factors and more contribute to where guest atoms will reside. For a protecting group application, it is essential that elements have a unique preferential location in the crystal structure and that they outcompete the intercalated Li ions for that site. With these considerations, Handy et al. have developed a strategy to selectively isolate specific Li ion sites and infer specific diffusion pathways from this analysis.[2] They do this by the pre- and co-intercalation of Cu and Ag ions into ζ-V_2O_5 at different stoichiometries.

The protection of lower-energy interstitial sites with Cu and Ag intercalants allows the observation of Li incorporation into four distinct crystallographic sites in the

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https://doi.org/10.1016/j.matt.2023.03.008

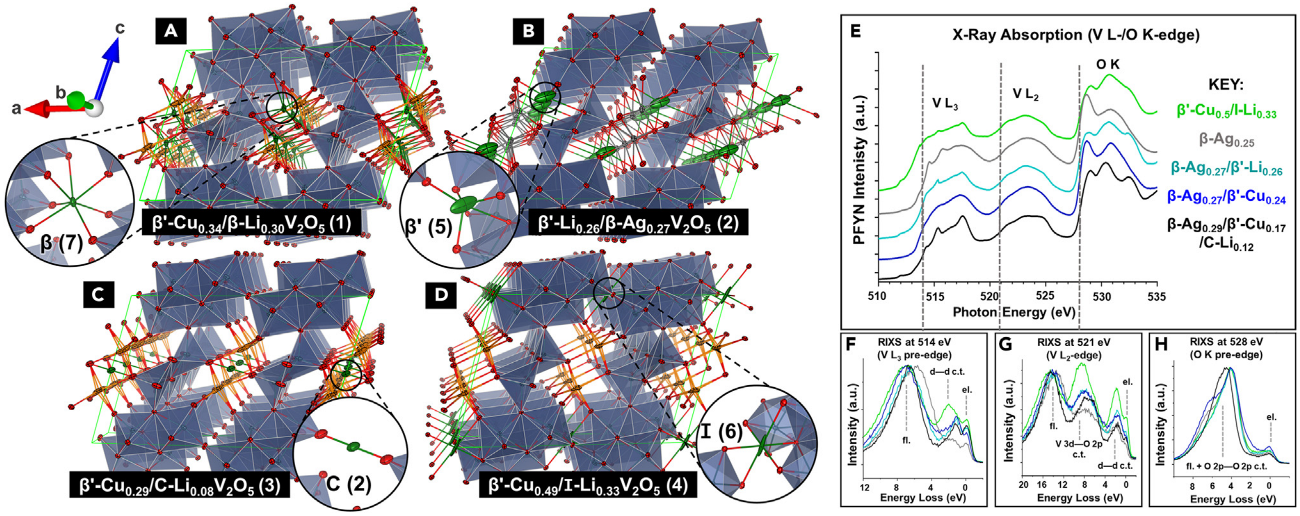

Figure 1. Site-selective occupation of Li ions within the V$_2$O$_5$ crystal structure

Li occupation in the β (A), β′ (B), C (C), and I (D) sites in ζ-V$_2$O$_5$ is pictured. XAS spectra of V L$_2$, V L$_3$, and O K edges for five intercalant concentrations are shown (E). RIXS spectra for the V L$_3$ (F), V L$_2$ (G), and O K (H) edges are also pictured. Reproduced with permission from *Matter*, 2023.[2] Copyright 2023 Elsevier.

ζ-V$_2$O$_5$ lattice. Li can be preferentially inserted into these four sites using a combination of of solid-state and topochemical lithiation methods. These sites, denoted as β (7 coordinate), β′ (5 coordinate), C (2 coordinate), and I (6 coordinate) are visualized in Figures 1A–1D; they can be accessed through the described methods including topochemical single-crystal-to-single-crystal transformations, which have emerged as a means of mapping entire atomic diffusion pathways traversed by Li ions.[4] Formation of β′-Cu$_{0.34}$/β-Li$_{0.30}$V$_2$O$_5$ is accessed through a solid-state reaction with Li$_2$CO$_3$, Cu metal, and α-V$_2$O$_5$. Swapping the Cu precursor for Ag in a similar solid-state synthesis allows incorporation of Li into the β′ site, with a stoichiometry of β′-Li$_{0.15}$/β-Ag$_{0.29}$V$_2$O$_5$. Topochemical reaction with *n*-butyllithium and pre-intercalated Ag leads to similar site preference and a stoichiometry of β′-Li$_{0.26}$/β-Ag$_{0.2}{}^{7}$V$_2$O$_5$.

However, with pre-intercalation of Cu into V$_2$O$_5$ β′ site, access to the β site for Li ions is impeded. Thus, other crystallographic sites are occupied. For lower concentrations of Cu, the Li ions are pushed to a different site in the main ion diffusion channel. In the β′-Cu$_{0.29}$/C-Li$_{0.08}$V$_2$O$_5$ configuration, the Li ion occupies an unusual 2-coordinate site (C-site) in the middle of the tunnel due to coulombic repulsions from the Cu ion in the β′ site. Further Cu incorporation causes complete removal of the Li ion from the main diffusion channel. Instead, it occupies an octahedral intralayer site (I). Li occupation in this location is previously unreported due to the instability of this intercalation site in V$_2$O$_5$, which is caused by a lack of structural integrity at the high lithiation concentrations required to access this site. However, structural support provided by Cu atoms in the β′ position allows the isolation of β′-Cu$_{0.49}$/I-Li$_{0.33}$V$_2$O$_5$.

Co-intercalation of Ag and Cu into the V$_2$O$_5$ structure highlights preferential ordering of Ag at the β site and Cu at the β′ site. Like the results seen from low Cu concentrations, lithiation in these materials demonstrates Li incorporation into the central channel. The resulting structure has a composition of β′-Cu$_{0.17}$/β-Ag$_{0.29}$/C-Li$_{0.12}$V$_2$O$_5$, representing the first reported quintenary V$_2$O$_5$ bronze.

Identification of these four distinct Li sites is done via magic angle spinning (MAS)-NMR; four distinct resonances for each species suggest unique crystallographic locations. X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) also help to identify site-selective positioning of Li ions. Modification of bond covalency and electronic structure with respect to the Li site occupied is evident through these analyses (Figures 1E–1H).

The work by Handy et al. calls attention to the inherent problem that high levels of Li intercalation are often followed by destabilization of the host lattice. Such an effect complicates structural analysis; practically, it can also be detrimental to the reversible intercalation process. Isolating specific crystallographic locations of Li in V$_2$O$_5$-based structures invites further research into ion pathways in intercalation compounds. Generalizing this approach to the plethora of cathode materials available as insertion hosts could generate a substantial wealth of information that can be used for rational atomistic design of electrode materials.

Selective intercalation through protecting groups may also find relevance in the field of beyond Li-ion battery (BLIB) research. Such a method could be used to determine preferential ordering of other ions, such as Na^+, K^+, Mg^{2+}, Al^{3+}, and others, which are important ions to consider for BLIB development. Lattice changes induced from these guest species tend to be more drastic than from Li, due to the larger size and/or charge introduced into the lattice.[5] Due to greater lattice strain imparted from these ions, understanding possible ion diffusion pathways in these systems could be of even greater importance than understanding Li transport.

Applying a protecting group method could also be used to stabilize solid-electrolyte interphase (SEI) layers that form on battery electrodes during the cycling process. These layers are known to have deleterious effects on battery performance, and yet many aspects of their formation remain poorly understood. They are particularly problematic for solid-state batteries, which cannot accommodate significant electrode morphology changes while retaining functionality. Blocking specific interfacial sites that may lead to irreversible SEI formation could lead to less capacity loss during battery cycling and be an important step for solid-state battery realization.

Use of a protecting group method to target Li incorporation into specific sites can reasonably be expected to shed light on Li diffusion in a variety of materials. Insights into lattice (de)stabilization with respect to ion incorporation indeed has implications for all of energy storage and will provide atomistic design rules needed to accommodate and/or mitigate ion-insertion-driven structural transformations that are at the heart of many degradation mechanisms.

ACKNOWLEDGMENTS

L.W.B. acknowledges support from the NSF under award numbers CHEM 2203926 and CBET 2016191. L.W.B. would also like to acknowledge the Sloan Foundation through an Alfred P. Sloan Research Fellowship in Chemistry and the Dreyfus Foundation through a Camille Dreyfus Teacher-Scholar Award.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Granular origami

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A sprinkling of dust may not give flight to its target like fictional characters, but with the right balance of elastic and cohesive interactions, a flexible sheet will bend and warp, enveloping granular matter on contact. In this issue of *Matter*, Guerra and Holmes explore a mechanism that is a new "twist" on classic approaches that deform elastic sheets into wrinkled or crumpled membranes.

Wrinkling, capillarity, aggregation. These words inspire simultaneous notions of simplicity and complexity. To a mechanician or materials scientist, each evokes the involvement of energy, force, and length scales at an interface, which are classical and easily identified yet also potentially geometrically complex. Let us consider a few "simple" soft matter and interfacial science scenarios.

Continuous solid-solid interfaces (Figure 1A): Combine a geometric constraint and a compressive stress at a solid-solid interface of two laminated films, and the result is a geometric change with a detectable length scale. This length scale defines a characteristic wavelength and amplitude of spontaneous wrinkles, forcing what seemingly should be a planar geometry

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https://doi.org/10.1016/j.matt.2023.03.011