

Ionic gating drives correlated insulator-metal transition

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The transport of matter is central to modern condensed-matter physics. Electronic transport is vital, enabling computer communication and playing a key role in interrogating material responses. A primary classification of matter is into metals, semiconductors, and insulators, based on their electronic conductivity, and electronic considerations underpin much of the current nanomaterials revolution (1). Transport anomalies have captured the imagination of scientists, engineers, and the public, from colossal (2) and giant (3) magnetoresistance and integer (4) and fractional (5) quantum Hall effects to topological insulators (6, 7) and semimetals (8). In particular, strongly correlated electronic states offer special opportunities for manipulating transport, including superconductivity and charge-ordering transitions, and perhaps enabling practical quantum computing (9). The Mott transition holds a unique place in modern electronic transport research. The Mott state (10) is an enigma—a system that naïve analysis suggests would be metallic. In a Mott insulator, nearby atoms appear to have electronic states at similar energies, suggesting easy charge flow. However, because the states are spatially localized, when an additional electron is added the energy cost is high, and the electron transfer is inhibited. This is related to “Coulomb blockade” (11) and is a type of strong electronic correlation that confers new ways of controlling electronic transport. It is now possible to envision new electronic devices (12) based on forming and disrupting the Mott insulating state, and this has been termed “Motttronics.”

Beyond electronic considerations, changes of composition via ion transport are of great interest as well. The flow of ions through membranes enables fuel cells, electrochemical devices that convert fuels to electricity without combustion. Batteries also involve coupled reduction and oxidation reactions that produce voltage and current in response to electrochemical differences. State-of-the-art rechargeable batteries (13, 14) rely on ion motion (often Li) from a state that holds high-energy electrons [e.g., $\text{Li}^+ + \text{e}^- + \text{C}_6$ (graphite) $\rightarrow \text{LiC}_6$ at the anode during charging] to one that stabilizes electrons at lower energy (e.g., $\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{e}^- + \text{CoO}_2$ at the

cathode during charging). One key challenge for batteries is the change in volume as Li ions are gained and lost; significant research currently examines these processes in situ and in operando to develop the next generation of batteries (15). More recently, flow batteries (16) are attracting great attention, combining the molecular electrochemistry of fuel cells with the reversibility of batteries.

Materials that exhibit concurrent electronic and ionic conductivity are relatively rare, with CeO_2 serving as a notable example (17). In addition, phenomena such as electromigration represent another coupling between electronic and ionic transport phenomena.

In PNAS, Sun et al. (18) describe a fascinating coupling between ionic and electronic conductivity. They demonstrate that by driving Li ion motion into and out of a perovskite oxide the material is transformed from a small band gap conductive semiconductor SmNiO_3 to a correlated Mott insulator Li-SmNiO_3 (Li-SNO). Pieces of this puzzle have emerged in the literature recently, including experimental investigations (19) of H-SNO and theoretical analyses (20) of SNO and Li-SNO, but this study provides a deeply integrated view of the relationships between ionic transport and electronic conductivity, motivating future investigation and development.

This study (18) draws on multiple state-of-the-art investigative techniques to make the case that Li transport induces a dramatic change in electronic transport. The team presents changes in resistivity versus Li concentration. As SNO is lithiated (ref. 18, figure 1), its resistivity rises by seven orders of magnitude. Another important finding is the gentle change of ionic conductivity with temperature. Arrhenius analysis suggests a small 0.24-eV barrier to Li motion. The team also provides interesting insights into the structural changes that accompany Li incorporation. The film appears to expand by only 9% upon full lithiation. Furthermore, theoretical and X-ray diffraction analysis suggest that octahedral rotations (ref. 18, figure 1C) accommodate the Li, facilitating its motion from cell to cell. The Li appears to move from one octahedron to

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another based on favorable rotations that bring the next O to a convenient spot, so that the Li hop is short and with low energy barrier, rationalizing the T dependence. This rotational accommodation and small volume change imply that the material could survive many cycles without damage. Furthermore, the team uses XANES spectroscopy to note distinct changes in the electronic properties of Ni, including the change of oxidation state from Ni^{+3} to Ni^{+2} upon lithiation. Therefore, these advanced spectroscopic techniques buttress the view that lithiation is stabilizing additional electrons on the Ni ions but also leading the resulting Li-SNO material into a Mott insulating state.

Relationship to Li Transport in Batteries

Many of the most important rechargeable battery anodes are transition metal oxides of Co or Fe. Li-SNO could also act as an anode, stabilizing low-energy electrons after discharge, but Ni brings significant additional interest and functionality. Because Ni is fairly electronegative, there is considerable debate about whether the O anions all get two additional electrons (O^{2-}), or whether Ni can steal some electrons, putting holes on the O. It is likely that the truth lies somewhere in between, but this issue is relevant because the enhanced covalency (Ni–O bonding with charge sharing) opens new opportunities for electronic transport control beyond that of other transition metal oxides.

Relationship to Intercalation

The term “intercalation” originates from the process of modifying a calendar by inserting days, weeks, or months to synchronize it with the Earth’s solar orbit or for other purposes. Here, intercalation refers to ion migration into materials without significant disruption of the underlying structure. The insertion of ions into graphite has led to rich discoveries. Intercalation is presently experiencing a renaissance, as ion insertion can lead to gentle exfoliation and the production of low-dimensional nanomaterials.

Relationship to Ion Transport in Perovskites

The authors suggest reversible diffusion of Li ions through the cubic perovskite structure without disrupting it permanently. Such diffusion is known for H in perovskites (21), with some oxide perovskites serving as effective proton conductors or mixed ion–electron conductors. Li migration in perovskites has been noted, especially in A-site deficient perovskites (22). There is also some evidence that H incorporation can lead to material degradation—certainly exposure to H_2 is known to lead to hydroxyls and O vacancies, while Li is gentler. An important aspect of this class of systems is the ability to take up a large amount of Li without significant structural degradation or even rearrangement.

Future Questions

Part of the importance of this study is that it suggests future work in so many different yet complementary scientific directions. The experimental and theoretical structural studies as presented are convincing, while raising new questions. Structural and ionic questions include the relationships of Ni oxidation state to cage distortions (e.g., Jahn–Teller effects), the impact of cage

distortions on Li mobility, and the interactions of Li ions and ligand holes on O.

The nature of the correlated electronic state is a continuing challenge. Further electronic investigations could reveal the nature of the strongly correlated states. Surely, more theoretical and experimental work understanding the electronic transport (and its dependence on temperature, electric and magnetic fields, material strain, etc.) can lead to findings of new conductivity anomalies and electronic functionalities. However, in this case, an extra handle is provided in the form of ion concentration, which can be

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tuned via applied voltage. For example, it appears possible that the electronic manifold could go through electronic transitions versus Li concentration, and then the I – V curves could be significantly different for different Li concentration ranges. The reversible entry into a Mott insulator regime is fundamentally interesting. The nature of the strongly correlated state merits investigation beyond the current theoretical treatment. The coupling of this state to ion motions could lead to interesting electron–phonon effects, including T dependence of the band gap.

In the near future, it will be exciting to explore how these functionalities (18) can be harnessed for applications. There will be growing interest in rapid ion redistribution associated with significant conductivity change. In principle, this could lead to history-dependent spatial conductivity patterns, which could enable neuromorphic applications and other systems that require rapidly reprogrammable circuitry. To some extent, the Li–Li interactions (for various applied fields) could enhance the nonlinearity of voltage–conductivity changes, and this remains an interesting open question. It even appears possible that this material and system could lead to gated redox catalysis, when certain electrochemical events turn others on or off via conductivity modulations.

This study by Sun et al. is likely to lead to cross-pollination between researchers interested in transport, electronics, electroceramics, metal–insulator transitions, battery materials, hysteresis, and neuromorphic computing. It serves as an interesting signpost for the high level of understanding of a complex material and its responses while also suggesting many unanswered questions and intriguing potential.

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