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Design and Preparation of Materials for Advanced Electrochemical Storage

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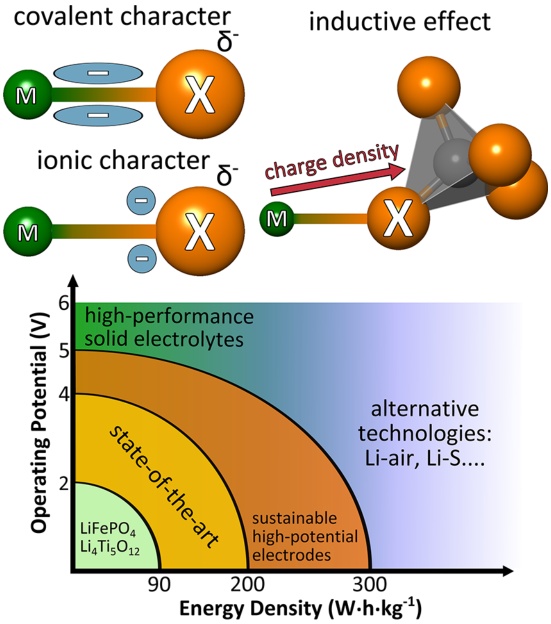
CONSPECTUS

To meet the growing global demand for energy while preserving the environment, it is necessary to drastically reduce the world's dependence on non-renewable energy sources. At the core of this effort will be the ability to efficiently convert, store, transport and access energy in a variety of ways. Batteries for use in small consumer devices have saturated society; however, if they are ever to be useful in large-scale applications such as automotive transportation or grid-storage, they will require new materials with dramatically improved performance. Efforts must also focus on using Earth-abundant and nontoxic compounds so that whatever developments are made will not create new environmental problems.

In this Account, we describe a general strategy for the design and development of new insertion electrode materials for Li(Na)-ion batteries that meet these requirements. We begin by reviewing the current state of the art of insertion electrodes and highlighting the intrinsic material properties of electrodes that must be re-engineered for extension to larger-scale applications. We then present a detailed discussion of the relevant criteria for the conceptual design and appropriate selection of new electrode chemical compositions.

We describe how the open-circuit voltage of Li-ion batteries can be manipulated and optimized through structural and compositional tuning by exploiting differences in the electronegativity among possible electrode materials. We then discuss which modern synthetic techniques are most sustainable, allowing the creation of new materials via environmentally responsible reactions that minimize the use of energy and toxic solvents. Finally, we present a case study showing how we successfully employed these approaches to develop a large number of new, useful electrode materials within the recently discovered family of transition metal fluorosulfates. This family has attracted interest as a possible source of improved Li-ion batteries in larger scale applications and benefits from a relatively "green" synthesis.



1. Introduction

The desire to reduce society's dependence on fossil fuels has made the field of energy storage one of the most important areas of research for the 21st century. Today, the fundamental concept of converting energy from the sun using photovoltaic, photocatalytic, or photosynthetic routes is very well-understood as are the basic principles of electrochemical storage using batteries,[1,2] supercapacitors,[3] and fuel cells.[4] Therefore, the challenge as it stands now is not to understand how to convert and store the energy we will need, but rather, what materials we will use and how they can be produced on a large scale with high-efficiency while still maintaining low-enough costs to ensure their worldwide adoption.[5,6] In addition to the need for more *energy-efficient* processes, there is also a significant demand for new synthetic methods which are *environmentally friendly*.

As with every new technology which begins to enjoy widespread application, it becomes increasingly clear that

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meeting these challenges requires innovation in the design and optimization of new materials. As far back as the 1960s, there was an adage at DARPA that said, "Technology is always limited by the materials available," and this holds true today. This call for new materials has generated a staggering number of papers dealing with the elaboration of better materials for water splitting, photon conversion, or electrochemical storage, but the need to aggressively search for new compounds still exists. Undoubtedly, this drive for new materials, with a broad focus on addressing the issue of electrochemical energy storage, will be of vital importance in the coming years.

In the following, we will discuss the hugely challenging process of creating new insertion electrodes: from the conceptual design and proper choice of chemical elements, through the optimization of the redox properties, and finally to the development of low-temperature synthetic processes that are environmentally sustainable. We will begin by outlining the current state-of-the-art in positive electrodes and identify the intrinsic materials limitations they present. This will be followed by a general strategy for the design of new phases with optimized redox properties with a particular view toward developing new and sustainable reaction pathways. We will then discuss how the rational approach to materials design and synthesis presented has been successfully employed in the context of the recently discovered family of transition metal fluorosulfates. In order to meet the goal of establishing a sustainable-energy economy, the ability of chemists to make use of their "green thumb" to prepare new phases and optimize their synthetic techniques will play a pivotal role.

2. Today's Status in Li-Batteries

The current state-of-the-art for positive electrodes relies on either $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, or $LiMn_2O_4$, with recently discovered polyanionic compounds like $LiFePO_4$ and $LiFeSO_4F$, though not as advanced, poised to play a major role in the near future (see Figure 1). While these phases perform well in practical applications, they are not without their limitations.

$LiCoO_2$, which is the most commonly used positive insertion electrode, has an extremely high theoretical capacity of 274 mA h g^{-1} due to its low molecular weight and with an operating voltage around 4 V displays one of the largest power densities available. Unfortunately, whenever more than 50% of the Li-ions are removed from between the layers, the structure tends to collapse due to a significant electrostatic repulsion between the transition metal polyhedra such that the reversible capacity is typically limited to approximately 150 mA h g^{-1}.[7] To overcome this problem, extensive efforts have been made to partially substitute a fraction of the Co in this phase with Ni or Mn so as to support the structure against decomposition at high potential. This technique has led i) to sustainably reversible capacities of 190 mA h g^{-1} with materials of formula $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ referred to as NMC,[8] ii) the synthesis of Li-rich layered oxides by embedding inactive Li_2MnO_3 component within layered $LiMO_2$ so as to prepare $xLi_2MnO_3\cdot(1-x)LiMn_{0.5}Ni_{0.5}O_2$ composites[9] displaying capacities of 250 mA h g^{-1}, this is the highest ever reported today for any reported Li-based inorganic compounds. Therefore, such materials are still suffering from sluggish kinetics (e.g., power rate capability) and limited cycled life owing to Mn dissolution.

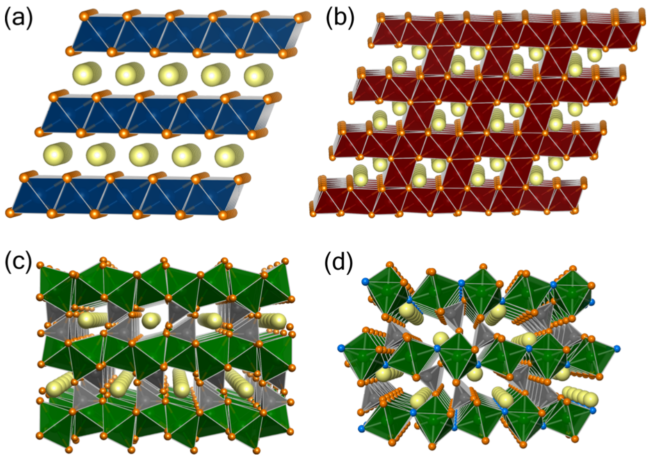

FIGURE 1. Illustration of the crystal structures of the best performing positive electrode materials: (a) $LiCoO_2$, (b) $LiMn_2O_4$, (c) $LiFePO_4$, and (d) the tavorite-phase of $LiFeSO_4F$. The common feature among the four is an open framework structure which allows for facile ionic transport. Li atoms are shown in yellow while the transition metals polyhedra, coordinated by oxygen atoms in orange, for Co, Mn, and Fe are shown in blue, red, and green, respectively.

In contrast, the structure of spinel $LiMn_2O_4$ proves to be much more robust against the removal of lithium, capable of reversibly removing and reinserting upwards of 95% of the theoretical capacity. However, this phase too has stability problems[10] when used in conventional Li-based liquid electrolytes, unless special postprocessing[11] is done to prevent dissolution by trace amounts of HF present in the electrolyte and has a significantly reduced theoretical capacity (148 mA h g^{-1}) compared to $LiCoO_2$. $LiFePO_4$, which has attracted considerable attention in recent years, has a great deal of potential, especially in the area of safe performance, but it cannot fully compete in power density due to its rather low operating voltage. Given these intrinsic limitations, it is

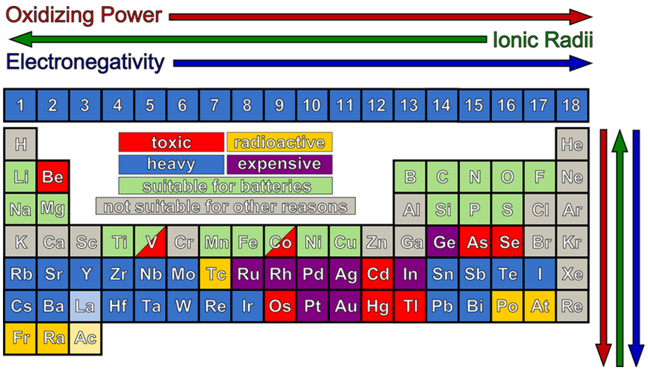

FIGURE 2. Periodic palette available for the design of new electrode materials. The colored squares are excluded due to either their high cost, low availability, toxicity, or radioactivity. This somewhat restricts the elements which are available for the design of new materials, but can be useful in guiding synthetic methods. Note that, despite their toxicity, some transition metals, such as V and Co, are still actively investigated.

clear that the future of electrochemical storage will critically depend on the design and discovery of new materials phases.

A close examination of the common structural features found across these compounds, which are illustrated in Figure 1, reveals an open-channel topology which allows for rapid ionic diffusion and enables cells to be cycled at higher rates for quicker charging or large bursts of power. These channels may result from layers of transition metals (as in $LiCoO_2$), from the packing of transition metal chains (as in $LiFeSO_4F$), or through a coherent network of empty interstitials within a close-packed anion lattice (as in $LiMn_2O_4$). While there are thousands of compounds which could meet this simple structural requirement, materials for energy applications must be held to a higher standard given that they will be distributed on a global scale. This implies that, beyond structure, composition, and morphology, the environmental impact of new materials must also be taken into account in designing new electrodes. As a consequence, new electrodes must consist of materials that are naturally abundant and non-toxic elements in order to meet the requirements for economic feasibility and environmental neutrality.

3. Fundamental Principles of Design

At the materials level, costs are principally determined by reaction temperature and pressure, abundance of the starting reagents, and the performance of the final device. As a consequence, using precious metals such as Ag, Au, and Pt (purple in Figure 2) would drastically increase the total cost of each cell and are simply not practical, while the toxicity of elements like Be, Hg, As, and Se (red in Figure 2) means they would never be safe enough to distribute in the volumes necessary. Simultaneously, concerns about the limited abundance of rare earth metals like La, Ce, and Pr in addition to their high molecular weights like the 4d and 5d transition metals (gray in Figure 2), which drastically reduces their theoretical capacities make them impractical. Just these few criteria already eliminate a significant portion of the periodic table as illustrated in Figure 2, and leaves chemists with a somewhat limited number of elements to work with. Nevertheless, these few elements still have the potential of producing a huge number of combinations, and sustainable 3*d* transition metals such as Mn ($LiMn_2O_4$), Fe ($LiFePO_4$, Li_2FeSiO_4), and even Ti (TiO_2, $Li_4Ti_5O_{12}$) have received a great deal of attention as candidates to replace the more expensive and somewhat toxic Co- or Ni-based electrodes.

Thus, the main question which remains is how to identify, among the numerous Fe- or Mn-based phases, the "winning" composition which exhibits not only exceptional performance, but can also be produced in a clean and eco-friendly way. In this pursuit, the periodic table (see Figure 2) acts as an excellent guide in designing compounds, but very often the trends it contains are neglected or forgotten as they have been less explicitly discussed in recent years. To help correct this, in the following we recall the most relevant properties for electrochemical materials.

First, it is well-known that the atomic radii of atoms decreases going from the left to the right and from the bottom to the top of the periodic table. As the radius of the element becomes smaller, the electronegativity and ionization energies correspondingly increase as the positively charged nucleus begins to pull more strongly on the valence electrons. The importance of electronegativity in the context of insertion electrodes is crucial as it determines the ionic/covalent character of the metal−ligand bonds and, as will be discussed in more depth later, is critical for tuning redox potentials. Indeed, the ionization energy is perhaps just as important as it dictates the oxidizing/reducing power of the atom. For example, monovalent ions, M^+, can act as stronger reducing agents than pentavalent ions, M^{5+}, which tend to be more oxidizing, because it is easier to remove electrons which sit farther away from the core and have lower ionization energies. Similarly 3*d* cations which possess the same charge have more oxidizing power from the left to the right of the periodic table, again, due to the atomic radius.

Size effects also play a role in stabilizing high-valence oxidation states by reducing the Coulombic repulsion as evidenced by the fact that V^{5+} is fairly common, whereas Co^{4+} is relatively unstable in air. Perhaps more importantly for the preparation of new materials, the acidic-basic character of oxides can be inferred by knowing that bonds with a

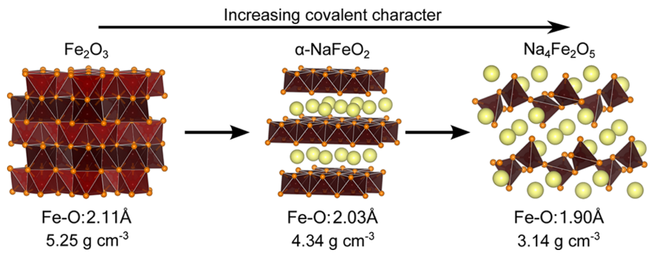

FIGURE 3. Density can be considered an indicator of the covalent and ionic character in materials. In going from a relatively dense oxide like Fe_2O_3 to a layered structured in α-$NaFeO_2$ to a chain structure in $Na_4Fe_2O_5$, the number of Fe−Fe neighbors is reduced. As Fe is replaced by the less electronegative Na, electron density is reintroduced into the bonds and the Fe−O bond length decreases as the orbital overlap increases thereby increasing the covalent character.

higher ionic character, such as Ni−O, tend to be more basic since the highly charged oxygen ions can easily capture protons. In contrast, more covalently bonded oxides, like SiO_2, have a stronger acidic character since the partial charge on the oxygen ions is more polarized toward the transition metal and thereby enables protons to depart more easily.

We also note that the character of bonds (ionic vs covalent) can actually be inferred from the density of a compound. Materials with more ionic metal−ligand bonds tend to have a dense structure and consist of edge- or face-sharing polyhedra, while those with covalently bound metals contain poorly packed structures with corner-shared or isolated polyhedra. This difference in bonding comes as a result of fewer metals atoms of similar electronegativity sitting farther apart from one another and is typified by the series of compounds illustrated in Figure 3.

While we have mentioned that Fe-based materials offer the most significant advantages with respect to environmental and economic considerations, the major difficulty in trying to base next-generation electrodes on the electrochemistry of Fe is the low voltage which is always obtained when compared to other transition metals. The reason for the reduced potential is best understood through examination of the relevant energy levels as illustrated in Figure 4. On discharge of an electrochemical cell (Li inserted into the positive electrode), electrons sitting at the Fermi energy of Li (dashed red line) move through the external circuit to populate the conduction band minimum on the cathode (dashed blue line). The position of these conduction band states, which are typically localized on a transition metal redox center, are effectively determined by the strength of the covalent character of the metal to ligand bonds as reflected in the interatomic distances, short distances imply stronger bonds. In the case of Fe, the states associated with the Fe^{4+}/Fe^{3+} redox couple generally sit too low in energy, which makes them incompatible with traditional electrolytes, while the states for the Fe^{3+}/Fe^{2+} couple are usually too high in energy, giving small potentials,[12] hence the need for a way to modify the position of these states.

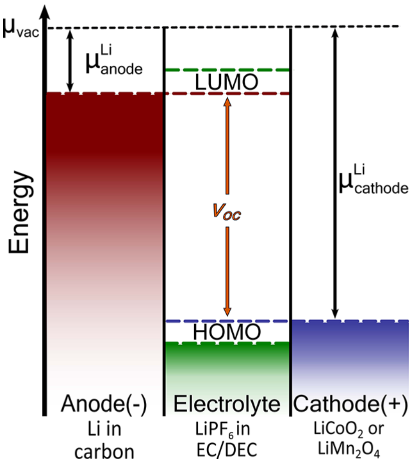

FIGURE 4. Schematic illustration of the energy levels involved in a typical Li-ion electrochemical cell. The dashed red, blue, and green lines correspond to the Fermi energy of Li in the anode, the lowest energy level of the transition metal antibonding states, and a typical placement for the voltage window for the electrolyte, respectively [i.e., the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)]. V_{OC} stands for the open circuit voltage of the cell, and μ is the chemical potential. Note the role of the solid−electrolyte interface is omitted in this figure for clarity. Inspiration for figure taken from ref 6.

A key way to overcome this problem was first introduced when Manthiram and Goodenough investigated Li intercalation in $Fe_2(SO_4)_3$.[13] In this seminal paper, the authors demonstrated that, compared to the 3.0 V found in $Fe_2(MoO_4)_3$ or $Fe_2(WO_4)_3$, the Fe^{3+}/Fe^{2+} redox potential could be increased to 3.6 V in the sulfate homologue. Given that all three compounds possess essentially the same metal to oxygen distances and formal charge, the authors rationalized that this increase was the result of the significantly larger electronegativity of the SO_4 groups increasing the ionic character of the Fe−O bonds. As mentioned earlier, this decrease in covalency reduces the separation between the bonding and antibonding orbitals and translates into a downward shift of the blue line shown in Figure 4 to give an increased cell potential (see Figure 5), which is defined by the difference in energy between the Li_{1s} and the lowest unoccupied 3d metal levels (σ*). Today this idea of exploiting the *inductive effect* of polyanions is well established, and, as shown in Figure 6, the increasing electronegativity of the polyanions has been demonstrated experimentally as an important way to tune redox potentials in a wide variety of systems.

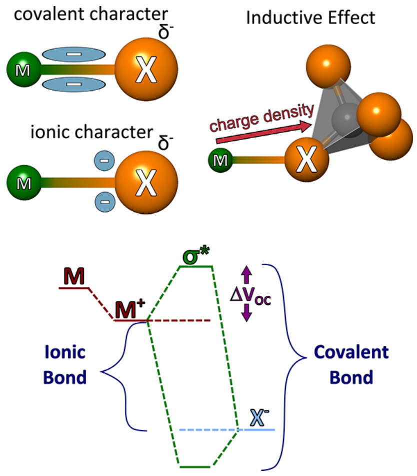

FIGURE 5. Illustration of the two extreme types of bonds typically found in insertion electrode materials. Covalent bonds form when the electronegativity of the metal, M, and the ligand X are approximately equivalent which results in an equal sharing of the electron. Ionic bonds form when there is a significant difference in electronegativity and as a result the electrons tend to localize closer to the most electronegative element. The inductive effect pulls some charge density out of the M–X bonds and allows for a tuning between ionic and covalent character depending on the difference in electronegativity between M and the polyanion. The difference between the energy associated with the stabilization in the two extremes sets the boundary for the maximum amount of tuning to the V_{OC} that can be obtained through structural modification.

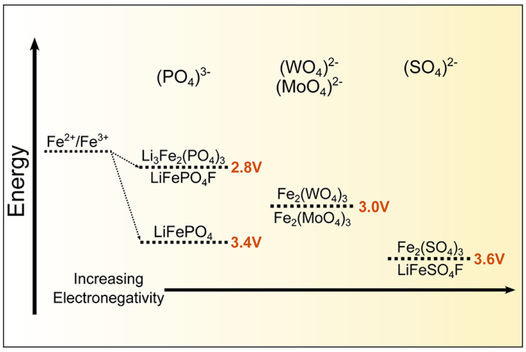

FIGURE 6. The electronegativity of polyanionic groups can be used as a way to directly change the position of unfilled states on the transition metal by reducing the covalency of the M–O bonds.

The very simple way in which the inductive effect alters the iono-covalent nature of the bonds explains why oxide-based insertion electrodes always display a larger potential than the corresponding sulfides, as well as why fluorides show still higher potentials. However, tuning the electronegativity is far from the only method available to tailor the electrochemical performance of a material. The character of bonds is also readily modified through the application of what is commonly called "chemical pressure". When smaller cations are replaced by larger ones in a close-packed structure, the result is a corresponding increase in unit-cell volume as expected from Vegard's law. This elongation of the bond corresponds to a decreased orbital overlap between the transition metals and the surrounding anions, thereby causing the bonds to take on an increasingly ionic nature. This effect is illustrated nicely by the work done by Muraliganth and Manthiram, where substitution of Mn into $LiFePO_4$ produced clear changes in the open circuit voltage as deduced via GITT measurements.[14] A similar effect has also been seen in the Li_2FeSiO_4 family[15] which consists of three different polymorphs, having slightly elongated Fe–O distances, with the long bond showing the highest redox potential. Indeed, inductive effects provide a convenient indicator to gauge the redox properties of an electrode material, yet it is important to remember that the properties of a compound can never be attributed to a single factor. Rather, the properties of a material are governed by a harmonious integration of the atomic structure, the elemental composition, as well as the microstructure and can never be fully understood by considering these facets by themselves.

4. Identifying and Preparing New Phases

Understanding the relationship between the atomic structure of materials and their applications has been a constant driving force in the field of inorganic synthesis and is sure to remain that way for the foreseeable future. With the tools we have just outlined in hand, we can now return to answering the question of how to identify new and promising compositions without testing every conceivable arrangement.

Computational and Theoretical Approaches. Given that the number of potential phases is virtually unlimited and the need is somewhat urgent, high-throughput computational tools for predicting and identifying promising new materials are gaining increasing prominence.[16,17] While still in their early stages, many of these initiatives, which rely heavily on experimental databases, aim to do for solid state chemistry what genomics has done for biology. However, despite the significant efforts that have been devoted to these approaches, there are still very few examples of new compounds which were purely the result of computational prediction (e.g., borophosphates and carbonosilicates[16]). This should serve as an impetus for computational chemists and theorists to continue working to improve their models and intensify their efforts to identify the key parameters that must be incorporated while maintaining close interactions with experimentalists to test and verify their predictions.

In the meantime, it is necessary to rely on the existing materials library, which consists primarily of naturally occurring mineral structures, to guide the discovery of new compounds, with their final preparation heavily dependent on intuition and the ability to manipulate thermodynamics, chemical affinity, and structural considerations. Recently, Long et al. described, through a careful analysis of an experimental database containing more than 3000 crystal structures, a way of exploiting dimensional reduction as a general mechanism for the prediction of new compounds.[18] This formalism explains that metal–anion (M–X) frameworks in a parent compound, MX_x, can be dismantled through reaction with an ionic reagent A_aX to form a family of $A_{na}MX_{x+n}$ compounds with reduced dimensionality. Hence, for numerous three-dimensional (3D) binary phases, one should be able to predict the existence of the 2D, 1D, and 0D homologues. Taking the silicate framework as an example,[16] subsequent additions of $1/2Li_2O$ produces compounds with frameworks of diminishing connectedness starting from corrugated sheets in $Li_2Si_2O_5$ (3D), moving to chains in Li_2SiO_3 (2D), singly connected $[Si_2O_7]^{6-}$ anions (1D) in $Li_6Si_2O_7$, until finally producing discrete molecular $[SiO_4]^{4-}$ tetrahedra (OD) in Li_4SiO_4.

Traditional Synthetic Techniques. Regardless of the aforementioned computational and theoretical approaches, the discovery of new inorganic materials has usually been the result of trial-and-error as solid state chemistry lacks a library of well-known and understood reactions with which to prepare new phases. When dealing with purely organic reactants, it is relatively trivial for modern chemists to prepare new target molecules when one considers the nucleo-(electro)philic character of the reactants in combination with the functional groups on the molecule. Inorganic chemists, in contrast, face significant challenges since traditional ceramic approaches rely solely on the steady-state diffusion of atoms in order to produce the most thermodynamically stable phase. Such approaches, commonly referred to as "shake and bake", have been widely used as a simple way to prepare several functional compounds as well as map out detailed binary, ternary, and quaternary phase diagrams. These phase diagrams are often the initial starting point from which researchers find inspiration by building intuition based around thermodynamic, structural, acid–base character, and bonding considerations. However, if one wishes to avoid getting trapped in the thermodynamic minima, as is a very significant challenge when searching for new materials, new synthetic approaches based on low temperature reactions must be employed.

As is often the case, crises can often give birth to new research directions in science as exemplified by the first oil crisis in 1976, which had a drastic impact on the field of inorganic synthesis with a departure from ceramic to low-temperature approaches or so-called *chimie douce*[19–22] to reduce energy demands. These low-temperature reactions offer many opportunities when compared to the ceramic methods since there are some rules which can be used to guide the design of reactions. These rules dictate that the reaction must preserve a structural relationship between the starting product and the target phase and are more commonly referred to as topotactic reactions. Therefore, the selection of the precursors in *chimie douce* reactions is vitally important and can give some control over the structure that one is attempting to produce. While finding a new material using this technique is often very exciting, it is extremely challenging to understand exactly how the reaction proceeds. Nevertheless, this is an essential part of being able to modify the reaction to become more general so that multiple new phases can be created and their properties determined.

This is best exemplified by the metal–organic hybrid compounds which are made of inorganic polyhedra joined together through organic linkers.[23] Once the importance of the connectivity of the organic linker and its nature were recognized in governing the dimensionality of the packing in the resultant phase, an entire new field of chemistry was unlocked. Because of the richness of carboxylate chemistry, such approaches have rapidly led to a vast array of metal–organic hybrid phases which are well-suited for a variety of applications as their typically porous structures are capable of storing gases like H_2,[24] reacting with Li,[25] absorbing CO_2, and may even serve as a vehicle for drug delivery. Further diversity is presently being explored through the introduction of various heteroatoms on the carboxyl linker and the types of new materials which will be produced is an exciting area of research.

At the very core of what enables Li-ion batteries, insertion reactions are chemically or potentiostatically driven redox reactions which can be done at room temperature and do not require the breaking of bonds to enable new metastable phases to be obtained.[26] Ion-exchange reactions, in contrast, do not involve redox-processes but provide a topotactic route to new phases in a similar way. In these reactions, Li-based compounds are prepared from the corresponding Na- or K-containing phases, where the driving force is the formation of a far more stable metal-halide byproduct when compared to the metal halide precursor. Compounds which are capable of undergoing these exchange reactions are particularly attractive for ionic conductors.[27,28]

Acid–base reactions, which alter the framework of a structure by forging new bonds between surfaces upon elimination of intervening terminal ligands, are also classified as condensation reactions. More than two decades ago, such a reaction was exploited and led to the discovery of the bronze polymorph of TiO_2 (typically denoted as TiO_2 B) which could be attractive as a negative electrode material via a hydroxylation–condensation process starting from $K_2Ti_4O_9$ and involving an ion exchange in acidic medium. In this example, while the reaction is not purely topotactic, there is a reconstructive transformation of the framework such that some parts of the parent and target phases remain structurally similar. A more recent example was reported by the group of L. F. Nazar in which they showed the transformation of $NH_4MPO_4 \cdot H_2O$ to $NaMPO_4$ could proceed via direct ion exchange between NH_4^+ and Na^+ using molten $NaCH_3CO_2 \cdot 3H_2O$.[29]

Hydro(solvo)thermal routes, which mainly involve reactions between metallic salts dissolved in aqueous (hydro) or nonaqueous (solvo) media, rely strongly on issues of solubility[30–32] and have significantly different kinetic and thermodynamic considerations compared to more traditional high-temperature routes. Solubility can clearly be manipulated by temperature or through adjusting the pressure depending upon whether the reaction is carried out under autogenous or applied pressure in the reaction vessel. Regardless, a strong knowledge regarding the solubility of the precursors is essential to properly planning hydro(solvo)thermal reactions and within this context Pearson's concepts of hard and soft acid-bases (HSAB) remain very useful to select suitable precursors. As an illustration, such concepts explain the lower solubility of LiF versus AgF (hard–hard/soft–soft) as opposed to the greater solubility of LiCl vs AgCl (hard–soft/soft–soft) with the salts made of either hard–hard or soft–soft cations–anions pairs always showing the lowest solubility. Generally, these hydro(solvo)thermal techniques have proven to be very efficient at producing monodisperse powders with well-defined shapes and sizes at temperatures in the range of 140 °C up to 250 °C. Solvothermal reactions can also benefit from the use of microwave heating to drive rapid changes in the temperatures as a way to increase the chances of trapping metastable phases, which may not be stable with slow initial heating or cooling. These low-temperature hydro(solvo)thermal reactions are typically conducted in water, because of its high solubilizing power, or in nonaqueous solvents of lower dielectric constant such as DMF, DMSO, or even acetamide when the target compound could present some solubility in aqueous media.

Since many of these solvents possess boiling points which are significantly higher than water, they can be easily exploited to facilitate reactions at temperatures up to 200 °C. However, to explore this 200–300 °C temperature gap, inorganic chemistry typically relies on a molten salt flux to provide the solubilizing media and numerous examples of metastable oxides, chalcogenides, have been produced over the years in this way. The problem with molten flux approaches is that they are often cumbersome as the number and choice of appropriate salts are limited since they must not react with the precursors or product and must be removable using washes which do not deteriorate the formed phase.

Synthetic Directions of the Future. Interestingly, ionic liquids, which are essentially just organic salts which exist in a liquid state at room temperature, have been extensively used in organic chemistry as a synthetic media.[33] However, the opportunities afforded by this reaction medium have been severely neglected by inorganic chemists despite the fact that ionic liquids: (i) have very low vapor pressures, enabling them to be used in open reaction vessels, (ii) have a decent solvating power, which makes them capable of solvating a wide variety of precursors, and (iii) are extremely diverse with more than 1500 members.[34,35] Like organic solvents, ionic liquids can be easily extracted, separated, purified, and are readily recovered and reused. Because of these positive attributes, ionic liquids, namely, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) (EMI-TFSI), have recently been exploited in preparing several different polyanionic electrode materials such as $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, Na_2FePO_4F, and $LiFePO_4F$.[36] It should also be noted that, just like any other solvothermal method, this technique allows for good control of particle size and morphology under atmospheric pressure and at temperatures as low as 200–300 °C. Costly ionic liquids as reacting media may seem uneconomical at first, but it should be emphasized that these liquids can be easily recovered and recycled. Besides, as the implementation of ionothermal synthesis to the field of inorganic synthesis is relatively new, significant improvements should be expected in terms of designing new low-cost ionic liquids for specific reaction condition. Combinations aiming at replacing imidazolium cations and highly expensive TFSI anions by quaternary ammonium cations and chlorine anions, respectively, are presently being explored while preserving their overall stability. We must also recognize that ionic liquids can be a renewable alternative to low-boiling solvents[37] and even more so for water-soluble compounds as will be discussed in greater detail later.

Considering that the drive toward low-cost processing should ideally give rise to effective synthetic approaches which can be carried out at room temperature, chemists have recently looked toward biological systems for inspiration. Nature is indeed rich with examples of nanometric iron oxide or calcite materials which are prepared by biomineralization reactions performed by bacteria. In an attempt mimic these processes, we recently tried to prepare $LiFePO_4$ in the presence of the bacteria *Bacillus pasteurii*. This bacteria, which slowly releases the enzyme urease, was combined with stoichiometric amounts of LiH_2PO_4, $FeSO_4 \cdot H_2O$, and urea in an effort to slowly produce the basic pH needed for the precipitation of $LiFePO_4$. The reactions were conducted in aerobic conditions in sealed vessels at 60 °C, and it was found that the color of the solution gradually became green after 8 h. A close examination of the product using HRTEM of the recovered solids revealed that the bacteria was surrounded by a biofilm within which needles of $LiFePO_4$ had formed. This demonstration proved that $LiFePO_4$ could be prepared near room temperature; however, it was difficult to establish highly reproducible results due to challenges in maintaining the performance of the bacteria. Such approaches, which are presently being applied to the synthesis of silicates and other phosphates, are encouraging. While there are still significant challenges to using this method, interdisciplinary collaboration with biologists in the years to come will prove extremely beneficial to the production of large-scale reproducible results.

Having reviewed the vast array of synthetic approaches available for the discovery of new phases, we now turn to a discussion on the most recently discovered class of positive electrode materials in the hope that the methodologies and rationale that were applied will encourage and assist other groups in their efforts to find new families of compounds.

5. Case Study: Discovery and Elaboration of the Fluorosulfates

With the first reports of the inductive effect and the subsequent discovery of $LiFePO_4$[38,39] came an explosion of work on polyanionic materials with recent reports on borate ($LiFeBO_3$) and silicate-based (Li_2FeSiO_4) compounds. However, many of these more recently discovered phases, in fact, show a lower redox potential than $LiFePO_4$ because the electronegativity of the B(2.0) and Si(1.9) atoms in the center of the polyanionic groups is not as large as that of P(2.1). In contrast, the substitution of phosphate $(PO_4)^{3-}$ groups by sulfate $(SO_4)^{2-}$ can be expected to increase the open-circuit voltage by as much as 0.8 V if one considers the example of early work on the NASICON framework structures due to the larger electronegativity associated with S which is 2.6.[40,41]

As recently as 2009, $LiMgSO_4F$ was the only fluorosulfate phase which had been reported in the literature and was prepared using a ceramic reaction at temperatures greater than 600 °C. Early attempts to make structural homologues based on 3d transition metals using similar conditions were completely unsuccessful so lower-temperature routes were pursued instead. Due to the issues of solubility of sulfates in aqueous media, initial attempts utilized nonaqueous reaction media in the form of ionic liquids. Following a survey of numerous parameters, including the type of hydrated precursors [$FeSO_4 \cdot nH_2O$ ($n = 1, 4, 7$)], the nature of the ionic liquids (hydrophobic vs hydrophilic), and the reaction temperature, pure $LiFeSO_4F$, having the same tavorite structure as $LiMgSO_4F$, was finally prepared following the reaction illustrated in Figure 7.

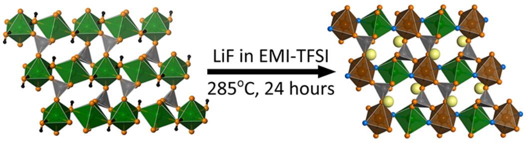

FIGURE 7. Illustration of the reaction to form the tavorite phase of $LiFeSO_4F$. $FeSO_4 \cdot H_2O$ is reacted with LiF in a hydrophobic ionic liquid above 285°. Note that the precursor phase and the resulting product are topologically related.

In order to understand the reaction mechanism, XRD, DSC, and IR spectroscopy techniques were heavily employed and revealed the critical importance of having both a very clean $FeSO_4 \cdot H_2O$ precursor and the presence of a hydrophobic reaction medium. The necessity for the monohydrate precursor, $FeSO_4 \cdot H_2O$, can be understood after comparing it to the structure of $LiFeSO_4F$ when oriented along the appropriate direction as seen in Figure 7. In both structures, chains of corner-sharing octahedra are joined together through commonly shared oxygens, which form SO_4 tetrahedra. The most important similarity lies in the position of the H_2O molecule at the shared-corner of the octahedra which corresponds to the fluorine site in $LiFeSO_4F$, implying that the reaction is completely topotactic with F^- ions replacing the H_2O and Li^+ inserting into the channels to maintain charge compensation.

The importance of the hydrophobic ionic liquid was recognized when TGA measurements revealed that the temperature at which the dehydration of $FeSO_4 \cdot H_2O$ occurred was shifted to higher temperatures when submerged in the ionic liquid. This lag in the kinetics of the dehydration led us to believe that the ionic liquid was encapsulating the water as it escaped and thereby was acting as a barrier to H_2O removal from the structure.[42] From this, it became clear that adjusting the rate of water departure and solubility of LiF dissolution was essential to obtain pure phases since if water

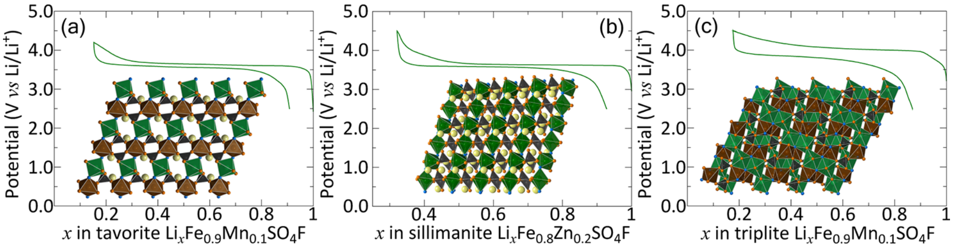

FIGURE 8. Illustration and comparison of the crystal structure and electrochemical performance of (a) $LiFeSO_4F$ in the tavorite phase, (b) $LiFe_{0.8}Zn_{0.2}SO_4F$ in the sillimanite phase, and (c) $LiFe_{0.9}Mn_{0.1}SO_4F$ in the triplite phase.

departure was allowed to happen too quickly, this led to the formation of anhydrous $FeSO_4$ which has consistently been found to be unreactive with LiF. Having finally determined the role of the ionic liquid, it was found that it could be easily substituted with polar polymers which were stable to temperatures as high as 320 °C or, alternatively, by doing a traditional solid state reaction within a pressurized atmosphere of four bars. It should be noted that these phases decompose at temperatures above 320 °C and are soluble in water, thus the complex role of water, which we will discuss in more detail later, and the need for water-free reaction media could explain why these phases have been previously unknown.

On the basis of this fundamental understanding of the topotactic reaction mechanism, we were able to successfully expand the reaction scheme to other 3d transition metal precursors which had similar structures to $FeSO_4\cdot H_2O$. Hence, in less than 18 months, we were able to obtain more than 15 different new phases; some of which presented attractive electrochemical properties like $LiFeSO_4F$[42] while others had interesting ionic properties like $LiZnSO_4F$.[43] Further building on this methodology, isostructural phases containing phosphate rather than sulfate polyanions were recently prepared by reacting $MnPO_4\cdot H_2O$ precursors with LiF.[44]

While the discovery of the tavorite phase of the fluorosulfates is exciting, caution should be exercised before blindly generalizing a rule for structure prediction. Indeed, while the hydrated Mn, Zn, and Fe precursors are completely isostructural, the $LiMnSO_4F$ and $LiZnSO_4F$ phases actually crystallize in two new polymorphs, isostructural to the triplite[45] and sillimanite[46] minerals, respectively. All three structures, illustrated along with their electrochemical performance in Figure 8 are composed of a similar close-packing of the SO_4 tetrahedra and merely differ by which interstitials are occupied, with the triplite-phase exhibiting a significant degree of atomic disorder. However, at a fundamental level, a topotactic relationship between the precursors and the products is still maintained since the underlying framework of the sulfate tetrahedra is maintained.

The competition between tavorite and triplite is actually more nuanced, as it was eventually found possible to stabilize $LiFeSO_4F$ in either the triplite or tavorite structure depending upon the reaction conditions used.[47] With respect to practical applications, this is an important finding given that the triplite $LiFeSO_4F$ shows a 3.9 V redox potential which is the highest voltage ever reported for the Fe^{3+}/Fe^{2+} couple.[45] Therefore, the delicate balance which exists between the kinetics of phase formation and the most thermodynamically stable phase required a careful examination of the role that water plays in the stabilization of the phase. Indeed, we found that the tavorite phase was readily obtained in sealed bombs providing the pressure reached 4 bars, and the release of water pressure on heating appeared to favor the nucleation and growth of triplite.

The competition between the triplite and travorite phases brings a great deal of complexity to the system but also opens new research directions for solid state chemists provided that we can find a way to adjust all of the key parameters, such as the rate of water departure, to be able to convert other compositions which crystallize in tavorite [$LiMXO_4$(F, OH) (M = Fe, Mn, Co; X = S, P)] into the triplite structure. This will stand as a significant synthetic challenge for the years to come and may also be achieved by playing with the atomic disorder. This is readily seen in triplite, where it may eventually be possible to replace Li with larger cations such as Na or K, so as to prevent the intersite mixing. This kind of logic could also be applied to the silliminite-phase where the main challenge still lies in identifying and controlling the key experimental parameters.

6. Summary and Perspective

With the recent birth of the seven billionth person, countries around the world were reminded of the need to more than double their energy production by the year 2050, if they wish to maintain the current standard of living. While the challenge of producing such a vast amount of energy seems daunting, the added complication that nearly all of the

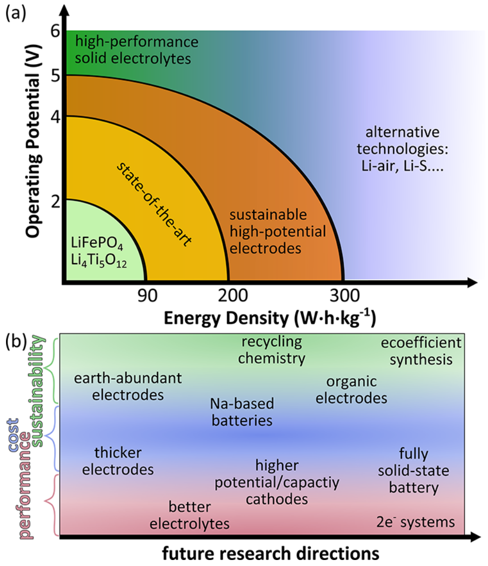

FIGURE 9. (a) Summary illustration of the materials challenges that must be overcome to push the boundaries of electrochemical storage further. Regions illustrated in green represent areas of safe operation whereas the orange regions present some safety concerns due to the possibility of oxidizing the liquid electrolytes, hence the drive toward solid electrolytes. Note that the maximum theoretical voltage is 6 V which would correspond to a cell cycling LiF. It should also be mentioned that surpassing an energy density of 300 W h kg^{-1} may eventually require the pursuit of technologies beyond Li-ion. (b) Illustration of the areas of research which must be pursued in the future. The green, blue, and red regions represent areas that would improve the sustainability, cost, and performance of batteries. Given that some developments could benefit more than one area, the colors are shown as a continuous field and the placement of each development on the vertical axis is meant to reflect the areas of impact.

world's energy is produced from nonrenewable fossil fuels, which emit huge amounts of CO_2 as a byproduct of combustion, only further complicates the problem. Thus, if society is to succeed in delivering this vast amount of energy while minimizing the impact on the environment, renewable sources such as wind, solar, tidal, and geothermal must play an integral role and automotive vehicles must become independent of petroleum-based fuels. Reaching this goal will require a staggering amount of work in the area of energy storage over the next few decades, but will principally require addressing the materials issues we have discussed.

With this in mind, the ultimate goal in designing new electrode materials is to eventually design a "superbattery" which can meet the needs of any application imaginable by possessing a large energy density and being capable of quickly delivering its charge in a safe way (Figure 9). Such a device will require electrodes of the future to either have significantly larger capacities or be capable of operating at much higher voltages than is possible today. While the intuition of chemists continues to play a central role in the search for new materials, this approach for discovering new materials is incredibly slow. Thus, computational approaches must continue to evolve, with the ultimate dream being the development of theoretical methods capable of predicting new compounds and their corresponding properties, but progress toward this ambitious goal will take some time. While theoretical chemists develop their techniques, experimentalists would do well to develop ways to better take advantage of the huge databases of structural information which are already avaible. In particular, programs which would enable a search for specific local coordination environment would prove extremely valuable given the importance of the local structure surrounding redox centers in unlocking high redox potentials as was recently reported.[48]

While much of the discussion has focused on increasing the operating voltage of electrodes, it should be noted that the upper limit for the voltage at which these electrodes can work is currently determined by the stability of existing electrolytes against oxidation. Developments in the area of liquid-based electrolytes has been extremely slow, however, and now may be the time to start pursuing solid electrolytes more vigorously. The design considerations for solid electrolytes are beyond the scope of this Account, but clearly much better ionic conductors with highly optimized interfaces and improved kinetics will be necessary before they can become commercially viable.[49]

An alternative way to increase the capacity of these electrodes would be to focus on materials which can accept more than one electron per 3d metal by accessing successive redox couples. V-based compounds such as Li_2VPO_4F are known to be capable of taking up two Li^+ per V, with redox voltages corresponding to the V^{3+}/V^{2+} and V^{4+}/V^{3+}, but these levels are separated by as much as 2 V which make it impractical for commercial cells.[50] It is conceivable that Mn-based compounds could also work, but in many cases, like Li_2MnSiO_4,[51] attempts to remove more than one Li^+ results in a breakdown of the structure. Two electrons can also been achieved by exploiting the oxidation of Ni^{2+} to Ni^{4+} as seen in the layered oxide $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; however, this only appears to work effectively when Ni is a dilute part of the cationic sublattice.[52]

Therefore, the pursuit of two electron processes should continue and further routes should consider exploring (i) the use of compounds with cations like Bi^{3+} which undergo a two-electron process due to the unstable Bi^{4+} oxidation state which disproportionates immediately on formation[53] or (ii) catalysts which could enable single-step $2e^-$ redox processes such as the direct conversion of Ti^{4+} to Ti^{2+}. For instance, this kind of effect has been seen when very small amounts of Fe is substituted into TiO_2 and results in a doubling of the capacity.[54]

Multielectron alkaline metals such as Mg^{2+}, Ca^{2+}, and Al^{3+} may seem like attractive routes for enhancing the capacity; however, using these elements would offer limited benefits as the electronic structure of the host would essentially limit the maximum number of electrons that could be taken up. Chevrel phases ($M_xMo_6S_8$) nicely illustrate this as you can insert either 4 Li^+ or 2 Mg^{2+} but the capacity is limited to 4 e^- due to the band structure of the host. Conversion electrodes may offer a way to break away from these limitations, since as many as 6 e^- per 3d metal have been achieved,[55] but the challenge here is that these electrodes do not tend to work at high potentials. Thus, significant improvements in the materials and electrode wiring designs are needed before they will be a realistic option.

While it is true that energy density has long been considered the most important figure-of-merit for new batteries, given the increasing demand for large-volume applications like electric vehicles and grid storage the ability to produce materials sustainably without environmentally toxic byproducts is quickly becoming a central concern as well. A recent analysis of the life cycle costs associated with the production and use of Li-based batteries estimated that 400 kW h of electricity are required and 75 kg of CO_2 are released for every 1 kW h of battery capacity produced. These numbers become worrisome when one considers that the electricity which will be used to produce and charge these batteries comes from coal-fired plants. Efforts focused on the development of low-temperature or biomineralization processes or the development of renewable organic electrodes that can be produced from biomass instead of mineralogical sources, offer a promising way to reduce the environmental impact.

Finally, it should be mentioned that today's Li-ion cells are only 50% by weight active electrode material and as little as 25% in the pack used in EVs due to all of the packaging. Thus, if a way could be found to allow for thicker electrode films, this would correspond to a direct increase in the energy density and translate into overall reduction in the costs. Increases in film thickness, however, would require some compromise in the form of nanostructuring or controlled porosity to maintain good kinetics for mass transport. Integrated experimental and theoretical efforts toward optimizing these systems have shown promising initial success.

Fears over potential shortages of Li should also encourage researchers to explore new chemistries for insertion electrodes, with special attention focused on using Na as a replacement for Li as it is far more abundant and easier to produce. In fact, despite its larger mass (22.99 g mol^{-1} compared to 6.94 g mol^{-1}) and the reduced redox potential (0.3 V) compared to Li, it is still realistic to imagine devices based on Na which can be just as attractive as those using Li. To make this a reality, better Na-based electrodes must be designed, particularly on the negative side, since today there are only three compounds (carbon, Pb, and $Na_2Ti_3O_7$) capable of reversibly accepting and releasing Na^+ ions. An alternative way to combat materials shortage would be to promote recycling owing to the staggering volume production of Li-ion batteries in the years to come; recycling will become mandatory. Due to its low melting point, recycling Li is not energetically demanding and hydrometallurgical processes are being developed to recover Li_2CO_3 out of which Li can be extracted. Nevertheless, recycling will necessitate unprecedented materials considerations in the conceptual design, namely, composition, of new electrode materials and the resurrection chemistry will form an integral part of the materials aspects associated to batteries. It should also be mentioned that while Li-ion has a great deal of potential, other promising electrochemical storage techniques such as Li-air and Li-S batteries offer a 10-fold increase in the theoretical energy density and are therefore likely to gain increasing attention in the near future. Yet again, just as in the case of insertion electrodes, these systems face significant difficulties in moving forward because of materials issues like the lack of suitable catalysts for better kinetics of oxygen reduction.

In summary, we have endeavored to provide some guidance to assist with the identification of new and higher-performing materials for electrochemical storage. We have reviewed the basic chemistry required and demonstrated through examination of a recently discovered family of compounds, how to identify and develop new phases in the context of both performance and sustainability. Research advances in the field of electrochemical energy storage will critically hinge on chemists designing new materials with very specific structures, compositions, and morphology, and it is our hope that the community of experimental and computational chemists will make use of the information presented to push the limits of electrochemical storage materials further in the future.

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BIOGRAPHICAL INFORMATION

Brent C. Melot received his Ph.D. from the Materials Department at the University of California, Santa Barbara under the supervision of Ram Seshadri. His research at UCSB focused on understanding the relationship between the atomic structure and magnetic properties of complex oxides. After completing his doctoral work (2010), Brent joined the Laboratoire de Réactivité et Chimie des Solides in Amiens as a postdoctoral research associate under Jean-Marie Tarascon. Starting July 2012, he begins an appointment as Assistant Professor in the Department of Chemistry at the University of Southern California in Los Angeles where his group will continue working to develop a deeper understanding of how the crystal structure and composition of materials influence their functional properties.

Jean-Marie Tarascon (1953) is a Professor at the University of Picardie Jules Verne, but much of his career was spent in the United States. He began as a postdoc at Cornell University (1980), then moved to Bell Laboratories, and finally to Bellcore until 1994 where he worked on the development of plastic Li-ion technology. He created the European network of excellence ALISTORE-ERI of which he was head until 2010 when he took over as director of the new LABEX "STORE-EX" and became in charge of the recently created French network on electrochemical energy storage (RS2E). His research deals with new electrode materials which can be prepared using eco-efficient processes for the development of sustainable and "greener" Li-ion batteries. He holds 73 patents and has authored more than 540 publications. He is the recipient of several awards with the most recent being his nomination to the college de France in 2010 as the Chair on Sustainable Energy and the 2011 ENI "Protection of the Environment" Prize.

FOOTNOTES

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