Research & Reviews in Electrochemistry
ISSN: 0974-7540

Research and Reviews in Electrochemistry

Mini Review Article|Vol 12 Iss 1

Materials Design and Preparation for Advanced Electrochemical Storage

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Received: 3-January-2022; Manuscript No. tsrre-22-64502; **Editor Assigned:** 17-January-2022; PreQC No. tsrre-22-64502 (PQ); **Reviewed**: 25-January-2022; QC No. tsrre-22-64502 (Q); **Revised:** 28-January-2022; Manuscript No. tsrre-22-64502 (R); **Published:** 30-January-2022, DOI No. 10.37532/0974-7540.22.12.1.233

Abstract

To meet the world's growing energy demand while protecting the environment, the world's reliance on nonrenewable energy sources must be drastically reduced. The ability to efficiently convert, store, transport, and access energy in a variety of ways will be at the heart of this effort. Batteries for small consumer devices have saturated society; however, if they are to be useful in large-scale applications such as automotive transportation or grid-storage, new materials with dramatically improved performance will be required. Efforts must also focus on the use of Earth-abundant and nontoxic compounds to ensure that any developments do not create new environmental problems.

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Keywords:* *Electronegativity; Metal fluorosulfates; Automotive transportation

Introduction

The desire to reduce society's reliance on fossil fuels has elevated the field of energy storage to the forefront of 21st-century research. The fundamental concept of converting solar energy via photovoltaic, photocatalytic, or photosynthetic routes is well understood today, as are the basic principles of electrochemical storage via batteries, supercapacitors [1], and fuel cells [2]. As a result, the current challenge is not understanding how to convert and store the energy we will require, but rather what materials we will use and how they can be produced on a large scale with high efficiency while maintaining low enough costs to ensure their global adoption.

As with any new technology that gains widespread adoption, it becomes clear that meeting these challenges will necessitate

Citation: Brown J. Material Design and Preparation for Advanced Electrochemical Storage. Res Rev Electrochem. 2022;12(1):233.

innovation in the design and optimization of new materials. DARPA had an adage in the 1960s that said, "Technology is always limited by the materials available," and this is still true today. This call for new materials has resulted in an astounding number of papers dealing with the development of improved materials for water splitting, photon conversion, or electrochemical storage, but the need to aggressively search for new compounds remains. This search for new materials, with a broad focus on addressing the issue of electrochemical energy storage, will undoubtedly be critical in the coming years.

In the following sections, we will go over the extremely difficult process of developing new insertion electrodes, from conceptual design and chemical element selection to redox property optimization. To begin, we will outline the current state-of-the-art in positive electrodes and identify the inherent material limitations they present. This will be followed by a general strategy for designing new phases with optimised redox properties, with the goal of developing new and sustainable reaction pathways. We will then discuss how the rational approach to materials design and synthesis presented has been successfully applied in the context of the recently discovered family of transition metal fluorosulfates. To achieve the goal of establishing a sustainable energy economy, chemists' ability to use their "green thumb" to prepare new phases and optimise their synthetic techniques will be critical.

Today's Li-Battery situation

The current state-of-the-art for positive electrodes is $LiCoO_2$, $LiNi1/3Mn1/3Co_1/3O_2$, or $LiMn_2O_4$, with recently discovered polyanionic compounds such as $LiFePO_4$ and $LiFeSO_4F$, while not as advanced, poised to play a significant role in the near future. While these phases perform admirably in practical applications, they are not without limitations.

Because of its low molecular weight, $LiCoO_2$, the most commonly used positive insertion electrode, has an extremely high theoretical capacity of 274 mA h g^{-1}. Unfortunately, whenever more than half of the Li-ions are removed from between the layers, the structure tends to collapse due to significant electrostatic repulsion between the transition metal polyhedra, limiting the reversible capacity to around 150 mA h g^{-1} [3]. To address this issue, extensive efforts have been made to partially substitute a fraction of the Co in this phase with Ni or Mn in order to support the structure against decomposition at high potential. This technique has resulted in i) sustainably reversible capacities of 190 mA h g^{-1} with materials of the formula $LiCoNi1/3Mn1/3O_2$ referred to as NMC, [4] and ii) the synthesis of Li-rich layered oxides by embedding inactive Li_2MnO_3 component within layered $LiMO_2$ to prepare xLi_2MnO_3• $(1-x)LiMn_{0.5}Ni_{0.5}O_2$. As a result of Mn dissolution, such materials continue to exhibit slow kinetics (e.g., power rate capability) and limited cycled life[5].

In contrast, the structure of spinel $LiMn_2O_4$ is much more resistant to lithium removal, capable of reversibly removing and reinserting up to 95 percent of the theoretical capacity. However, this phase, like $LiCoO_2$, has stability issues when used in conventional Li-based liquid electrolytes unless special postprocessing [6] is performed to prevent dissolution by trace amounts of HF present in the electrolyte, and has a significantly lower theoretical capacity (148mAh g^{-1}) when compared to $LiCoO_2$. $LiFePO_4$, which has received a lot of attention in recent years, has a lot of potential, especially in terms of safe performance, but it can't compete in terms of power density due to its relatively low operating voltage. Given these intrinsic limitations, it is clear that the design and discovery of new material phases will be critical to the future of electrochemical storage.

Fundamental design principles

At the materials level, costs are primarily determined by reaction temperature and pressure, the abundance of starting reagents, and the performance of the final device. As a result, precious metals such as Ag, Au, and Pt would significantly increase the total cost of each cell and are simply not practical, whereas the toxicity of elements such as Be, Hg, As, and Se means they would never be safe enough to distribute in the volumes required. Simultaneously, concerns about the scarcity of rare earth metals such as La, Ce, and Pr, as well as their high molecular weights such as the 4d and 5d transition metals, make them impractical. Simply applying these few criteria eliminates a significant portion of the periodic table, as illustrated in, leaving chemists with a somewhat limited number of elements to work with. Nonetheless, these few elements have the potential to produce an enormous number of combinations, and sustainable 3d 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 lot of attention as candidates to replace the more expensive and somewhat toxic Co- or Ni-based electrodes.

Thus, the main question is how to select, from among the numerous Fe- or Mn-based phases, the "winning" composition that not only exhibits exceptional performance but can also be produced in a clean and eco-friendly manner. The periodic table is an excellent guide in designing compounds in this pursuit, but the trends it contains are frequently overlooked or forgotten because they have been less explicitly discussed in recent years. To help correct this, we've compiled a list of the most important properties of electrochemical materials.

To begin, it is well understood that the atomic radii of atoms decrease as one moves from left to right and from bottom to top of the periodic table. The electronegativity and ionisation energies increase as the positively charged nucleus begins to pull more strongly on the valence electrons as the radius of the element decreases. The importance of electronegativity in the context of insertion electrodes is critical because it determines the ionic/covalent character of metalligand bonds and, as will be discussed further below, is critical for tuning redox potentials. Indeed, the ionisation energy is perhaps equally important in that it determines the atom's oxidizing/reducing power. Because it is easier to remove electrons that are further away from the core and have lower ionisation energies, monovalent ions, M^+, can act as stronger reducing agents than pentavalent ions, M^{5+}, which tend to be more oxidising. Similarly, 3d cations with the sams charge have more oxidising power from left to right on the periodic table, due to the atomic radius.

Size effects also play a role in the stabilisation of high-valence oxidation states by reducing Coulombic repulsion, as evidenced by the fact that V^{5+} is relatively common in air whereas Co^{4+} is relatively unstable. Perhaps more importantly for the creation of new materials, the acidic-basic character of oxides can be deduced from the fact that bonds with a higher ionic character, such as $Ni^{\neg}$–O, tend to be more basic because the highly charged oxygen ions can easily capture protons. More covalently bonded oxides, such as SiO_2, have a stronger acidic character because the partial charge on the oxygen ions is more polarised toward the transition metal, allowing protons to depart more easily.

Identifying and planning for new phases

Understanding the relationship between the atomic structure of materials and their applications has been and will continue to be a driving force in the field of inorganic synthesis for the foreseeable future. With the tools we've just described in hand, we can now return to the question of how to find new and promising compositions without testing every possible arrangement.

Computational and theoretical approaches

Given the virtually infinite number of potential phases and the pressing need, high-throughput computational tools for predicting and identifying promising new materials are gaining traction [7]. Many of these initiatives, which rely heavily on experimental databases and are still in their early stages, aim to do for solid state chemistry what genomics has done for biology. Nonetheless, despite significant efforts devoted to these approaches, there are still very few examples of new compounds that were solely the result of computational prediction (e.g., borophosphates and carbonosilicates) [8]. This should serve as motivation 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, the existing materials library, which primarily consists of naturally occurring mineral structures, must be relied on to guide the discovery of new compounds, with their final preparation heavily reliant on intuition and the ability to manipulate thermodynamics, chemical affinity, and structural consideration Long et al. recently described a method for utilising dimensional reduction as a general mechanism for the prediction of new compounds by carefully analysing an experimental database containing over 3000 crystal structures. This formalism explains how metal anion (M–X) frameworks in a parent compound, MX_x, can be disassembled via reaction with an ionic reagent A_aX to form a family of $A_{na}MX_{x+n}$ compounds with reduced dimensionality. As a result, for a large number of three-dimensional (3D) binary phases, one should be able to predict the existence of 2D, 1D, and 0D homologues. Using the silicate framework as an example,16 subsequent additions of $1/2Li_2O$ produce compounds with decreasingly connected frameworks, beginning with corrugated sheets in $Li_2Si_2O_5$ (3D), progressing to chains in Li_2SiO_3 (2D), singly connected $[Si_2O_7]^{6-}$ anions (1D) in $Li_6Si_2O_7$, and finally producing discrete molecular $[SiO_4]^{4-}$ tetrahedra (OD) in Li_4S.

Summary and analysis

With the recent birth of the seven billionth person, countries around the world were reminded that if they want to maintain their current standard of living, they must more than double their energy production by 2050. While the task of producing such vast amounts of energy appears daunting, the fact that nearly all of the world's energy is produced from nonrenewable fossil fuels, which emit massive amounts of CO_2 as a byproduct of combustion, only complicates matters. Thus, if society is to succeed in delivering this vast amount of energy while minimising environmental impact, renewable sources such as wind, solar, tidal, and geothermal must play an important role, and automotive vehicles must become independent of petroleum-based fuels.

With this in mind, the ultimate goal of developing new electrode materials is to eventually create a "superbattery" that can meet the needs of any application imaginable by having a high energy density and the ability to deliver its charge quickly and safely. To power such a device, future electrodes will need to be significantly larger in capacity or capable of operating at much higher voltages than are currently available. While chemists' intuition remains important in the search for new materials, this approach is extremely slow. Thus, computational approaches must evolve further, with the ultimate goal of developing theoretical methods capable of predicting new compounds and their corresponding properties, but progress toward this lofty goal will be slow. While theoretical chemists develop their techniques, experimentalists would benefit from improving their use of the massive databases of structural information that are already available. Programs that enable the search for specific local coordination environments, in particular, would be extremely valuable given the importance of the local structure surrounding redox centres in unlocking high redox potentials, as recently reported [9].

While much of the discussion has centred on increasing the operating voltage of electrodes, it should be noted that the upper limit for the voltage at which these electrodes can function is currently determined by the oxidation resistance of existing electrolytes. However, progress in the field of liquid-based electrolytes has been extremely slow, and now may be the time to begin pursuing solid electrolytes more aggressively The design considerations for solid electrolytes are beyond the scope of this Account, but clearly much better ionic conductors with highly optimised interfaces and improved kinetics will be required before they can become commercially viable [10].

In conclusion, we attempted to provide some guidance to aid in the identification of new and higher performing materials for electrochemical storage. We reviewed the fundamental chemistry required and demonstrated, using a recently discovered family of compounds, how to identify and develop new phases in the context of both performance and sustainability. Advances in the field of electrochemical energy storage will be critically dependent 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 use the information presented to push the limits of electrochemical storage materials further in the future.

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