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Systematic Studies on “Abundant” Battery Materials: Identification and Reaction Mechanisms

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ABSTRACT

"Abundance" is an important keyword in materials development. This is particularly the case for the energy storage sector, where materials themselves function as a storage host. The amount of materials is directly linked to the amount of energy stored in the device. In rechargeable batteries, transition metal elements are necessary to accommodate a large number of electrons/holes in a reversible redox reaction. Iron, as the fourth most abundant element in the earth's crust, is an ideal redox center, but practical storage electrodes with Fe redox have long been the "holy grail" of the lithium-ion battery since its commercialization in 1991. In this review article, the history of replacing Co with Mn and/or Fe in lithium battery electrodes is briefly reviewed followed by recent technical achievements toward more sustainable batteries using Na⁺ as a guest ion, where the goal would be to discover a high voltage electrode material composed of Na and Fe without compromising the energy density. Further, our ultimate destination is set to high energy density aqueous lithium/sodium ion batteries, where the hydrate-melt electrolyte enables surprisingly high-voltage operation over 3 V. During materials identification and optimization, reaction mechanisms should be understood in a systematic way to provide a firm direction for strategic design. With this regards, important physicochemical properties of key materials will be introduced.

Keywords: Battery, Abundance, Sustainability, Hydrate Melt

1. Introduction

There is a pressing need to use renewable energy (solar, wind, geothermal, etc.) as well as to provide efficient storage and supply of mobile energy to enable the application of consumer electronics to commuter vehicles. In the energy-storage sector, electrochemical energy storage based on the reversible conversion of chemical energy and electrical energy both having a common carrier, i.e., electrons, has dominated over two centuries. Lithium ion batteries, which have been commercialized by Sony in 1991, have far outperformed other technologies in terms of energy density with adequate rate capability, longevity, and large-scale commercial applications. Thus, Li-ion batteries hold the promise and burden to sustain our energy-demanding society.

As this review article illustrates a road toward rechargeable battery with ultimate sustainability, let us first spotlight on the principle of present lithium-ion battery system. As illustrated in Fig. 1, there are three main components: positive electrode (also termed as cathode), negative electrode (anode) and organic electrolyte. In this system, Li ions can intercalate to both the electrodes, which act as hosts and this mechanism is known as intercalation. The role of organic liquid electrolytes, which always consist of a solution of a lithium salt dissolved in an inert solvent, is to act as an ionic conductor to transport lithium ions back and forth between the two electrodes as the batteries are repeatedly charged and discharged. It employed low-voltage carbonaceous material without Li as anode and LiCoO₂ as cathode acting as a source of Li. This kind of lithium-ion battery possess a working voltage exceeding 3.6 V and gravimetric energy densities between 120 and 150 Wh/kg, which is two or three times of those usual Ni-Cd batteries. During the charge process, the chemical reactions occurring at both electrodes can be expressed as following.

(Cathode) LiCoO₂ → Li₁₋ₓCoO₂ + xLi⁺ + xe⁻  (1)
(Anode) C₆ + xLi⁺ + xe⁻ → LiₓC₆  (2)

And during discharge process, the reactions go in reverse direction.

In the following sections, achievements and problems in elemental strategy will be discussed toward (simultaneous) replacements of Co to Mn/Fe and Li to Na, as well as organic electrolyte to hydrate melt electrolytes.
2. Spinel LiMn$_2$O$_4$

A classical low-cost and stable cathode material for lithium-ion batteries, LiMn$_2$O$_4$, is also an interesting research subject in terms of typical phase diagram dominated by oxygen equilibrium and sensitive Jahn-Teller phenomena driven by high spin Mn$^{3+}$ ($d^4$) depending on several extrinsic factors such as lithium content, oxygen stoichiometry, and temperature.

2.1 Phase diagram

Figure 2 is the phase diagram of LiMn$_2$O$_4$ in the temperature–oxygen partial pressure system ($T$–$P_0$) obtained by TG/DTA analysis. The metastable samples of high-temperature phases were obtained by quenching from the corresponding temperatures in the regions B and C in Fig. 2. A linear Arrhenius behavior of $\ln P_0$ versus $1/T$ indicates the diagram is dominated by the oxygen equilibrium. The X-ray diffraction study revealed that line 1 in Fig. 2 represents the onset of oxygen extraction and line 2 corresponds to the formation of orthorhombic LiMnO$_2$. Oxygen extraction in region B leads to the formation of a tetragonal spinel with the nominal composition LiMn$_2$O$_{3.86}$ ($c/a = 1.07$).

2.2 Jahn-Teller transition

In trivalent manganospinels, e.g., MgMn$_2$O$_4$ and ZnMn$_2$O$_4$, a cooperative JT transition from cubic to tetragonal takes place at temperature $T_t \sim 1400$ K and the tetragonal distortion ($c/a$) is as large as 1.15 at room temperature. The transition temperature $T_t$ and the distortion $c/a$ have a moderate correlation to the electronic structure of the MnO$_6$ octahedron in the ground state because of the thermal excitation of electrons over the energy gap $\Delta$ ($d_{x^2-y^2}$ orbital in tetragonal $D_{4h}$ symmetry), $\Delta \sim k_BT_t \propto (c/a - 1)$, i.e., $\Delta/k_BT_t$ is approximately $\sim 1400$ K (see Fig. 3).

The replacement of the trivalent manganese ions by divalent ($t_{2g}^2e_{g}^2$) or tetravalent ($t_{2g}^3e_{g}^0$) manganese ions reduces the instability. Consequently, $T_t$ decreases and the magnitude of $c/a$ decreases and approaches unity as the average manganese valence number increases from 3.0 to 3.5 (Fig. 4). In the lithium manganospinel system, LiMn$_2$O$_4$ is of particular interest because it takes the threshold manganese valence, 3.5, where the cubic lattice is apt to exhibit JT distortion when the manganese valence is slightly reduced by lithium insertion or oxygen extraction. This situation led us to an investigation of the low temperature structure of LiMn$_2$O$_4$ and the discovery of the unique Verwey-like charge-ordering transition with large local JT distortion in the vicinity of $T_t = 280$ K (Fig. 5).

3. Olivine LiFePO$_4$

Defeating some negative perspectives raised at an early stage of the development, LiFePO$_4$ has been commercialized and received the common agreement of the battery community as most promising for the next generation lithium battery cathode. Operation under very high rate condition is possible, in spite of its insulating nature. This has been achieved by several technical modifications as carbon coating on particles with smaller size. Through investigations show there seems to be essential thermodynamic and structural aspects behind them. The latest body of knowledge will be briefly demonstrated below.

3.1 Phase diagram

In order to understand the unexpected fast kinetics in the inherently insulating material, the pervasive trends in research into LiFePO$_4$ basically fall into understanding the mechanism of charge transport and the phase diagram. The pursuit of intensive research have established (i) existence of solid solution in Li$_x$FePO$_4$ over...
the entire compositional domain (0 < x < 1) at temperatures above 520 K (Fig. 6); (ii) incomplete miscibility gap at room temperature sandwiched by two small solid-solution compositional domain at 0 < x < α and 1 − β < x < 1; (iii) the miscibility gap shrinks systematically with decreasing particle size and increasing temperature (Fig. 6). Thermodynamically, the dependence can be explained by the increasing contribution of the elastic energy induced along coherent two-phase interphase in the smaller particles by a factor of \( r^2 \alpha(x)/V(x) \), where \( r \) is the particle radius, \( \alpha(x) \) is the interface area, and \( V(x) \) is the particle volume.

3.2 Lithium diffusion

Intuitive expectations based on the polyhedral network in the structure provide two possible continuous lithium pathways, along the [010] and the [001] directions. However, analysis of solid solution phase of Li_{0.6}FePO_4 at 620 K, where Li is the exclusive motional atom, have led to the strict conclusion that the probability density of lithium nuclei distributes into the continuous curved one-dimensional chain along the [010] direction (see Fig. 7). This was also supported by the independent ab initio study using the nudged elastic band (NEB) method.

3.3 Optimization

As described above, two major drawbacks of LiFePO_4 were recognized as easily blocked one-dimensional lithium diffusion and low electronic conductivity in slow hopping sequence, but these were successfully overcome as shown in the ideal charge-ordering structure of LiMn_2O_4.

Figure 6. (Color online) Phase diagram of Li_xFePO_4. (a) Lithium composition vs. temperature. (b) Room-temperature size-dependency diagram.

Figure 7. (Color online) (A) Three-dimensional Li nuclear density data calculated by MEM using neutron powder diffraction data measured for Li_{0.6}FePO_4 at 620 K. The brown octahedra represent FeO_6 and the purple tetrahedra represent PO_4 units. (B) Two-dimensional contour map sliced on the (001) plane at z = 0.5; lithium delocalizes along the curved one-dimensional chain along the [010] direction, while Fe, P, and O remain near their original positions. (C) Two-dimensional contour map sliced on the (010) plane at y = 0; all atoms remain near their original positions.
discharge curves realized by particle downsizing and carbon coating (Fig. 8). After 2006, high-rate Li-ion batteries with a LiFePO4 cathode became commercially available and are widely used for power tools and larger scale applications.

3.4 Metastable intermediate: structure, transport, and optical properties

As speculated from the aforementioned sensitive change of the phase diagram, the ground state two-phase separation and the metastable solid-solution are energetically competitive in the Li$_x$FePO$_4$ system, and the solid solution phase is induced in a non-equilibrium electrochemical reaction (Fig. 9). However, structural and transport properties of the metastable solid solution phase are hard to measure due to its short lifetime; it easily relax into the ground-state phase separation within 10 second. We overcame this limitation by quenching Li$_{2/3}$FePO$_4$ ($x = 2/3$, the eutectoid magic number) at 350°C to room temperature. This quenched phase remained stable for a couple of weeks, which enabled sufficient time to measure the several intrinsic properties.

The structural analysis of metastable Li$_{2/3}$FePO$_4$ (see Fig. 10a) revealed that the charge-ordered stripes at the Fe sites and the disordered configuration of lithium resulted from the electrostatic frustrations among the lithium and Fe$^{3+}$ ions. Metastable Li$_{2/3}$Fe-PO$_4$ phase was found to have approximately 2 orders of magnitude increased conductivity over the two end members of LiFePO$_4$ and FePO$_4$. Our research reveals that the single-phase transformation mechanism not only relaxes the interface strain energy but also improves the intrinsic charge transport (Fig. 10b), enabling the high-rate capability of olivine LiFePO$_4$. Inclusion of Fe$^{3+}$/Fe$^{2+}$ mixed valence state modify the electronic density of state to induce optical absorption caused by inter-valence charge transfer transition, leading to a deeper color of the sample powder.

4. New Polyanion Cathodes

Inspired by the success of LiFePO$_4$, several compounds were explored to further utilize the redox reaction of Fe more efficiently toward higher energy per weight/volume. Major directions were (1) increasing the number of redox electrons per transition metal, (2) minimizing the weight and volume of the host framework, and...
few reports claim reversible two-electron reaction in Li₂Mn₂O₄ are also included. The practical capacity in a battery does not show any correlation to the theoretical capacity.

(3) raising the redox potential. The present status of these approaches is summarized in Fig. 11.

4.1 Exploration for >1e⁻ reaction

In order to overcome the capacity limit by the one-electron Fe³⁺/Fe²⁺ redox reaction, several compounds with the ratio Li/Fe = 2 were explored, including Li₂₋ₓFeSiO₄ (2.8 V),22 Li₂₋ₓFePO₄F (3.2 V),23 and Li₂₋ₓFeP₂O₇ (3.5 V).24 However, access to tetravalent iron, Fe⁴⁺, by removing a second lithium atom from the lattice is very difficult because of the too high Fe⁴⁺/Fe³⁺ potential and/or structural instability upon deep oxidation. Stable reversible reactions were confirmed only for the one electron reaction at 0 < x < 1. A few reports claim reversible two electron reaction in Li₁₋ₓFeSiO₄ (0 < x < 2) but with sluggish kinetics, which may be caused by a framework breaking surface reaction with atomic rearrangement. Such parasitic slow reactions are observed exclusively at very small nanoparticles that do not warrant application to practical electrode because of significant sacrificial decrease in volume energy density.

4.2 Lightening and compaction of host framework

In comparison to the oxide cathodes, the polyanionic framework compounds invariably suffer from lower theoretical capacity owing to the weight and volume penalty of constituent polyanion units. The metal borate (LiMBO₃) family forms a special class of polyanionic cathodes with the lowest-weight polyanions (BO₃)³⁻ with a molecular weight of 58.8, which is significantly lighter than the larger tetrahedral (PO₄)³⁻ unit with a molecular weight of 95.0. A large theoretical capacity of 220 mAh/g is calculated based on the LiFeBO₃ chemical formula, which is much higher than the 170 mAh/g for LiFePO₄. Furthermore, the true density of LiFeBO₃ is 3.46 g/cm³, which is close to that of LiFePO₄ and suitable for maximizing the volume energy density due to the minimum volume occupation of the planar triangle BO₃ oxygen unit. Carefully prepared LiFeBO₃ shows room temperature activity as a cathode with a capacity of >190 mAh/g at around 3 V versus Li.25,26 A significant positive impact is realized by avoiding surface poisoning due to contact with the ambient atmosphere. However, the voltage window of 1.5–4.5 V to cover large polarization is too large for practical applications. Moisture sensitivity is another important factor that needs to be investigated before its application in commercial products can be considered. Once these problems are solved, borates, rather than heavier and larger phosphates, could be a new avenue for the exploration of novel electrode materials.

4.3 Raising the Fe³⁺/Fe⁴⁺ redox potential

The cell voltages with M = Fe show the trend LiFeBO₃ < Li₃FeSiO₄ < Li₃FePO₄F < LiFePO₄ < Li₂FeP₂O₇ < LiFeSO₄F,27,28 This trend roughly follows the formal charges of the central atoms in the polyanions, which is consistent with the idea of the inductive effect. More essentially, the voltage is defined as the difference between the lithium chemical potential in the cathode and in the anode, leading to the simple thermodynamic definition ignoring PV and TS terms (P = pressure, V = volume, T = temperature, and S = entropy),

\[ E = (G_{\text{charged}} - G_{\text{discharged}})/nF. \]

Where, \( G_{\text{Li}} \), \( G_{\text{charged}} \), \( G_{\text{discharged}} \) are Gibbs free energies of lithium metal, charged cathode, discharged cathode, respectively, \( n \) is the number of electron to the redox reaction, and \( F \) is the Faraday constant. The overall thermodynamic scheme for voltage generation is summarized in Fig. 12 based on the Born Haber cycle. A shorter Fe⁺⁺–Fe³⁺ distance in the charged state is effective for enlarging \( G_{\text{charged}} \) and hence the operating voltage \( E \), while the influence of the discharged state \( G_{\text{discharged}} \) with smaller charge Fe⁵⁺ can be subordinated in energetics.29 Of particular interest is the trivalent phase of LiFeSO₄F and metal doped LiFePOₓ, which possess edge sharing Feₐ octahedra to minimize the Fe–Fe distance as distinguished from other lower voltage Fe-based polyanion cathodes with corner-sharing octahedra.

5. Alluaudite Na₃Fe₂(SO₄)₃: A 3.8 V Earth-Abundant Sodium Battery Cathode

At the present stage, Na-ion batteries are not a strong competitor for Li-ion chemistry by only considering sodium’s greater abundance compared to the well-established state-of-art Li-ion power packs. However, it has rapidly attracted the attention of many materials scientists. Both weak Lewis acidity and the large polarizability of the Na-ion allow fast charge transfer reactions at electrode/electrolyte interfaces and in bulk diffusion. Furthermore, unlike the incremental progress of the mature Li-ion systems, researchers of the immature Na-ion systems based on Na-ion intercalation are likely to discover new electrodes with ordered functional structures due to the difference in the ionic radius of Na and 3d transition metals, which may enable Na-ion batteries to surpass Li-ion batteries.

5.1 Li versus Na: Similarities and Differences

Renewed interest in sodium-ion chemistry has seen extensive research on various P2- and O3-type oxide layered compounds and their solid-solutions. Different from the lithium case, Na₂FeO₂ satisfies the tolerance criterion for layered structure, \( r_{\text{Na}}/r_{\text{Fe}} \approx 0.86 \), due to the larger ionic radius of Na⁺ (\( r_{\text{Na}} = 120 \text{ pm} \)) and Fe⁺⁺ (\( r_{\text{Fe}} = 76 \text{ pm} \)). To date, O3-type NaFeO₂30 and P2-type Naₓ[Fe₁₋ₓMnₓ]O₂ have
been reported, both suffering from low operating potential even by using a Fe4+/Fe3+ redox couple, and the stable reversible capacity is limited. In spite of the great success with olivine LiFePO4, the sodium analogue with the same structure has turned out to be unsuitable for an electrode. Although the switch to Na from Li is not easy with several technical difficulties. Unlike the oxides and various polyaniions (BO43−, PO43−, SiO44−) compounds, the SO42−-containing systems are acutely prone to thermal decomposition above ~400°C (leading to SO2 gas evolution). Additionally, inherent dissolution of SO42− in water makes it unstable in aqueous solution. Thus, we used low temperature (<350°C) solid-state methods to search new compounds in Na-Fe-S-O system.

5.2 Exploring Na-Fe-S-O system

Newer Fe-based compounds with higher electrode potential can be realized by replacing phosphate PO43− with sulphate SO42− units taking advantage of their higher electronegativity. This avenue was not easy with several technical difficulties. Unlike the oxides and various polyaniions (BO43−, PO43−, SiO44−) compounds, the SO42−-containing systems are acutely prone to thermal decomposition above ~400°C (leading to SO2 gas evolution). Additionally, inherent dissolution of SO42− in water makes it unstable in aqueous media. It rules out conventional high-temperature solid-state and aqueous solution-based synthetic routes. Thus, we used low temperature (Ti ≤ 350°C) solid-state methods to search new compounds in Na-Fe-S-O system.

During the search along the Na2SO4-FeSO4 tie line, we discovered the first sulfate compound with Alluaudite-type framework (Fig. 13). Deviating sharply from most of the AXMo6(XO4)3 type compounds adopting the NASICON-related structures, Na2Fe2(SO4)3 does not contain the lantern units [M6(XO4)3]. It would be convenient to denote AA′B2M2O12 as general alluaudite-type compounds, where A = partially occupied Na(2), A′ = partially occupied Na(3), B = Na(1), M = Fe2+, and X = S in the present case.

5.3 The highest Fe3+/Fe2+ redox potential

The Na2Fe2(SO4)3 cathode offers an average potential of 3.8 V (vs. Na/Na+) with smooth slopy charge-discharge profiles over a narrow voltage range in 3.3–4.3 V window, which is the highest-ever Fe3+/Fe2+ redox potential in any materials environment (Fig. 14). Abnormally high generating voltage can be explained by thermodynamic definition of voltage explained in section 4.3.; the edge sharing geometry of the Fe octahedra in Na2Fe2(SO4)3, will push up G°red due to the strong Fe3+–Fe2+ repulsion, leading to high E. Additionally, it offers excellent rate kinetics and cycling stability without demanding any additional cathode optimization. It forms an open framework host for efficient (de)intercalation of Na+ ions with very low activation energy.

Complementing this electrode performance, Na2Fe2(SO4)3 can be easily prepared and up scaled by low-temperature solid-state methods, though care should be taken on the hygroscopic nature. The sustainability of Na2Fe2(SO4)3 further arises from its economic Na–Fe–S–O elemental constitution. In earth’s upper crust, Na and Fe are the most abundant and geographically distributed alkali and (3d) transition metal respectively. Talking about sulphur and sulphate compounds, they are very economic and widely used in fertilizers, pesticides and chemical industries. In fact, they are extremely cheap, being a byproduct of fuel combustion, coal power plants and oil/petrochemical industries. Thus, Na2Fe2(SO4)3 form an ideal material for economic production and large-scale battery manufacturing.

6. Room-Temperature Hydrate Melt Electrolyte

Ever-increasing demand for better batteries has set extraordinarily high standards for electrolyte materials, which are far beyond the realm of a conventional electrolyte design. Superconcentrated (or highly concentrated) solutions are emerging as a new “realistic” class of electrolytes with various unusual functionalities beneficial for advanced battery applications. We have demonstrated several technical advances towards it versatile salt/solution combination.

Figure 13. (Color online) Comparison of PO4 vs. SO4-based Alluaudite-type compounds with general chemical formula AAXBM2(XO4)3.

Figure 14. (Color online) (a) Galvanostatic charging and discharging profiles of Na2Fe2(SO4)3 cathode cycled between 2.0 and 4.5 V at a rate of C/20 (2 Na in 20 h) at 25°C. (b) Overall comparison of the Fe-based cathode materials that can function as Na sources in Na-ion battery system.
reaction of Li$_4$Ti$_5$O$_{12}$ was demonstrated for the LiCoO$_2$ batteries. As a proof of concept, charge-discharge cycling of 2.4 V class of stable aqueous electrolyte, the reversible Li with 160 Wh kg$^{-1}$ fully selecting Li salt anions and exploring their eutectics.42 As a new way for the highest energy density (Fig. 15). As a new class of high-energy-density yet highly safe aqueous (Fig. 16), both of which were the consequence of the unusual aqueous liquid state unique to hydrate melts, where all water molecules are coordinated with Li$^+$ and thus free (un-coordinated) water molecules disappear. Further exploration of hydrate melts to optimize the synergetic effect, in combination with engineering approaches (e.g., surface coating), will enable us to suppress the residual water electrolysis even upon prolonged cycling at low rates. Anyhow, these significant features will open up a new field of hydrate melt electrochemistry, as well as an expanded research avenue for safe and high energy density aqueous batteries. Huge impact for the manufacturing is being released from highly dry atmosphere, which will significantly reduce the total cost including initial investment and daily electricity for mass production.

7. Toward Sustainable Batteries

Seeking for an extremely high-energy density rechargeable battery (based on an ideal desk calculations) far exceeding the present lithium-ion batteries, several candidates are under investigation including multi-valence guest batteries, lithium/sodium air battery, lithium sulfur battery, and all solid-state battery. However, these are not new technology at all, but the original concept had been proposed and explored several decades ago and unfortunately completely defeated by the smart lithium-ion technology. Thereby, we may call them “classical innovative batteries”. Based on the conventional concepts with decades of unsuccessful history, performances are tardily improved by applying more and more complicated-specific materials and processes. Naturally, none of these are truly recognized as a future realistic solution.

On the other hand, for batteries required for the coming IoT society, where the ownership of things will lose its value, the huge energy density might not be of paramount importance anymore. Technical priority would rather be put on price destruction, extreme durability/lifetime, high throughput productivity, and absolute avoiding of major social risks, i.e., natural resources, environmental issues, toxicity, and explosion. From such bird’s-eye view based on the authentic social requirements, materials exploration with “abundant” elements introduced in this article has already led to some commercial products or serious industrial development. Our present ambition is to construct aqueous battery with higher energy density than those of present non-aqueous lithium-ion battery; a prototype in my laboratory has now reached the target with stable operation over hundreds of cycles.
References


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