The Pathway to Discovering Practical Cathode Materials for the Rechargeable Li^+-ion Battery

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John B. Goodenough
The University of Texas at Austin, Austin, Texas, USA.

A BATTERY STORES electric power as chemical energy in two electrodes, the anode and the cathode, which are separated by an electrolyte. The chemical reaction between the electrodes has an ionic and an electronic component. The electrolyte transports the ionic component inside a cell and forces the electronic component to traverse an external circuit. This chemical reaction is reversible in a rechargeable battery. The following is a personal narrative of the insights that led to the development of the first practical rechargeable Li^+-ion battery cathode, $LiCoO_2$, and the following research that developed from this discovery.

In the 1960s, Jean Rouxel in France and Robert Schroeder in Germany were exploring the chemistry of reversible insertion of lithium into the van der Waals gap of layered transition-metal sulfides. At that time, rechargeable batteries used strongly acidic (H_2SO_4) or alkaline (KOH) aqueous electrolytes that offered fast hydrogen-ion (H^+) diffusion. The most stable cells used an alkaline electrolyte and a layered nickel oxyhydroxide (NiOOH) as the cathode into which H+ is inserted reversibly to form the hydroxide

Ni(OH)2. However, an aqueous electrolyte limits the voltage of the cell and, therefore, the density of electric power that a battery can deliver.

In 1967, Joseph Kummer and Neill Weber of the Ford Motor Company discovered fast sodium-ion diffusion above 300°C in a ceramic electrolyte and assembled a sodium–sulfur rechargeable battery that used this solid ceramic as the electrolyte, molten sodium as the anode and a carbon felt with molten sulfur as the cathode. Their battery was commercially impractical owing to its high operating temperature of above 300°C, but it stimulated research into solid electrolytes and alternative battery strategies. At the time, I was working on transition-metal oxides at the MIT Lincoln Laboratory, and I was asked to monitor the development of this battery. The assignment introduced me to electrochemistry and to the challenge of developing a better oxide-based sodium-ion conductor. In response, Henry Hong and I developed a $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ electrolyte that had a framework structure and supported fast sodium ion conductivity; it was dubbed NASICON (NA SuperIonic CONductor) by colleagues after I left for the University of Oxford in 1976.[1]

In the early 1970s, an oil crisis exposed the vulnerability of US society, among others, to its dependence on imported oil and subsequently prompted investigations into solar and wind energy as potential sources for electric power. However, the intermittency of solar and wind meant that this power must be stored if these renewable sources were to be useful. Thus, there was a desire for rechargeable batteries that could serve this purpose efficiently.

At Oxford, I was free to work on problems related to energy. Initially, I selected two primary targets for my research program: the direct methanol-air fuel cell and the photoelectrolysis of water. The former requires a solid proton (H^+-ion) conductor for its electrolyte that is an electronic insulator and can operate near 300°C or an anode that is chemically stable in an acidic solution and catalytically active for the oxidation of methanol below 80°C. I soon found that good proton conductivity in a solid electrolyte can only occur when the solid is wet, which means operating below 80°C for fear of drying the solid. Our search for a sufficiently active and chemically stable anode for a direct methanol-air fuel cell proved unsuccessful, but it introduced me to the field of electrochemistry. Our attempt to realize a practical electrode for photoelectrolysis also involved electrochemistry. I had hoped to be able to use most of the spectrum of visible light by using a filled as well as a nearly empty d-electron band; however, the lower lying filled energy band proved to be too narrow for this strategy to be practical. The alternative was to attach a dye to the surface of the oxide. This exercise provided a good D. Phil. thesis, but it did not give a practical solution. I realized it would probably be better to separate the steps in the process by coupling a photovoltaic cell to an electrolysis cell to store solar energy as chemical energy in hydrogen gas as a portable fuel. More successful was my effort to identify a suitable cathode material for a lithium battery, an effort that has done much to bring together the solid-state chemist and the electrochemist.

The H^+ ion is the most mobile working ion in a rechargeable battery. However, protons are only mobile in an aqueous acidic or alkaline electrolyte. To avoid electrolysis of the water within a rechargeable battery with an aqueous electrolyte, the single cell voltage is restricted to less than 1.5 V if the battery is to have a long shelf life. A schematic of the open-circuit energy diagram of such a battery is shown in Figure 1.[2] This restriction limits the energy density of a rechargeable battery, which is why the advent of the cell telephone and the laptop computer had to await the arrival of the lithium rechargeable battery. The working Li^+ ion in a lithium battery is mobile in a nonaqueous electrolyte, which permits single-cell voltages over 4 V. Primary batteries using a lithium anode and an organic-liquid electrolyte were known at the time, so the next step was to use the chemistry demonstrated in Europe of reversible lithium-ion insertion into transition-metal layered sulfide cathodes to create a rechargeable battery. However, realization of a competitive rechargeable lithium battery required the identification of a cathode material into/from which Li^+ could be inserted/extracted reversibly over a large solid-solution range. Moreover, the active redox couples of the insertion compound electrode must have energies matched to the allowable energy of the electrolyte if larger voltages are to be achieved. Before I left Lincoln Laboratory, M. Stanley Whittingham had demonstrated intercalation of lithium into TiS_2 at the EXXON research laboratory.[3] The structure of TiS_2 consists of sheets of edge-shared $TiS_{6/3}$ octahedra held together by weak dipole-dipole (van der Waals) forces; lithium can be inserted/extracted reversibly between the layers over the solid-solution range Li_xTiS_2 $(0 \leq x \leq 1)$. With a metallic Lithium anode and a TiS_2 cathode, the TiS_2/Li single cell has a voltage of about 2.4 V over most of the solid-solution range. However, it was soon discovered that a metallic Lithium anode cannot be used in a practical rechargeable battery. On repeated charge/discharge cycles, dendrites from the anode grow across the electrolyte to the cathode to short-circuit the battery explosively. Therefore, this effort to realize a lithium battery was abandoned.

I had realized that it would not be possible to obtain a layered sulfide with a higher voltage versus a Lithium anode and, therefore, that an alternative insertion-compound anode would lower the output voltage to a value where the battery would not be competitive with a nickel/metal-hydride aqueous electrolyte system. A competitive lithium battery would require an oxide into/from which lithium can be inserted/extracted reversibly at a high rate over a large solid-solution range for its cathode.

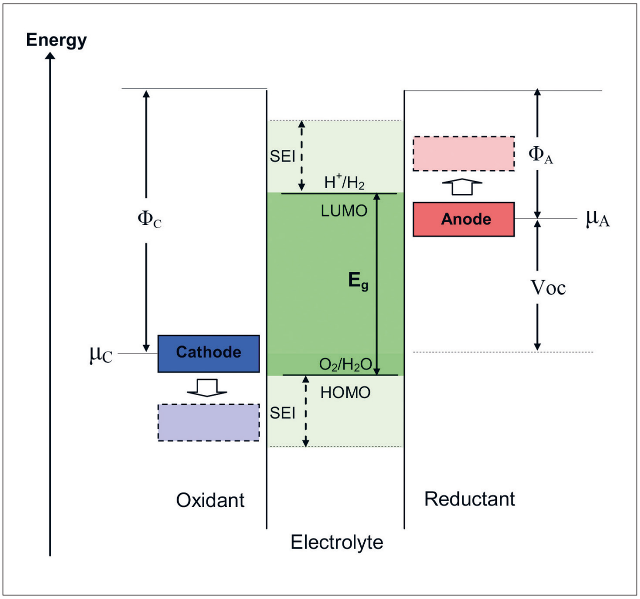

Figure 1. Schematic open-circuit energy diagram of an aqueous electrolyte. ΦA and ΦC are the anode and cathode work functions. E_g is the thermodynamic stability window of the electrolyte. A μ_A > LUMO[a] and/or a μ_C < HOMO[b] requires a kinetic stability by the formation of a solid electrolyte interphase (SEI) layer. Reprinted with permission from Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* 2010, **22** (3), 587–603. https://doi.org/10.1021/cm901452z.. Copyright 2010 American Chemical Society.

In 1978, an undergraduate thesis at Oxford on the structure of the $LiMO_2$ oxides reminded me of work I had done with Donald Wickham in the 1950s on $Li_xNi_{2-x}O2$.[4] The MO_2 oxides are not layered as is TiS_2; the electrostatic energy between the O^{2-} ions of MO_2 sheets is larger than the dipole-dipole van der Waals binding energy. However, layered $LiMO_2$ is stabilized by the Li^+ ions between the MO_2 sheets, and the ions are well-ordered provided the sizes of Li^+ and M^{3+} ions are sufficiently different from one another. I decided to investigate how much lithium can be extracted reversibly from a well-ordered $LiMO_2$ layered oxide. I knew that to maximize the working voltage of the battery, we wanted to choose a material with an M^{4+}/M^{3+} redox couple that had an energy well below the Li^+/Li^0 couple of a metallic Lithium anode. My prior experience working on transition-metal oxides at Lincoln Laboratory provided me with the knowledge to know that chromium, cobalt, and nickel each had a d-band redox energy sufficiently far below the Fermi level of lithium to be inter-

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[a] Lowest Unoccupied Molecular Orbital
[b] Highest Occupied Molecular Orbital

esting to study as the M atom. An experimental physicist, Koichi Mizushima, had just come from the University of Tokyo to work with me at Oxford. I teamed him with my chemist post-doctoral assistant, Phillip Wiseman, to work on this investigation. We found that over half of the lithium could be removed reversibly from the structure with cobalt or nickel as the M atom; each of these $Li_{1-x}MO_2$/Li half-cells gave an output voltage near 4 V.[5,6] $LiCoO_2$, the structure of which is provided in Figure 2, was particularly interesting owing to the fact that it could be synthesized with the lithium layers and CoO_2 layers completely separate and ordered, with little presence of cation mixing. This feature allows for lithium to be reversibly inserted/extracted without hindrance within the lithium layer. $LiNiO_2$ is difficult to make in this way directly from lithium precursors; some Ni^{3+} ions always reside in the lithium layer, disturbing the perfect ordering desired for the layered $LiMO_2$ structural motif. However, no battery company in England, Europe, or the U.S. was interested in licensing a patent for these cathode materials; they could not imagine starting with a discharged battery even though the battery was to be rechargeable.

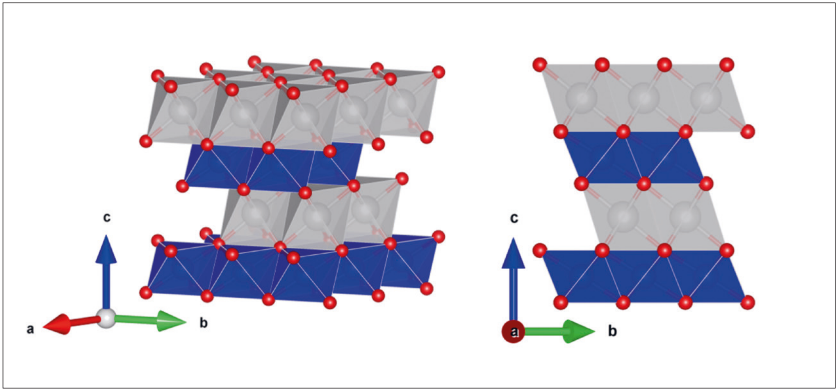


Figure 2. The structure of layered $LiCoO_2$. The $LiO_{6/3}$ octahedra are represented in silver and the CoO6/3 octahedra are represented in blue.

In 1982, Rachid Yazami and Philippe Touzain reported the dendrite-free intercalation of lithium into graphitic carbon with a potential near that of metallic lithium – see Figure 3a–b.[7] It did not take long for Akira Yoshino at Asahi Kasei Corporation to realize that this graphitic carbon electrode could be used as a discharged anode to go with our discharged $LiCoO_2$ cathode, and he assembled the first C/$LiCoO_2$ Li-ion cell. This battery cell was then licensed and developed by the SONY Corporation, who were hoping to find a rechargeable battery of high energy density so that they could market a wireless telephone. Thus, the wireless revolution was born.

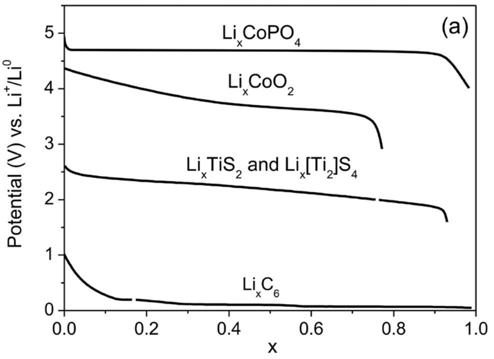
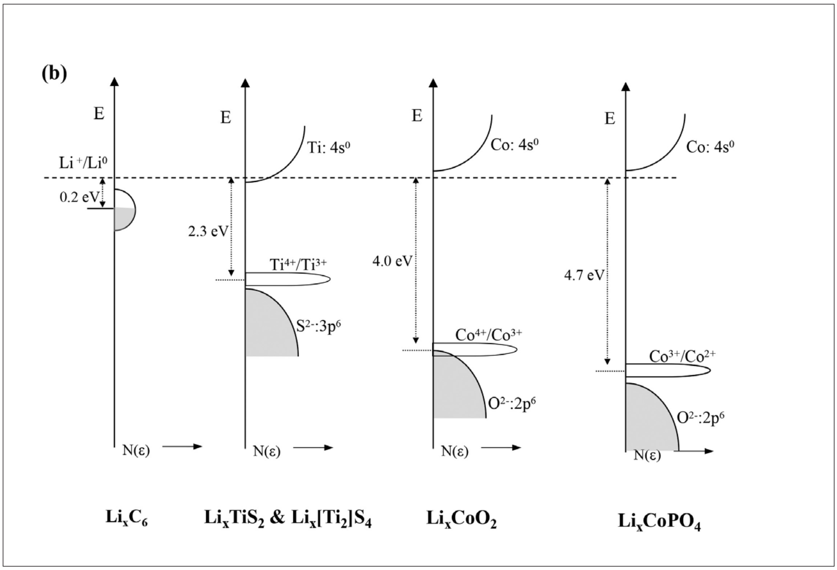


Figure 3. (a) Voltage profiles versus Li^+/Li^0 of the discharge curves of Li_xC_6, Li_x-TiS_2 and $Li_x[Ti_2]S_4$, Li_xCoO_2, and $Li_xC_oPO_4$. (b) Schematic of their corresponding energy vs density of states showing the relative positions of the Fermi energy in an itinerant electron band for LixC6, the Ti^{4+}/Ti^{3+} redox couple for Li_xTiS_2 and $Li_x[Ti_2]S_4$, the Co^{4+}/Co^{3+} redox couple for Li_xCoO_2, and the Co^{3+}/Co^{2+} redox couple for $Li_xC_oPO_4$. Reprinted with permission from Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* 2010, 22 (3), 587–603. https://doi.org/10.1021/cm901452z. Copyright 2010 American Chemical Society.



Cobalt is expensive and toxic. In 1981, Michael Thackeray came from South Africa to work with me on inserting lithium into the ferrospinel magnetite, Fe_3O_4. He wanted to develop a less expensive cathode than $Li_{1-x}CoO_2$. Bruno Scrosati of Rome had reported a similar experiment in a seminar I had learned of two weeks prior to Thackeray's arrival. I was skeptical of this result as I knew that the spinel structure cannot tolerate excess cations. Therefore, I asked Thackeray to repeat this experiment in my laboratory. When he confirmed the insertion of lithium into magnetite, I realized that the insertion of lithium must be displacing the tetrahedral-site iron to the empty octahedral sites of the structure to form an ordered rock-salt phase. This insight made me realize that the spinel octahedral-site $[M_2]O_4$ array represented a three-dimensional framework into/from which lithium could be inserted/extracted reversibly. Therefore, I asked Thackeray to insert lithium into the manganese spinel $Li[Mn_2]O_4$.[8] The $Li_{1+x}[Mn_2]O_4$/Li half-cell gave a flat 3V open-circuit voltage. Thackeray would later extract lithium from the tetrahedral sites; the $Li_{1-x}[Mn_2]O_4$/Li half-cell gave a 4 V open-circuit voltage.[9] A sharp shift of 1 eV in the energy of the Mn^{4+} /Mn^{3+} couple occurs where the Li^+ ions change their occupancy cooperatively from all-tetrahedral to all-octahedral sites. Donald Murphy of the Bell Telephone Laboratory had independently prepared the spinel framework $[Ti_2]S_4$ by extracting copper chemically from $Cu[Ti_2]S_4$. In the sulfospinel framework, lithium enters only octahedral sites and the $[Ti_2]S_4$/Li half-cell gives a voltage identical to that of the original TiS_2/Li half-cell (Figure 3 a–b). In Li_xTiS_4, lithium occupies only octahedral sites. Chemical instability on cycling $Li[Mn_2]O_4$ over the 4-V solid-solution range $0 \leq x \leq 1$ prevented its commercial adoption as a lithium battery cathode.

Frameworks containing $(XO_4)^{n-}$ polyanions instead of oxide ions can not only open up the interstitial space for fast Li^+ -ion or Na^+-ion transport, but also provide the strong oxygen covalent bonding needed to lower the top of the O-2p or, with $(XS_4)^{n-}$, the top of the S-3p bands sufficiently to provide a $V_{oc} > 5.0$ V versus lithium. In our earlier search for a framework oxide giving fast 3D Na^+-ion transport in Lincoln Laboratory, we showed that $Na_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$ with $x = 2/3$ gives a superior Na^+-ion conductivity.[1] Therefore, I suggested exploring Li^+-ion insertion into $Fe_2(XO_4)_3$ frameworks with X = Mo, W, or S. Arumugam Mathiram showed that the voltage of these compounds jumps from $V_{oc} \approx 3.0$ V with X = Mo or W to 3.6 V versus lithium with X = S, each operating on the Fe^{3+}/Fe^{2+} couple.[10, 11] This experiment demonstrated the influence, through the inductive effect, of the counter cation X on the Fe^{3+}/Fe^{2+} redox energy. At the University of Texas at Austin, I assigned to my engineering student, Akshaya Padhi, and my post-doctoral fellow, Kirakodu Nanjundaswamy, the task to explore the relative energies of transition-metal redox couples in the NASICON framework: $M_2(XO_4)_3$. Different transition-metal atoms and polyanions (XO_4) can be accommodated in the framework with the charge of the framework being balanced by Li^+-ion guests over the range $0 \leq x \leq 5$ in $Li_xM_2(XO_4)_3$.[12] In this framework, the energy of the redox couples appear to be essentially insensitive to the location and number of lithium ions in the interstitial space. I was also interested in knowing how these redox energies shifted on changing from $(SO_4)^{2-}$ to $(PO_4)^{3-}$ or $(AsO_4)^{3-}$ polyanions. During the course of this work, Padhi found that Lithium can be extracted reversibly from $LiFePO_4$, which has the olivine structure.[13] The Li_xFePO_4/Li cell gives a constant 3.45 V open-circuit voltage over the range $0 \leq x \leq 1$. Made as small platelet particles, this cathode is capable of extremely fast rates of charge and discharge owing to the one-dimensional Li+-ion conduction channel being perpendicular to the face of the platelet. This discovery prompted the investigation of many other phosphate and pyrophosphate framework structures to elucidate further the effect of anion-framework on the energy of transition-metal redox couples in these materials, the results of which are summarized in Figure 4 for the Fe^{2+}/Fe^{3+} couple.[14]

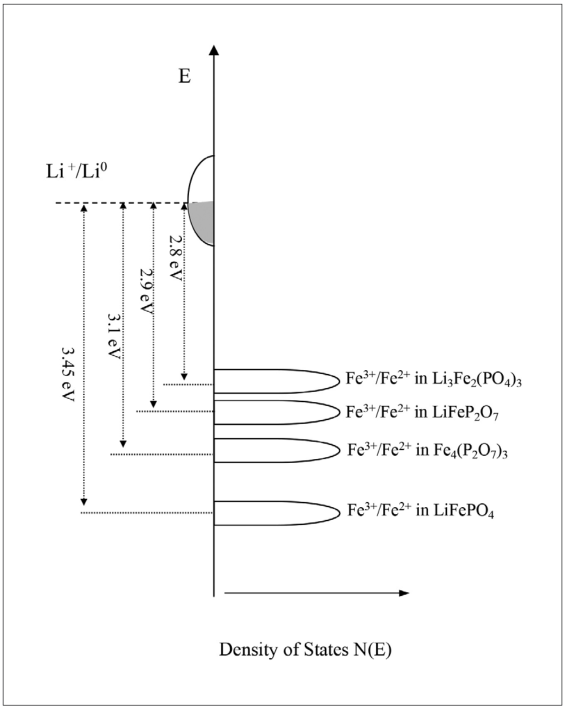


Figure 4. Relative energy levels of the Fe^{3+}/Fe^{2+} redox couple in different phosphate framework structures. Reprinted with permission from Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, 22 (3), 587–603. https://doi.org/10.1021/cm901452z. Copyright 2010 American Chemical Society.

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