Synthesis and Electrochemical Performance of a Lithium Titanium Phosphate Anode for Aqueous Lithium-Ion Batteries

Colin Wessells,* Fabio La Mantia,* Heather Deshazer,** Robert A. Huggins,**,z and Yi Cui**

Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA

Lithium-ion batteries that use aqueous electrolytes offer safety and cost advantages when compared to today's commercial cells that use organic electrolytes. The equilibrium reaction potential of lithium titanium phosphate is -0.5 V with respect to the standard hydrogen electrode, which makes this material attractive for use as a negative electrode in aqueous electrolytes. This material was synthesized using a Pechini type method. Galvanostatic cycling of the resulting lithium titanium phosphate showed an initial discharge capacity of 115 mAh/g and quite good capacity retention during cycling, 84% after 100 cycles, and 70% after 160 cycles at a 1 C cycling rate in an organic electrolyte. An initial discharge capacity of 113 mAh/g and capacity retention of 89% after 100 cycles with a coulombic efficiency above 98% was observed at a C/5 rate in pH-neutral 2 M Li_2SO_4. The good cycle life and high efficiency in an aqueous electrolyte demonstrate that lithium titanium phosphate is an excellent candidate negative electrode material for use in aqueous lithium-ion batteries.
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The high power output and energy density of lithium-ion batteries have led to their widespread use as power sources for portable electronics. Most commercial lithium-ion cells rely on a highly flammable organic electrolyte. Concerns about the safety of these cells have largely precluded their adoption on larger scales. Improvement of the safety of lithium-ion batteries must occur if they are to be utilized for applications such as electric vehicles and industrial-scale energy storage.

The replacement of the organic electrolytes found in commercial lithium-ion cells with an aqueous electrolyte would resolve the safety concerns surrounding these devices. Aqueous lithium-ion batteries could therefore be used for applications that require excellent safety.

Prior Work

Several research groups have studied aqueous lithium-ion batteries, starting with demonstration of a full cell using $LiMn_2O_4$ and VO_2 electrodes in an aqueous lithium nitrate solution by Li et al.[1-4] In later years, other research groups investigated the behavior of common cathode materials such as $LiMn_2O_4$, $LiFePO_4$, and $LiCoO_2$.[5-9] Our own research group recently demonstrated a favorable performance of $LiCoO_2$ in aqueous lithium nitrate.[10]

The narrow electrochemical stability range of water limits the choice of lithium intercalation materials that may be used as electrodes in aqueous cells. $LiMn_2O_4$ and $LiCoO_2$ react with lithium at potentials near the upper limit of the electrochemical stability range of aqueous electrolytes. This allows their successful use as cathode materials in aqueous cells. However, the choice of a suitable anode material for an aqueous lithium-ion battery is more difficult. At a pressure of 1 atm, ambient temperatures, and a neutral pH, aqueous electrolytes will start to decompose below potentials of about -0.4 V with respect to the standard hydrogen electrode (SHE) or 2.6 V with respect to metallic lithium.

It has been shown that $LiTi_2(PO_4)_3$ (LTP) reacts with lithium at an open-circuit potential of 2.5 V with respect to lithium.[11] Thus it is among only a handful of materials currently known to intercalate lithium at potentials near the lower limit of the electrochemical stability range of pH-neutral aqueous electrolytes. The Nasicon crystal structure of LTP has good ionic conductivity, so early interest in this material focused on its development as both a solid electrolyte and an intercalation electrode.[11-15] More recently, LTP has been explored as a negative electrode material in aqueous lithium-ion batteries.[7,16,17] However, these studies examined the performance of a full cell that incorporated LTP, rather than focusing on the behavior of LTP alone.

To examine the behavior of just one electrode in a battery, reference and counter electrodes must be chosen carefully. Previous study of the performance of LTP in aqueous electrolytes used a saturated calomel electrode (SCE).[17] One disadvantage of the use of an SCE or Ag/AgCl reference electrode is that they typically require a flooded cell. In flooded cells the electrodes are generally not tightly constrained, so active material may gradually lose electrical contact with the current collectors. In addition, the vast excess of electrolyte used in a typical flooded cell may mitigate the effects of electrolyte decomposition.

In this study, partially delithiated Li_xFePO_4, obtained from Hydro-Quebec, was used as a reference electrode in aqueous cells. This material undergoes a reconstitution reaction with lithium at a reaction potential that is constant over a wide range of composition. A small change in composition will not affect the potentials of materials such as Li_xFePO_4 and $Li_{4+x}Ti_5O_{12}$, which operate by two-phase reconstitution reactions. This is crucial for the reliability of the reference electrode. Therefore, once their potentials are accurately measured they may be used as reference electrodes. The choice of a Li_xFePO_4 reference electrode allows construction of "coffee bag" or "pouch" cells that have a pressed geometry, allowing the use of minimal electrolyte while ensuring good electrical contact to the electrodes.

Previous studies of LTP in aqueous electrolytes used a platinum counter electrode.[16,17] Charge transfer between Pt and an aqueous electrolyte results in a change in pH, which may be detrimental to the performance of an aqueous cell. Our research group recently demonstrated the use of a large mass of partially delithiated $Li_xMn_2O_4$ as a counter electrode in an aqueous cell.[10] This helps to ensure that the composition of the electrolyte does not change, as $Li_xMn_2O_4$ reacts with Li^+ rather than water. If the mass of the $Li_xMn_2O_4$ in the counter electrode is much larger than the mass of the active material in the working electrode, then the potential of the counter electrode will not change substantially. A large mass of $Li_xMn_2O_4$ can therefore act as a reversible lithium sink in an aqueous cell. This is analogous to the use of a metallic lithium counter electrode in a cell containing organic electrolyte.

Experimental

Synthesis of lithium titanium phosphate.— $LiTi_2(PO_4)_3$ was synthesized by a Pechini method similar to one reported by Mariappan et al.[18] Approximately 3 g of titanium isopropoxide was added under constant vigorous stirring to a solution containing 40 mL of 30% hydrogen peroxide and 15 mL of 30% ammonium hydroxide.

The solution instantly turned yellow due to the formation of titanium peroxy complexes. After stirring for 20 min, citric acid was added to the solution in a 2:1 molar ratio with respect to titanium. After stirring for an additional 20 min, a stoichiometric amount of lithium carbonate dissolved in 10 mL of concentrated nitric acid was added to the solution. Immediately following the addition of this lithium precursor, a stoichiometric amount of ammonium phosphate monobasic dissolved in 10 mL of water was added. The solution was bright orange after the addition of the lithium and phosphate precursors. After stirring for 20 min, ethylene glycol was added to the solution in a 2:1 molar ratio with respect to titanium.

The temperature of the solution was then raised from room temperature to 80°C and held for 2 h. The temperature was then ramped to 140°C in 1 h and held for 20 min to polymerize the citric acid and ethylene glycol. The brown, foamy product was heated at 300°C for 2 h in air, ground, and then sintered at 800 or 900°C for 4 h in air. This produced a fine white powder, which was then ball-milled for 1 h.

The LTP was coated with conductive carbon by mixing it with a polymer of glucose in ethylene glycol before heating at 800°C in N_2. The details of the carbon coating method are a subject of active research and will be described thoroughly in a future publication. Thermogravimetric analysis found that the carbon-coated material was 96% LTP and 4% carbon.

Electrode preparation and cell construction.— A slurry containing the carbon-coated LTP was prepared by ballmilling it with amorphous carbon (Super P), poly(vinylidene fluoride) (PVDF), and graphite for 1 h before dispersing this mixture in 1-methyl-2-pyrrolidinone. The composition of the slurry was 76% carbon-coated LTP, 10% amorphous carbon, 10% PVDF, and 4% graphite by weight. The relatively large amount of carbon was present in order to assure that the properties that were measured were not perturbed by lack of electronic contact. The slurry was stirred at room temperature and was sonicated for 1 h immediately prior to electrode preparation. Electrodes containing LTP were prepared by dipping stainless steel mesh or foil into the slurry. The electrodes were then dried at 100°C for 1 h and roll pressed. The electrodes had mass loading of 5–10mg/cm².

Pouch cells were constructed to study the electrochemical properties of LTP in an organic electrolyte. Half-cells that contained an LTP working electrode, a lithium foil counter and reference electrode, and an organic electrolyte [1 M LiPF$_6$ in 1:1 ethylene carbonate (EC): diethyl carbonate (DEC) from Ferro] were prepared. Cyclic voltammetry and galvanostatic cycling were performed to determine the electrochemical properties of LTP in this organic electrolyte.

Cells utilizing an aqueous electrolyte containing *p*H-neutral 2 M Li$_2$SO$_4$ were also constructed. For cyclic voltammetry measurements, a flooded cell geometry with a Ag/AgCl reference electrode and a platinum counter electrode was used. For longer term galvanostatic cycling measurements, a constrained pouch cell geometry with a large Li$_x$Mn$_2$O$_4$ counter electrode was used. There was not sufficient space to use a commercial Ag/AgCl reference electrode, so a reference of LiFePO$_4$ was used instead.

To prepare the LiFePO$_4$ reference electrode, a slurry of LiFePO$_4$, amorphous carbon, and PVDF was deposited on stainless steel mesh. Galvanostatic cycling was performed on the LiFePO$_4$ and was halted when half of the lithium was removed from the material. The open-circuit potential of the LiFePO$_4$ was then measured against a Ag/AgCl electrode for 24 h immediately before the insertion of the LiFePO$_4$ electrode into the cells containing LTP. The Li$_x$Mn$_2$O$_4$ counter electrode was prepared as reported previously.[10]

Results

Physical characterization of lithium titanium phosphate.— The powder X-ray diffraction spectrum of the LTP matched the previously reported spectrum for this material. However, it was found
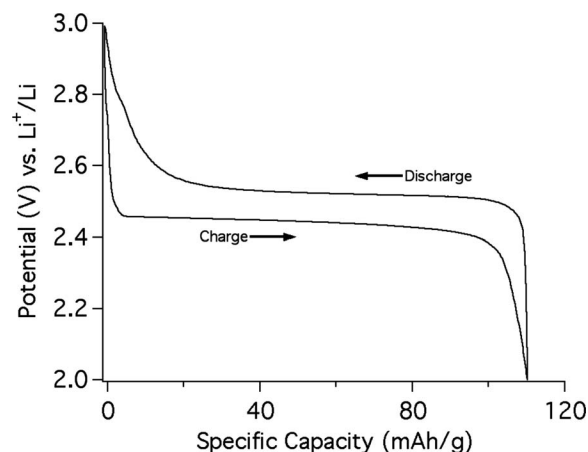

Figure 1. The voltage profile of the 30th galvanostatic cycle of LiTi$_2$(PO$_4$)$_3$ at a 1 C rate in organic electrolyte.

that if the temperature ramp between 80 and 140°C was performed too quickly, there were small additional peaks that indicated the presence of a second phase, TiP$_2$O$_7$.

Previous studies suggested that the formation of this impurity phase is due to a loss of lithium from the material at high temperature.[12,19] Scanning electron microscopy of the synthesized LTP showed large agglomerations (several micrometers) of fine particles. After ballmilling, the microstructure showed dispersed fine particles with sizes between 100 and 300 nm.

Electrochemical measurements of lithium titanium phosphate.— In order to confirm the electrochemical properties of the LTP that was synthesized in this way, cyclic voltammetry scans were performed at 0.1 mV/s on electrodes containing LTP powder in both organic and aqueous electrolytes. The reaction potential of the LTP was found to be approximately −0.5 V vs the SHE, and thus 2.5 V vs Li$^+$/Li, in agreement with previous studies.[11]

Galvanostatic cycling was performed on electrodes containing LTP in the organic electrolyte between 2 and 3 V with respect to Li$^+$/Li.

A first-discharge capacity of 115 mAh/g was observed at a cycling rate of 1 C. This is quite close to the maximum theoretical capacity, which is 138.8 mAh/g, based upon the insertion of two lithium ions into the crystal structure. The reaction of LTP with lithium during the 30th cycle of galvanostatic cycling at a 1 C rate in the organic electrolyte is shown in Fig. 1. A difference of 75 mV between the charge and discharge curves was observed at this cycling rate.

The decay of the discharge capacity of LTP during 160 cycles at the 1 C rate in the organic electrolyte is shown in Fig. 2. It can be seen that 84% of this initial discharge capacity was retained after 100 cycles, while 70% was retained after 160 cycles. The coulombic efficiency remained above 0.99 throughout cycling.

The X-ray diffraction of LTP samples after prolonged cycling found no apparent structural change. This suggests that the decay in capacity was due to the loss of electrical contact with some of the LTP particles.

Subsequent to this confirmation of the behavior of LTP in organic electrolytes, its electrochemical performance in an aqueous electrolyte was examined. Galvanostatic cycling was performed on electrodes containing LTP in *p*H-neutral 2 M Li$_2$SO$_4$ between −0.05 and −0.65 V with respect to SHE. The lower limit cutoff potential was 0.4 V higher for aqueous cells than for organic cells to avoid electrolyte decomposition.

In the aqueous electrolyte, an initial discharge capacity of 113 mAh/g was found. The 30th cycle at a C/5 rate is shown in Fig.
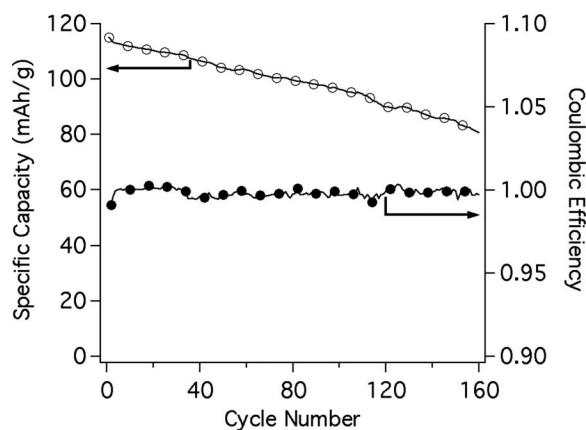
Figure 2. Specific capacity and coulomb efficiency of $LiTi_2(PO_4)_3$ at a 1 C rate in organic electrolyte vs cycle number.

Figure 5. Specific capacity and coulombic efficiency of $LiTi_2(PO_4)_3$ in pH-neutral 2 M Li_2SO_4 at various current densities.

3, while the cycle life and coulombic efficiency are shown in Fig. 4. It is seen that 89% of the initial capacity was retained after 100 cycles.

The coulombic efficiency was found to be ~0.98 in this electrolyte at the C/5 rate. This is somewhat lower than that found in the organic electrolyte and was presumably related to a minor amount of electrolyte decomposition in the potential range that was employed.
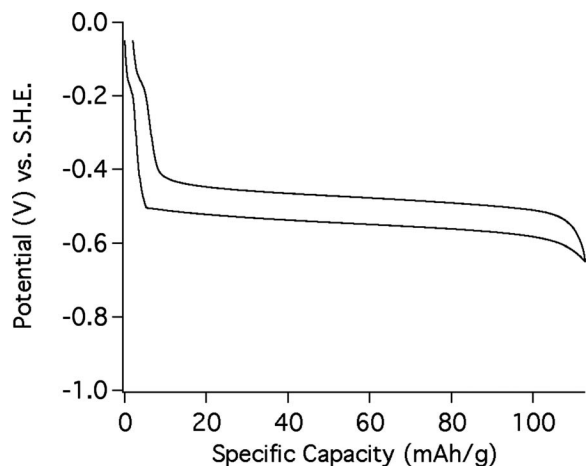

Figure 3. The voltage profile of the 30th galvanostatic cycle of $LiTi_2(PO_4)_3$ at a C/5 rate in pH-neutral 2 M Li_2SO_4.
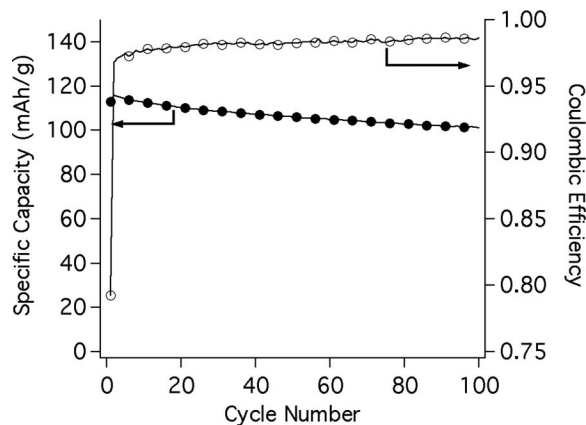

Figure 4. Specific capacity and coulombic efficiency of $LiTi_2(PO_4)_3$ at a C/5 rate in pH-neutral 2 M Li_2SO_4 vs cycle number.
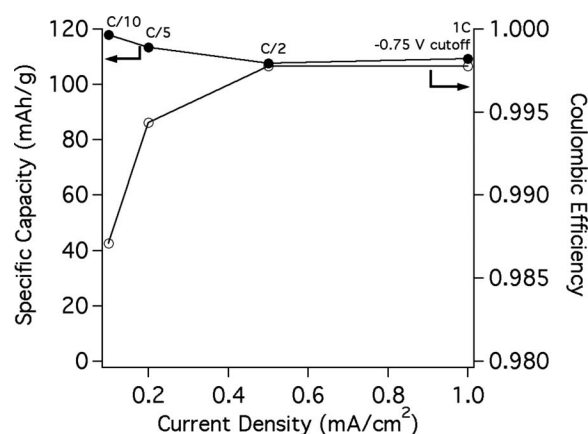
The measured coulombic efficiency should increase with the current rate, as the time spent outside the stability window of the electrolyte decreases by increasing the current rate.

This was confirmed by measurements made over a range of different charge–discharge rates, as seen in Fig. 5. It can also be seen in that figure that extending the lower cutoff voltage to −0.75 V with respect to the SHE provided a capacity of 110 mAh/g at a 1 C rate.

Summary and Discussion

Aqueous lithium-ion batteries can offer improved safety and lower cost when compared to cells utilizing organic electrolytes. It has been shown that a number of well-known materials can be used as positive electrode reactants in aqueous electrolyte lithium cells. The major challenge is to find materials with comparable properties for use in the negative electrode. The reaction potential and the relatively large theoretical capacity of lithium titanium phosphate (LTP) make it an attractive candidate material for this purpose.

In this work, LTP was synthesized using a Pechini type of method, followed by the deposition of a thin carbon coating. This material was made into a slurry containing additional carbon and deposited onto a stainless steel substrate to produce electrodes for electrochemical testing. Experiments were undertaken to evaluate its behavior in both a standard organic electrolyte and a pH-neutral 2 M lithium sulfate aqueous solution.

A partially delithiated Li_xFePO_4 reference electrode was used in the aqueous electrolyte experiments. This allowed the construction of three-electrode pouch cells. The use of this electrode and the compressed geometry gave improved performance compared to that observed with more a conventional flooded-cell arrangement.

Capacity values not far from the theoretical maximum value of 138.8 mAh/g were measured in both the organic and aqueous electrolytes. Cycling experiments also showed good capacity retention in both electrolytes. After 100 cycles, experiments at a 1 C rate in the organic electrolyte showed a capacity loss of only 16%, and those in the aqueous electrolyte at a C/5 rate had a capacity loss of only 11%.

It was found that the coulombic efficiency during cycling in the aqueous electrolyte was greater at higher charge and discharge rates, contrary to what is generally found in lithium-ion batteries. The reason for this is that there is some steady-state self-discharge in aqueous cells in which the electrode potential is beyond the equilibrium stability range of the electrolyte. The magnitude of this phenomenon varies with the extent of this deviation.[20]

Slower experiments, during which the electrode potential was in this range for longer times, showed greater capacity losses upon cycling. This loss can be minimized by constraint of the low end of

the potential range during cycling to that at which most of the capacity is found, rather than driving it down further to attain slightly greater apparent capacities.

Acknowledgments

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