



Short communication

## Recent results on aqueous electrolyte cells

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## ABSTRACT

The improved safety of aqueous electrolytes makes aqueous lithium-ion batteries an attractive alternative to commercial cells utilizing flammable and expensive organic electrolytes. Two important issues relating to their use have been addressed in this work. One is the extension of the usable voltage range by the incorporation of lithium salts, and the other is the investigation of a useful negative electrode reactant,  $\text{LiTi}_2(\text{PO}_4)_3$ .

The electrochemical stability of aqueous lithium salt solutions containing two lithium salts,  $\text{LiNO}_3$  and  $\text{Li}_2\text{SO}_4$ , has been characterized using a constant current technique. In both cases, concentrated solutions had effective electrolyte stability windows substantially greater than that of pure water under standard conditions. At an electrolyte leakage current of  $10 \mu\text{A cm}^{-2}$  between two platinum electrodes in 5 M  $\text{LiNO}_3$  the cell voltage can reach 2.0 V, whereas with a leakage current of  $50 \mu\text{A cm}^{-2}$  it can reach 2.3 V.

$\text{LiTi}_2(\text{PO}_4)_3$  was synthesized using a Pechini method and cycled in pH-neutral  $\text{Li}_2\text{SO}_4$ . At a reaction potential near the lower limit of electrolyte stability, an initial discharge capacity of  $118 \text{ mAh g}^{-1}$  was measured at a C/5 rate, while about 90% of this discharge capacity was retained after 100 cycles. This work demonstrates that it is possible to have useful aqueous electrolyte lithium-ion batteries using the  $\text{LiTi}_2(\text{PO}_4)_3$  anode with cell voltages of 2 V and above.

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### 1. Introduction

The wide electrochemical stability range of organic electrolytes allows lithium-ion batteries to operate at high voltages, which are useful in achieving the energy values necessary to power portable electronic devices. However, these organic electrolytes are highly flammable, and safer alternatives are needed if lithium-ion batteries are to be used on larger scales.

Aqueous electrolytes are inherently nonflammable, can have significantly higher ionic conductivity, and can cost significantly less than the common organic electrolytes. Aqueous electrolytes are generally thought to be electrochemically stable over a narrower voltage range than organic electrolytes. Aqueous lithium ion batteries are therefore considered for applications that require excellent safety at a low cost, and perhaps high power, but in which the specific energy and energy density are not critical.

The Dahn group was the first to demonstrate an aqueous lithium-ion battery, pairing  $\text{LiMn}_2\text{O}_4$  and  $\text{VO}_2$  electrodes in concentrated lithium nitrate [1–4]. Since that time, several research groups have reported aqueous lithium ion batteries using common lithium-ion positive electrode materials such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ , and  $\text{LiFePO}_4$  [5–10]. However, these materials react with lithium reversibly at potentials outside the 1.23 V electrochemical stabil-

ity window of pure water under standard conditions. This suggests that the electrochemical stability range of some aqueous lithium electrolytes may be substantially larger than that of pure water. In this work, the electrochemical stability limits of aqueous electrolytes containing lithium salts were determined using a constant current technique [11].

Whereas several of the common positive electrode reactants have been used in aqueous electrolyte cells, information on suitable negative electrode reactants is much more sparse.

Lithium titanium phosphate, originally studied for use as a solid-state electrolyte, has recently attracted attention for possible use as an anode in aqueous lithium-ion batteries, as it reacts at about 2.5 V versus pure lithium [12–18]. It is one of few lithium electrode materials currently known with a reaction potential suitable for that purpose. In addition,  $\text{LiTi}_2(\text{PO}_4)_3$  was shown to offer high capacity and long cycle life while reacting with lithium at a potential near the limit of the electrochemical stability of pH-neutral aqueous electrolytes [19].

### 2. Experiments on aqueous electrolytes containing lithium salts

One method that is sometimes used to examine the electrochemical stability of electrolytes is cyclic voltammetry (CV). However, this is a dynamic technique, and is often not sufficiently sensitive to observe the potential dependence of the onset of

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**Table 1**

Estimated full cell voltages of 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub> at various leakage current densities, found by extrapolating from measured full cell voltages at higher current densities. The measured full cell voltages at 50 μA cm<sup>-2</sup> are also included.

Current density	5 M LiNO <sub>3</sub> full cell voltage	2 M Li <sub>2</sub> SO <sub>4</sub> full cell voltage
1	1.52	1.72
5	1.85	1.95
10	1.99	2.05
25	2.17	2.18
30	2.30	2.26

electrolyte decomposition processes. In addition, batteries are generally operated at relatively constant voltages, rather than under potential scan conditions. Thus the CV scan method is not a useful way to determine the electrochemical stability window of a battery electrolyte.

Instead, it is better to examine the potential-dependent decomposition of battery electrolytes under steady-state conditions. In the work described here, constant current, rather than constant potential, measurements were used. It was found that constant potential experiments sometimes took a long time to reach equilibrium, during which a substantial amount of electrolyte had evaporated, and thus its composition had changed. In addition, constant current measurements allow a direct evaluation of the maximum cell voltage that can be used for an acceptable rate of electrolyte decomposition.

A three-electrode cell with excess electrolyte was used. Aqueous solutions of salts containing various concentrations of lithium nitrate and lithium sulfate were prepared using reagent grade commercial salts (Aldrich) and deionized water. The working and counter electrodes were platinum foil, while the reference electrode was Ag/AgCl. All reported potentials are with respect to the standard hydrogen electrode. Before each measurement the platinum foil was first washed with acetone, and then repeatedly washed in concentrated sulfuric acid, before being rinsed with deionized water. To accurately control the current density at the electrodes, all but 1 cm<sup>2</sup> of the platinum was masked with nonconductive nitrile cellulose. The platinum electrodes were immersed in excess electrolyte approximately 1 cm apart, with the reference electrode between them.

Constant current steps were applied to the platinum electrodes, and their equilibrium potentials were measured with respect to the reference electrode. Each current step was held for 1 h, enough time for the potentials of the working and counter electrodes to reach equilibrium. The full cell voltage was determined by the sum of the equilibrium potentials of the working and counter electrodes.

In all measurements, higher current densities led to higher working electrode potential, lower counter electrode potential, and larger full cell voltage. In addition, the potentials of the working and counter electrodes were found to vary linearly with the logarithm of the current density, in agreement with the Tafel relation. This behavior is shown for 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub> in Fig. 1. For 5 M LiNO<sub>3</sub>, a current density of 50 μA cm<sup>-2</sup> produced equilibrium working and counter electrode potentials of 1.75 and -0.55 V, respectively, yielding a full cell voltage of 2.30 V. Even larger equilibrium full cell voltages were measured at higher current densities. Similar behavior was observed for both 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub>.

For current densities that are not too small, the potential of an electrochemical reaction at a given current density can be estimated using the Tafel relationship to extrapolate from measured potentials at known current densities. Both 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub> were found to have behavior consistent with the Tafel relation over a wide range of current densities. Table 1 shows the estimated electrode potentials and full cell voltages at lower current densities for 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub>. Thus at a leakage current density of 10 μA cm<sup>-2</sup>, the estimated electrochemical sta-

bility windows of 5 M LiNO<sub>3</sub> and 2 M Li<sub>2</sub>SO<sub>4</sub> are 1.99 V and 2.05 V, respectively.

A battery electrode with a specific capacity of 1 mAh cm<sup>-2</sup> will require 100 h to discharge at 10 μA cm<sup>-2</sup>. In an actual 2 V aqueous battery, self-discharge due to electrolyte decomposition would take longer, as the platinum electrodes catalyze water decomposition and actual batteries are not continuously held at their maximum voltage. This suggests that aqueous lithium ion batteries of up to 2 V may be operated without rapid capacity loss due to electrolyte decomposition.

### 3. Synthesis and characterization of lithium titanium phosphate

The effective stability window of pH-neutral aqueous lithium electrolytes was found to range from about -0.5 V to over 1.5 V with respect to the standard hydrogen electrode. Common high potential materials such as LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> can be used as cathode reactants in these aqueous lithium electrolytes. However, anode materials such as graphite and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> have reaction potentials that are far too low to allow their use in aqueous electrolytes. Lithium titanium phosphate reversibly intercalates lithium at 2.5 V with respect to lithium, or -0.5 V with respect to the standard hydrogen electrode. This makes LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> an ideal candidate for use as a low potential electrode reactant in aqueous electrolytes of neutral pH.

LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was prepared using a Pechini method similar to that developed by Mariappan et al. [20]. Briefly, 3 g titanium isopropoxide was dissolved in 40 mL 30% H<sub>2</sub>O<sub>2</sub> and 15 mL 30% NH<sub>4</sub>OH under constant stirring. The solution immediately became bright yellow as titanium peroxy complexes formed. Citric acid was added to the solution in a 2:1 molar ratio versus titanium. After approximately 30 min, stoichiometric quantities of Li<sub>2</sub>CO<sub>3</sub> in 10 mL concentrated HNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>PO<sub>4</sub> in 10 mL H<sub>2</sub>O were added. Ethylene glycol was added to a 2:1 molar ratio with respect to titanium, and the temperature of the solution was raised to 80 °C and held for 2 h. Then the temperature was ramped to 140 °C over 1 h, and then held at 140 °C for 20 min while a viscous brown gel was formed. This intermediate product was heated at 350 °C for 3 h, ground, and heated at 800 °C for 12 h. Powder X-ray diffraction found that the material was phase pure, while scanning electron microscopy found polydisperse particles ranging from 100 to 300 nm.

To improve the electronic conductivity of the material, the particles were coated with conductive carbon. After 1 h of high impact ball milling, the LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was sonicated in a solution containing a polymer of glucose and ethylene glycol. The particles were filtered, dried in vacuum, and heated at 800 °C for 1 h in flowing N<sub>2</sub>. Thermogravimetric analysis found that the carbon-coated LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was about 4% carbon by weight. Electrodes of carbon-coated LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, amorphous carbon (Super P), and PVDF were prepared on stainless steel foil, with a mass loading of 5–10 mg cm<sup>-2</sup>.

To confirm the electrochemical properties of the carbon-coated LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, half cells using a lithium counter electrode and an organic electrolyte of 1 M LiPF<sub>6</sub> in 1:1 ethylene carbonate/diethyl carbonate were constructed. The voltage profile of the thirtieth cycle of galvanostatic cycling at a 1C rate in an organic electrolyte half cell is shown in Fig. 2. Due to the conductive carbon coating, a very low hysteresis of 75 mV was achieved at this cycling rate. An initial discharge capacity of 115 mAh g<sup>-1</sup> was observed at a rate of 1C. After 100 cycles, 84% of this initial capacity was retained, and 70% was retained after 160 cycles (Fig. 3).

Three-electrode coffee-bag cells were constructed to evaluate the performance of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in an aqueous electrolyte, 2 M Li<sub>2</sub>SO<sub>4</sub> at a pH of 8. The working electrode was LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, while

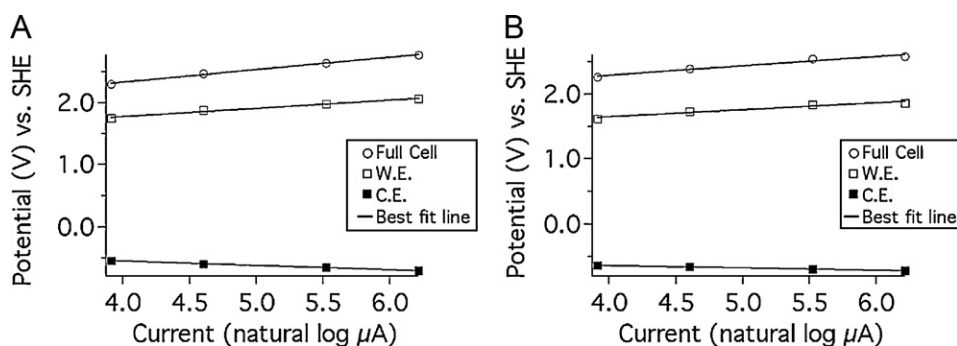


Fig. 1. Equilibrium full cell voltage and working (W.E.) and counter electrode (C.E.) potentials of 5 M LiNO<sub>3</sub> (A) and 2 M Li<sub>2</sub>SO<sub>4</sub> (B) as a function of current density.

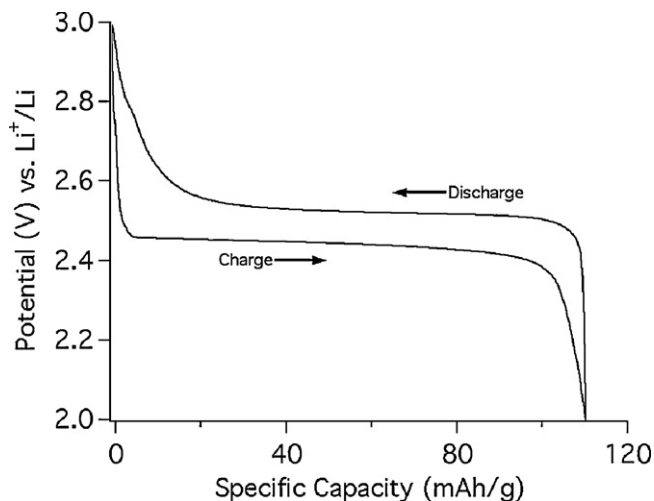


Fig. 2. The thirtieth galvanostatic cycle of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> at a 1C rate in an organic electrolyte.

the counter electrode was a large mass of partially delithiated Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>, produced by electrochemically charging LiMn<sub>2</sub>O<sub>4</sub> in the Li<sub>2</sub>SO<sub>4</sub> solution to remove some of the lithium. The mass of the Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> counter electrode was approximately 10 times the mass of the LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> working electrode, so neither its composition nor its potential changed substantially during cycling. Thus, it acted as a reversible lithium sink analogous to the lithium metal used in the half cell containing the organic electrolyte.

Typical reference electrodes such as Ag/AgCl are large and require a flooded cell geometry. A large excess of electrolyte may hide the effects of electrolyte decomposition on cell performance. To allow the use of pressed cells, a partially delithiated Li<sub>x</sub>FePO<sub>4</sub> reference electrode was used instead. Electrode materials such as LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> undergo reconstitution reactions, and their potentials do not change over a large composition range. Therefore, any small change in the composition of a Li<sub>x</sub>FePO<sub>4</sub> electrode should not alter its potential, and it may be used as a reference. A slurry of LiFePO<sub>4</sub> (Hydroquebec), Super P, and PVDF was deposited on stainless steel mesh. This electrode was then charged in 2 M Li<sub>2</sub>SO<sub>4</sub> until half of the lithium was removed. The potential was measured for 24 h immediately before the construction of full cells containing the Li<sub>x</sub>FePO<sub>4</sub> reference electrode, a Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> counter electrode, and the LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> working electrode. The electrodes were separated by filter paper (2 μm pore size) containing approximately 1 mL of electrolyte.

The voltage profile of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cycled at a C/5 rate between –0.05 and –0.65 V with respect to the standard hydrogen electrode in an aqueous electrolyte cell is shown in Fig. 4. An initial discharge capacity of about 118 mAh g<sup>–1</sup> was observed. At about –0.5 V with respect to the standard hydrogen electrode, the reaction potential of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is near the limit of the electrochemical stability of the electrolyte at a pH of 8. Ninety percent of the initial discharge capacity was retained after 100 cycles at a C/5 rate, while the coulombic efficiency was above 98% for most of cycling (Fig. 5). The loss in coulombic efficiency is due to electrolyte decomposition, so by raising the lower voltage cutoff of cycling (and therefore giving up some electrode capacity), higher efficiencies may be achieved.

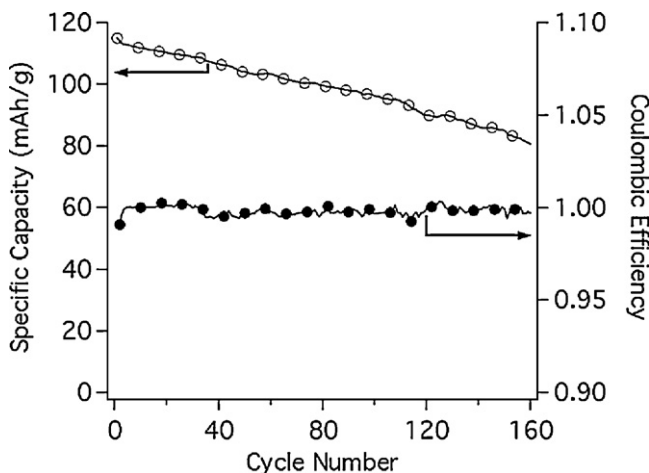


Fig. 3. Specific capacity and coulombic efficiency of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> during 1C galvanostatic cycling in an organic electrolyte.

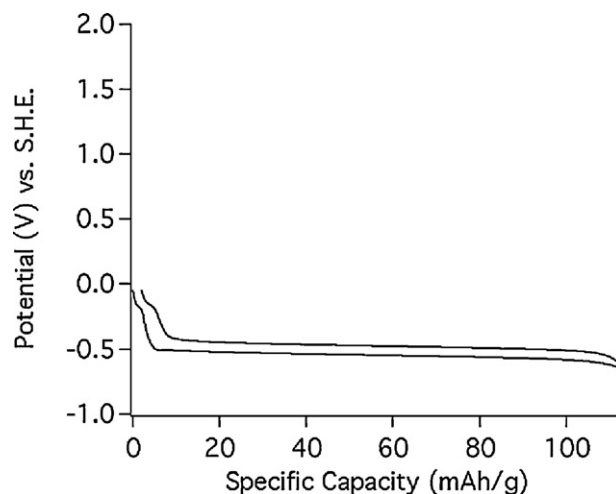


Fig. 4. The thirtieth galvanostatic cycle of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in 2 M Li<sub>2</sub>SO<sub>4</sub> at pH 8 at a C/5 rate.

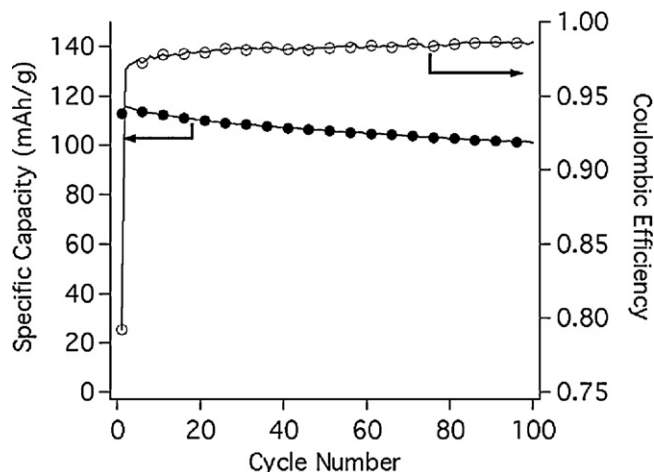


Fig. 5. Specific capacity and coulombic efficiency of  $\text{LiTi}_2(\text{PO}_4)_3$  during C/5 galvanostatic cycling in 2 M  $\text{Li}_2\text{SO}_4$  at a pH 8.

The total amount of electrolyte decomposed at an electrode at constant potential depends on the amount of time the electrode is held at a very low potential, so better coulombic efficiency is possible at higher cycling rates. For example, at C/2 cycling ( $500 \mu\text{A cm}^{-2}$ ), coulombic efficiency of over 99.5% is reached (Fig. 6).

#### 4. Summary and conclusions

Two electrolytes suitable for use in aqueous lithium-ion batteries were found to have useful electrochemical stability ranges substantially larger than the 1.23 V thermodynamic stability window of pure water under standard conditions.

At high salt concentrations a large fraction of all of the water molecules in solution participate in the hydration shells of the various ions, greatly reducing the water activity, and extending its thermodynamic stability range.

Low leakage current densities across concentrated aqueous lithium salts allow the use of large cell voltages. The widths of the stability windows of both concentrated lithium nitrate and lithium sulfate were found to increase with the logarithm of the allowable leakage current density. Extrapolating to low leakage current densities, both of these electrolytes were found to have useful voltage windows of about 2 V at leakage current densities of  $10 \mu\text{A cm}^{-2}$ . If leakage current densities up to  $50 \mu\text{A cm}^{-2}$  can be tolerated, the

useful voltage can be up to 2.3 V. This demonstrates that given the correct choice of electrode materials, aqueous lithium ion batteries may successfully operate at voltages well above the nominal thermodynamic stability of pure water.

$\text{LiTi}_2(\text{PO}_4)_3$  is an example of a negative electrode reactant that may be successfully operated near the limit of the electrochemical stability of a neutral aqueous lithium electrolyte. Its reaction potential of  $-0.5 \text{ V}$  versus the standard hydrogen electrode makes it ideal for neutral-pH electrolytes. The cells described here used a  $\text{Li}_x\text{MnO}_4$  counter electrode, so the full cell voltage was about 1.5 V. However, by the use of a cathode with a higher reaction potential, aqueous lithium ion batteries utilizing a  $\text{LiTi}_2(\text{PO}_4)_3$  anode could operate up to 2 V.

The  $\text{LiTi}_2(\text{PO}_4)_3$  synthesized here possesses high discharge capacity and long cycle life. As it is electronically insulating, particles of  $\text{LiTi}_2(\text{PO}_4)_3$  must be carbon-coated to allow good cycling performance. A gradual loss in capacity was observed during cycling of  $\text{LiTi}_2(\text{PO}_4)_3$  in both organic and aqueous cells. A possible cause for this capacity loss is the loss of electrical contact to some of the  $\text{LiTi}_2(\text{PO}_4)_3$  particles. X-ray diffraction of  $\text{LiTi}_2(\text{PO}_4)_3$  after many cycles did not show a change in crystallinity.

Aqueous lithium-ion batteries can offer excellent safety at low cost. Aqueous electrolytes are inherently nonflammable, and are therefore safer than contemporary commercial lithium-ion batteries containing organic electrolytes. In addition, aqueous electrolytes and the salts and separators used with them are significantly less expensive than the electrolytes and separators used in organic electrolyte cells. While pure water has a thermodynamic stability window of 1.23 V under standard conditions, concentrated lithium salt electrolytes can have a useful stability window of about 2 V, extending from  $-0.5 \text{ V}$  to over 1.5 V with respect to the standard hydrogen electrode at a pH of 7. Concentrated lithium nitrate and lithium sulfate perform similarly. Carbon-coated  $\text{LiTi}_2(\text{PO}_4)_3$  synthesized by a Pechini method can achieve high capacity and long cycle life in aqueous electrolytes, with a reaction potential near the lower limit of electrolyte stability. This demonstrates the principle of utilizing the entire effective stability window of an aqueous lithium electrolyte. If paired with an appropriate cathode material, future aqueous cells containing  $\text{LiTi}_2(\text{PO}_4)_3$  may operate up to 2 V.

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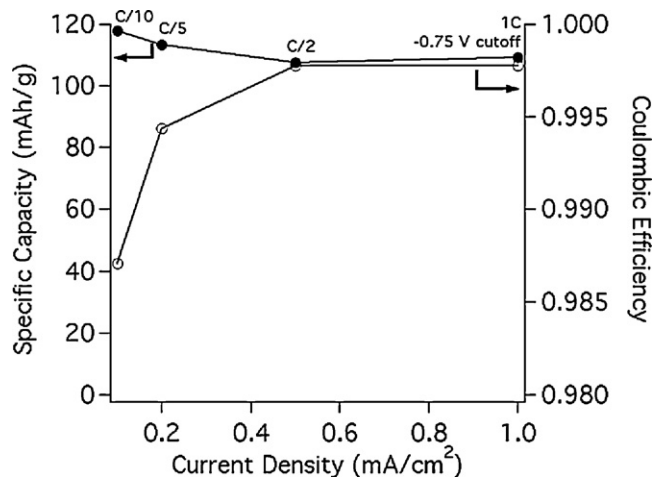


Fig. 6. Specific capacity and coulombic efficiency of galvanostatic cycling of  $\text{LiTi}_2(\text{PO}_4)_3$  in 2 M  $\text{Li}_2\text{SO}_4$  at a pH 8 at various current densities.

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