



## Letter to the Editor

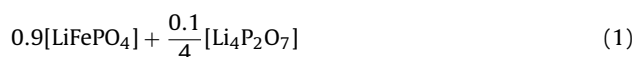
**Unsupported claims of ultrafast charging of LiFePO<sub>4</sub> Li-ion batteries**

Energy storage by batteries has become an issue of strategic importance. A scientific breakthrough in this context is the lithium-ion battery. Indeed, lithium-ion batteries can store up to three times more electricity and generate twice the power of nickel–metal–hydride batteries now in use, making possible great improvements in energy storage for electric vehicles and portable electronics. Major investments are being made for the commercial development of Li-ion batteries and there are government funds available offering \$billions in grants for research, development, and manufacturing. In this context, we wish to call attention to a deceptive paper that recently appeared in *Nature* [1], which has received much publicity since it announced an impossibly high recharging rate capability for a Li-ion battery of 9 s! Close examination of the work [1] shows that the authors have no direct evidence in support of such a high recharging rate, but imply their dramatic conclusion only from the high discharge rate. Experienced battery materials scientists would understand that the charge and discharge processes of batteries are basically asymmetric, resulting in rates of discharge that are generally much higher than rates suitable for recharge! The ability of a battery to be recharged in a few seconds, as the authors claim, would indeed be of great benefit, but this goal remains unmet despite the claims of Kang and Ceder [1] as we will explain herein.

The olivine material LiFePO<sub>4</sub>, used in the work reported by Kang and Ceder [1] is a very promising material that was first proposed in 1996 [2]. Hydro Quebec (HQ) recognized the potential of this material for Li-ion batteries after discussions with Professor John Goodenough in the same year. HQ has much experience with this material and has invested in R&D to promote this material for battery applications in order to make it practical for lithium rechargeable batteries by coating it with carbon [3].

We wish to specifically bring the following points to the attention of the battery community in order to correct numerous errors and claims in the work of Kang and Ceder [1], including their unsupported claims of an impossibly high 9-s charging-rate capability:

- (1) The authors in [1] claim to have made LiFe<sub>0.9</sub>P<sub>0.95</sub>O<sub>4-δ</sub> by creation of an iron:phosphorus deficiency. That is not true: the material is not this solid solution, and the material can be broken down as:



with  $\delta = 0.24$  (not specified in the paper). The material consists of well-recognized LiFePO<sub>4</sub> particles with a Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> impurity phase that, as with any impurity in such powders, is stuck on the surface. This situation is quite similar to the case where the

off-stoichiometry is Li excess, which also results in an impurity phase, this time Li<sub>3</sub>PO<sub>4</sub> [3]. A counter example is Li excess that results in a true solid solution [4].

- (2) This misunderstanding may have come from a mistake in the phase diagram presented in the supplement of [1]: one of the corners of the triangle is Fe<sub>2</sub>O<sub>3</sub>, which should have been FeO because it is in FeO that iron is divalent.
- (3) Eq. (1) opposes the idea expressed on page 190 of [1] according to which Mössbauer experiments suggest Fe<sup>3+</sup> in a pyrophosphate glass environment. Such an environment implies the existence of Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> since the juxtaposition of Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and LiFePO<sub>4</sub> involves a negligible amount of Fe at the interface between these two components. However, there is no evidence of Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> in the sample of [1]. On the other hand, the validity of Eq. (1) is confirmed by the photoelectron spectra and with the conclusion on page 191 of [1] that Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is present in their sample. However, let us point out that Eq. (1) does not explain the presence of Fe<sup>3+</sup> at the surface.
- (4) The presence of Fe<sup>3+</sup> in the surface layer of LiFePO<sub>4</sub> has been systematically observed and reported for years [5], and it has been discussed in [6]. In particular, even a short exposure to the humidity of ambient air is sufficient to delithiate a disordered surface layer owing to a reaction with water as has been investigated in [7]. This reaction is also the reason why Fe<sup>3+</sup> is systematically detected, even in a surface layer that does not contain any impurity phase of pyrophosphates; in [8], the absence of pyrophosphate was proven by the absence of any band in the gap between 700 and 900 cm<sup>-1</sup> of the FTIR spectra. In addition, lithium at the anode plays the role of a reservoir for lithium, so that a full discharge allows the lithium from the anode to re-lithiate the surface layer [7] provided that the exposure to humidity is not too long (less than a few months). That is the very reason why the capacity at 2C at full discharge is recovered (unexplained in [1]).
- (5) The main problem with the paper, however, comes from the part of reference [1] devoted to the electrochemical properties, which has a remarkable ambiguity in the captions of Fig. 3a and b that needs to be deciphered to understand how the experiments have actually been done. Fig. 3a is the discharge rate capability after charging at C/5 and holding at 4.3 V until the current reaches C/60. The next sentence explains that C/n denotes the rate at which a full charge or discharge takes n hours. Then comes Fig. 3b: capacity retentions when performing full charge–discharge cycles at 20C and 60C. The ambiguity is the following: does “full” refer to the cycle or to the charge and discharge. The text in page 191 mentions “C/n denotes the rate at which full charge or discharge takes n hours”, which is misleading since it suggests to the reader that the charge–discharge cycle at nC means both the charge and dis-

- charge portions are at  $nC$ , which is not true. The procedure used is provided by the fact that the 20C capacity in Fig. 3a is exactly that of the first cycle in Fig. 3b, so that the experimental procedure is the same. Therefore, “full” means that the charge is performed until the current reaches  $C/60$ , so that the charge has been performed at the slow rate of  $C/5$ , and only the discharge has been performed at the 20C, 60C . . . up to 400C rates.
- (6) It is true that a fast discharge can be obtained from nanoparticles of  $\text{LiFePO}_4$ , but not for the reasons invoked in [1], i.e., a fast-ion-conducting surface phase through controlled off-stoichiometry. It is well known that a surface layer a few nanometers thick is more or less disordered [6]. The degree of disorder can even be monitored by carbon coating and heating [6], and measurements of electrochemical properties for different degrees of structural disorder of the carbon have shown that the disorder does not improve the electrochemical performance. In any case, the surface layer is not a barrier for the lithium ions. Only the electronic conductivity of the surface layer is critical, which is why the particles are usually carbon-coated. Note that the carbon layer is porous so that it does not damage the ionic transport, and carbon allows electronic transport through the surface layer [3].
- (7) The authors [1] assume, on the basis of their theoretical model, that the ionic mobility of Li in  $\text{LiFePO}_4$  is  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$  so that a particle of 50 nm in diameter would lithiate or delithiate quasi-instantaneously (1 ms). The reality is very different. Such high ionic mobility may be encountered in single-phase solid solutions (like  $\text{LiAl}$  or  $\text{TiS}_2$ ), but not in  $\text{Li}_{1-x}\text{FePO}_4$ , in which two phases coexist. The diffusion coefficient (with restrictions for this meaning to two-phase materials) has been measured by different techniques. The experimental values are in the range  $10^{-14} \text{ cm}^2 \text{ s}^{-1}$  [8] to  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$  [9], for reasons that have been explained in [10]. And actually, the decrease of the capacity when discharging at a high rate may come from the fact that the lithium ions do not have enough time to enter into the core of the material (the plateau at 3.6 V has been lost, and the system is clearly out of equilibrium).
- (8) In addition, the calculation of the diffusion coefficient in [1] was made on the basis of diffusion in a homogenous solution, which is irrelevant to the case of  $\text{LiFePO}_4$  since the  $\text{LiFePO}_4/\text{FePO}_4$  system is bi-phasic under normal conditions. The lithiation/delithiation process is not a simple diffusion of uncorrelated  $\text{Li}^+$  ions. We have shown [11] that disorder favors the formation of a solid solution inside the surface layer. It is then possible that the resulting homogenous solution  $\text{Li}_x\text{FePO}_4$  in the surface layer supports a faster  $\text{Li}^+$  diffusion process, but not in the core region that is crystallized. The lithiation/delithiation process in the core region is not diffusion by isolated  $\text{Li}^+$  ions, but is a correlated motion that can be described in the framework of percolating modulated structures that are formed in a process similar to spinodal decomposition [12]. This, in essence, is the reason why fast discharge is possible in this material and the reason why it has been so extensively studied for a decade. We have pointed out in [12] that anomalous transport will take place where the size of the particle is reduced to the characteristic wavelength of this modulated structure. The existence of a lithium intercalation voltage of 3.4 V versus lithium metal in the electrochemical curves at low rates in papers [1,12] shows, however, that this anomalous situation has not yet been reached. And finally, the concept of a well-defined diffusion coefficient for ultrafast discharge experiments envisioned in [1] where the system is out of equilibrium is meaningless because, in that case, the diffusion coefficient strongly depends on time [13,14].
- (9) The authors in [1] claim that the conductivity comes from a coating of the particles with  $\text{Li}_4\text{P}_2\text{O}_7$ . That is unlikely.  $\text{Li}_4\text{P}_2\text{O}_7$  is usually the co-signature of  $\text{Fe}_2\text{P}$  impurities, which results in a poor life cycle of the batteries [15]. This degradation is not surprising because  $\text{Li}_4\text{P}_2\text{O}_7$  is not an electronic conductor.  $\text{Fe}_2\text{P}$  has been detected by XRD if the sintering temperature is raised to  $700^\circ\text{C}$ . At  $600^\circ\text{C}$ , the authors do not detect  $\text{Fe}_2\text{P}$  by XRD, but we have already shown that  $\text{Fe}_2\text{P}$  is an impurity that can poison the material even if it is not detected by XRD [16]. The authors claim that the performance is slightly improved with respect to stoichiometric  $\text{LiFePO}_4$ . However, the amount of  $\text{Fe}_2\text{P}$  is known to be quite sensitive to all the synthesis parameters [17], and deviation from stoichiometry is one of them. In particular, a small amount of  $\text{Fe}_2\text{P}$  that does not generate a significant amount of  $\text{Li}_4\text{P}_2\text{O}_7$  is known to improve the performance of  $\text{LiFePO}_4$  [15], at least in the short term before the iron of  $\text{Fe}_2\text{P}$  dissolves in the electrolyte.
- (10) There is no reason to believe that the  $\text{Li}_4\text{P}_2\text{O}_7$  impurity will coat the particles. Instead, impurities usually form nanoparticles that stick on the surface. This has been first deduced for  $\text{Fe}_2\text{P}$  and  $\text{Fe}_2\text{O}_3$  impurities in [16] from the analysis of magnetic properties, and observed experimentally in [18] by TEM images showing a 3-nm-thick impurity particle stuck at the surface of  $\text{LiFePO}_4$ . Actually, the thickness of the surface layer in [1] varies, with bumps about 5 nm thick, which is an additional indication that the impurities form nanoparticles at the surface of  $\text{LiFePO}_4$ . Indeed, in the absence of impurities, the surface layer is regular. Therefore, the results displayed in the paper suggest that the  $\text{Li}_4\text{P}_2\text{O}_7$  does not coat the particle, but is present as nanoparticles that stick at the surface of the particles like other impurities.
- (11) If the  $\text{Li}_4\text{P}_2\text{O}_7$  does not play a positive role, where does the possibility of fast discharge come from? Maybe, once again, it is the carbon coating. Synthesis of the samples has been made with precursors ( $\text{Li}_2\text{CO}_3$ ,  $\text{FeC}_2\text{O}_4$ ) that contain carbon, which is liberated upon heating from the disproportionation of CO and may generate such a carbon coating. The electronic conductivity of the carbon depends on the synthesis temperature. At  $600^\circ\text{C}$ , which is the synthesis temperature used in the experiments [1], Raman spectroscopy has shown that the carbon is essentially coke [17], which is considered to be a conductive form of carbon and can do the job.
- (12) The discharge results of 200C and 400C have been obtained by adding up to 65 wt.% carbon. On the one hand, the authors recognize that so much carbon is not appropriate for real batteries. Indeed, in a commercial cell, obvious practical considerations oppose more than 10 wt.% carbon. On the other hand, the reason why the authors could discharge at such high rates is due to the 65 wt.% carbon: so much carbon is needed to carry the current it transforms the battery into a carbon supercapacitor. There is no hope that such high discharge rates can be achieved in a commercial battery that contains less than 10 wt.% carbon.
- (13) Our efforts in research, however, are not only to make a battery that discharges fast. We are also looking for the opposite; the driver of an electric car wants a battery that can be charged as quickly as possible. In Ref. [1] the reader is led to think that if a battery can be discharged at rate  $nC$ , it could as well be charged at the same rate. The red line is crossed on page 192 where the authors speak about “the ability to charge and discharge batteries in a matter of seconds”, although they have not actually been able to charge a battery at this rate (see comment 5). In fact, there is no hope of charging the battery in [1] at such a high rate because it would generate dendrites on the anode and hence generate a short-circuit after a few cycles. That is the very reason why charging has to be at a slow rate and why only the discharge curves have been reported in [1].

The substitution of lithium by graphite for the anode would not help because formation of a passivation layer at the interface between graphite and electrolyte prevents the battery from surviving fast charging rates, which plate Li on the anode to promote dendrite formation that again can short-circuit the battery. This phenomenon illustrates that the anode is limiting the rate at which the battery can be charged.

- (14) The most misleading conclusion in [1], apart from the title of the work, is: “the rate at which very large batteries such as those planned for a plug-in hybrid vehicle can be charged is likely to be limited by the available power: 180 kW is needed to charge a 15 kWh battery in 5 min” (note that 5 min = 1/12 h, so in fact the authors have switched from 400C to 12C). We note that  $P = 180 \times 10^3 \text{ W}$  is the power mentioned above. So if the plug-in operating voltage is 200 V, the current is 900 A. However, one must remember that the internal resistance of the battery will be of the order of  $R = 1/4 \Omega$  so that the power dissipated by the Joule effect is  $R I^2 \sim 200 \text{ kW}$ , so that the energy lost to Joule effect heating after  $t = 5 \text{ min} = 300 \text{ s}$  (to end of charge) is  $R I^2 t = 60 \times 10^6 \text{ J}$ . Unfortunately, this is typically what you need to heat a four-story building! The problem is further exacerbated by the heat being concentrated in the small volume of the battery, so that this heat must be removed if you do not want your battery to be volatilized before the end of the first charge. To water-cool the battery, for instance, dissipation of  $60 \times 10^6 \text{ J}$  would cause 170 l of water to rise from room temperature to boiling point. So, an electric current of 900 A on recharging is not recommended for safety even if charge storage at his rate were possible.

## 1. Conclusions

An important performance target for a battery is a fast charge, but the laboratory cell in [1] has been tested at a rather slow charge rate of  $C/5$  that is very far from the “ultrafast charging” mentioned in the title and elsewhere in this work.  $\text{LiFePO}_4$  is a very important material for storing energy in Li-ion batteries, which justifies the efforts that are currently being made in R&D. Goodenough has promoted the  $\text{LiFePO}_4$ -cathode on the basis that “made as small particles, this cathode is capable of extremely fast rates of charge and discharge” [19]. However, this does not mean, like the authors [1] have claimed, that a Li-ion battery equipped with this cathode is capable of the same performance because the limiting rate at which a Li battery can be charged/discharged does not come from the cathode; it comes from the anode. To suggest that it is possible to charge lithium batteries for an electric vehicle in seconds or even minutes is a misleading conclusion that is not justified in the paper by Kang and Ceder [1]; and although appealing, is particularly deceptive for those less experienced in Li-ion battery technology.

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