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COMPARISON OF LiFePO$_4$ FROM DIFFERENT SOURCES

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ABSTRACT

The lithium iron phosphate chemistry is plagued by the poor conductivity and slow lithium diffusion in the solid phase. In order to alleviate these problems, various research groups have adopted different strategies including decreasing the particle sizes, increasing the carbon content, and adding dopants. In this study we obtained LiFePO$_4$ electrodes from six different sources and used a combined model-experimental approach to compare the performance. Samples ranged from one with no carbon coating to one with 15% coating. In addition, particle sizes varied by as much as a order of magnitude between samples. The study detailed in this manuscript allows us to provide insight into the relative importance of the conductivity of the samples compared to the particle size, the impact of dopant on performance and ideas for making materials in order to maximize the power capability of this chemistry.
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INTRODUCTION

Lithium iron phosphate (LiFePO$_4$) is a promising candidate for low-cost lithium batteries because it has a high theoretical capacity (170 mAh/g), excellent stability during cycling and expected to be safer compared with LiCoO$_2$ [1]. The major drawback with this material has been that it has low electronic conductivity, on the order of 10^{-9} S/cm [2]. This renders it difficult to prepare cathodes capable of operating at high rates. Significant research has recently been focused on the incorporation of conductive carbon into the active material powders [3-5] or the doping of the LiFePO$_4$ structure to improve its electronic conductivity [2,6]. Our group has been studying the LiFePO$_4$ invented at Hydro Quebec [3] and now supplied by PhosTech (Montreal, Canada) in our lab in pouch cells prepared with natural graphite anodes and either liquid [7] or gel electrolytes [8]. Nazar *et al.* reported the preparation of LiFePO$_4$ in a carbon gel matrix where the active material is dispersed in a carbon prepared from a resorcinol gel [4]. More recently, other labs are reporting excellent results from carbon-coated LiFePO$_4$'s made by other techniques such as gel-coating [9] and a carbo-thermal technique [10]. In addition to having low electronic conductivity, lithium diffusion in the active material has been reported to be slow, with considerable loss in utilization with increasing current [11].

Because of the low electronic conductivity of the active material, LiFePO$_4$, the performance of a LiFePO$_4$ cathode will depend on the <u>amount</u> of carbon in the structure, either *in-situ* or mixed in with the binder etc. However, Doeff *et al.* also found that the relative quality of the *in-situ* carbon on the LiFePO$_4$ particles also plays a major role in cathode performance [12]. The quality of the carbon, resulting from the addition of different organic precursors, was compared by measuring the sp2/sp3 character of the carbon in the LiFePO$_4$ after firing, by Raman spectroscopy.

In another approach to the problem, Chiang *et al.* found that doping of part of the Li in the structure for Nb, Zr, or Mg resulted in an increase in the electronic conductivities

by 8 orders of magnitude [2]. However, the improvement of the electronic conductivity of an active material powder is difficult to measure since most preparations involve organic precursors that result in residual carbon. In addition, the conductivity measurement requires dense pellets that in turn require higher temperatures (for sintering) than what is used to prepare cathode-active powders. This increases the risk that part of the $LiFePO_4$ will be converted into other (highly conductive) phases such as Fe_2P [13].

A low electronic conductivity active material, such as $LiFePO_4$, will require an excellent dispersion of conductive diluent, such as carbon, to prepare a high-performance cathode. In addition, the poor lithium diffusion means that the utilization of the active material will be a strong function of the solid-phase conductivity achieved as well as the loading and thickness of the structure. This dependence on loading makes it very difficult to compare the merits of different preparation techniques for $LiFePO_4$. In this work, we prepared cathodes from many sources of $LiFePO_4$. Performance at different rates was measured in half cells and the inevitable differences in cathode design were normalized through the use of a mathematical model of the discharge process in the $LiFePO_4$ cathode.

The model is based on the one developed previously by Doyle *et al.* in that it incorporates charge and mass balance in the porous electrode and reaction at the interface [14]. While the previous models have described the solid-phase phenomenon using intercalation behavior (diffusion in spherical coordinates), the present model describes the phase change that is known to occur in $LiFePO_4$ using the 'shrinking core' approach in keeping with X-ray diffraction (XRD) evidence of the existence of two phases [11].

EXPERIMENTAL

$LiFePO_4$ powders with varying amounts of in-situ carbon (carbon resulting form the phosphate preparation) were used as-received from the Institute of Chemistry (Lubjiana, Slovenia), Hydro Quebec (Quebec, Canada), U. of Waterloo (Waterloo, Canada), and SUNY (Binghamton, NY). The $LiFePO_4$ powders were combined with carbon black (Shawinigan) and/or graphite (SFG-6) and mixed into a slurry with Polyvidelyne fluoride (PVDF) (Kureha)/ N-Methyl Pyrrolidone (NMP). Slurries were cast with a knife-edge coater onto carbon-coated Al current collectors, prepared in-house from a very thin coating of PVdF-bonded Shawinigan black. In addition, pre-made cathodes were received from MIT and LBNL-MSD. The MIT cathode was prepared from 1% Zr-doped $LiFePO_4$ [2], and the LBNL cathode was prepared with the sol-gel technique with the addition of pyromelitic acid to the precursor mix [12].

The powders were analyzed with XRD to verify phase-purity and get an estimate of the average crystallite size by whole pattern fitting. Cathode performance was tested in a Swagelok half-cell containing Li reference and counter electrodes, with either 1 M $LiPF_6$ or 1 M $LiBF_4$ in ethylene carbonate/diethyl carbonate electrolyte and Celgard separators. Electrode capacity was determined at C/25, and high-rate utilization was measured at discharge rates from C/5 to 10C.

MODEL

The model developed describes the diffusion of lithium in the solid phase and the phase change in the material using the 'shrinking-core' approach, with a shell of one phase covering a core of the second phase. The model solves for the diffusion of lithium in the shell and the movement of the phase interface by assuming that the concentration

at the phase interface is at equilibrium. In addition, the distributed reaction in the porous electrode is described using porous electrode theory and the change in concentration of the electrolyte is accounted for using concentrated solution theory, as described previously [14]. Two particle sizes are included in the model in order to approximate the behavior of a true particle-size distribution.

We have previously used a well characterized cell based on the HQ material, where the particle sizes, area for reaction, loading and thicknesses were known, to compare the model to the data and extract unknown parameters. This cell was used to estimate the equilibrium-potential expression and the composition ranges of the single-phase regions in the material. The diffusion coefficient of lithium in the material was extracted by fitting the model to the experimental utilization with rate, resulting in a value of 8×10^{-18} m^2/s, consistent with values reported in the literature. The kinetics was assumed to be large, keeping with the prevalent view that the Li reaction is facile. These two values were then maintained for all the fits reported in this manuscript.

The comparison of the various materials reported here was performed by first fitting the model to experimental data at various rates to extract the particle-size distribution, the matrix conductivity and the contact resistance and then using these numbers to simulate behavior for a fixed cell design. We first fit the model to the utilization at the largest current to find the size of the small particle. Subsequently, we fit the utilization at the lowest current to find the size of the large particles. The parameters are then tested by predicting the utilization at other currents. The slope of the voltage-capacity curve at intermediate capacity values at the largest current is then used to extract the matrix phase conductivity. This slope occurs because of a changing reaction distribution in the porous electrode as discharge proceeds. Subsequently, we fit the voltage drop at this current to find the contact resistance. These two values are then tested by predicting the voltage and the slope at all other currents. For each material, the C/25 discharge curve was assumed to represent the equilibrium potential and a curve fit to an equation was used in the model. These were was also used to calculate the maximum capacity of each electrode. Once these parameters are extracted and tested, the comparison of the various materials is performed by simulating their behavior for a single thickness, porosity, and volume fraction of active material.

RESULTS AND DISCUSSION

LiFePO$_4$ Materials Properties

The samples were received over a period of a year and do not necessarily represent the best LiFePO$_4$ from any of the labs. The sample from SUNY was included as a baseline material to show the performance of pure LiFePO$_4$. The sources of LiFePO$_4$, the percentage of in-situ carbon (that resulting from the preparation process), estimates of the primary particle sizes taken from the literature or from the supplier and the measured XRD crystallite sizes are summarized in Table 1.

Electrochemical Studies

The compositions and loadings for the cathodes tested are also listed in Table 1. The fraction of active material in the cathode matrix fell in the range of 75 to 82%. It was not possible to keep the carbon content the same since the Waterloo material already contained 15% carbon and the MIT cathode only 10%. All of the cathodes were tested

with two cycles at C/25, and the second of these cycles is compared in Fig. 1. A specific capacity close to 150 mAh/g was observed for all of the cathodes except for the no *in-situ* carbon sample and the 15% *in-situ* carbon sample, as summarized in Table 1. The capacity of the Waterloo material was much lower than reported previously [4] and may hint at a degradation process in this material. Note the differences in the shape of the C/25 curve at the end of discharge. While the drop in potential is very sharp for the materials prepared by HQ and Slovenia, the other samples show a more gradual drop. Although a C/25 discharge may not be a true thermodynamic measurement, this may indicate differences in the phase composition in these materials.

Our standard protocol for variable rate measurements uses a constant charge at C/2, so that all the discharges start from the same place and the test can finish in a timely fashion. However, for modeling purposes, it is more convenient to assume that the cathode starts at a fully charged state before each variable rate discharge. Therefore, except for the MIT cathode, several cycles were also carried out with C/25 charging before the variable rate discharges. The discharge curves for the C/5 and 5C discharges for the six $LiFePO_4$ are compared in Fig.s 2A and 2B, respectively. It is clear that some treatment of the $LiFePO_4$, either doping or *in-situ* carbon, is necessary for adequate performance of $LiFePO_4$. This is consistent with the early work with the uncoated samples [11]. However, further comparison of these data is difficult, wince the best discharge curve (for the MIT cathode) is also for the lowest cathode loading.

Model Fitting and Predictions

The model was run for all six sets of cathode discharge data. Two of these fits are shown for the HQ material (Fig. 3a) and for the LBNL material (Fig. 3b). The excellent model predictions for the HQ material is expected considering that this is similar to the material that the unknown parameters were extracted from. The knee in the low-rate curve in Fig. 3a is caused by the two particle sizes in the model. As discharge proceeds the small particles fill up faster than the larger ones. Typically this mismatch in the state-of-charge can be expected to result in a greater change in the equilibrium potential of the small particles compared to the large, resulting in a larger overpotential, thereby allowing the larger particles to 'catch up'. However, the relatively flat potential for this two-phase system does not allow this to occur, and the mismatch between the two particles increases until the small particles are almost completely filled, at which point the potential drops, and the reaction shifts to the larger particles, resulting in a second plateau. Clearly incorporating more particle sizes into the model would remove this artifact.

The model predictions for the LBNL material [Fig. 3 (b)] are also excellent, especially in predicting the voltage drops with current. The fit is lacking in predicting the final drop in potential, especially at low rates. The particle sizes extracted for this material had the largest range among all the materials studied here (see Table 2). This suggests that the model would need to incorporate more particle sizes in order to predict this final decrease in voltage accurately.

Table 2 summarizes the particles sizes and matrix conductivities extracted using the model for all the materials. Its should be noted that this is an indication of the smallest length scale over which diffusion occurs and is therefore different from an agglomerate size, typically reported in the literature. The sizes extracted are of the order of the crystallite size for the various materials (Table 1). Note that in some cases (*e.g.,* LBNL) the small particle size extracted is smaller than the crystallite size. This is a consequence

of using two sizes to approximate a true distribution. It is clear that the MIT cathode data were fit with the smallest size and smallest range of particle sizes. This feature is the cause for the excellent behavior of the MIT material. The agreement with their particle size data (from Transmission Electron Microscopy) is remarkable. The particle sizes for the no-carbon sample are not significant due to the fact that the electrode was so ohmically limited. The fits of the HQ and the Slovenia cathodes were similar, although that for the HQ gave a significantly higher matrix conductivity. Note that the matrix conductivity value for the HQ electrodes is large enough that there is little ohmic drops.

The fitting parameters from each source of LiFePO$_4$ were used to calculate the expected performance for a cathode with a thickness of 85 μm and active material loading of 9.175 mg/cm^2 (same as the HQ electrode). The calculated C/5 and 5C curves are shown in Fig. 4 and can be compared to the experimental results in Fig. 2. Note that the Waterloo material is seen to have almost *ca.* 140 mAh/g in Fig 4 (a) as the mass of all the materials has been normalized in order to provide a fair basis for the comparison. The excellent utilization of the MIT material is clearly seen in Fig 4 (b), although the potential drops are more significant. The impact of the decreasing utilization and the drop in voltage with current can be captured in one plot by estimating the energy of the cell (area under the voltage-capacity curve, to a cut-off to 2.5 V) and plotting it against the average power (energy divided by the time of discharge), in the form of a Ragone plot, as shown in Figure 5.

As expected, the electrode with no *in-stiu* carbon shows the worst performance, while the electrodes from HQ and Slovenia show the best high-rate capability. While the MIT material shows much better intermediate rate behavior, a consequence of its smaller particle size, at higher rates, ohmic drops become more important, and the energy decreases. The two materials that have the widest particle size range, LBNL and Waterloo, shows poor intermediate rate capability, with the Waterloo material, with its lower average particle size, performing better. In order to give the reader an estimate of what can be achieved for this material, we perform a hypothetical simulation by using the best features of these different materials and represent it by the dotted line marked 'ideal' in Figure 5. This line was generated by using the particle size of the MIT material and the conductivity of the HQ material. As much as a doubling of the power capability can be achieved by better material preparation techniques. In summary, Figure 5 suggests that for this chemistry to be made more competitive three strategies need to be pursued (i) particle size should be made smaller (ii) the particle size ranges should be minimized, and (iii) the matrix conductivity needs to be improved. Figure 5 also suggests that all three factors are equally important. However, decreasing the particle size can lead to electrode fabrication issues and could lower the volumetric energy density, caused by the decreasing tap density, as suggested by Chen and Dahn [15]. This aspect is beyond the scope of this study.

CONCLUSIONS

Six LiFePO$_4$ electrodes having different particle size, carbon content, porosity and thickness were examined in this study in order to understand the mechanism that improves the power capability of this chemistry. This insight is provided by combining experimental data at various rates with a mathematical model. The study suggests that carbon coating is critical as it provides the electron with a more conductive path, thereby decreasing ohmic drops. While the amount of carbon coating seems immaterial as long as a coating is achieved, the quality of the carbon is important. However, the coating can be eliminated if the active material can be made more conductive, via doping. However,

carbon is still needed to carry the electron from the current collector to the reaction site, and therefore, electrode construction can be significant to performance. Finally, the utilization of the material can be poor if the particle size is large, or if the distribution of particles is wide.

ACKNOWLEDGEMENTS

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Table 1 Properties of LiFePO$_4$ Powders and Cathodes (NA- Not available)

Source	In-situ Carbon (%)	Particle Size (nm)	Crystallite Size (nm)	Active Loading (mg/cm^2)	Total Carbon (%)	Electrode Thickness (μm)	C/25 Capacity (mAh/g)
SUNY	0	NA	43	10.4	9	90	91
LBNL	0.9%	700	200	7.3	12.7	70	149
MIT	<1%	50 to100	36	4.4	10	55	150
HQ	1-2%	200	77	9.2	9	85	144
Slovenia	6.1%	<100	30	8.9	10	85	144
Waterloo	15%	100 to 200	81	7.8	17.2	80	130

Table 2 Model Fits and Comparisons

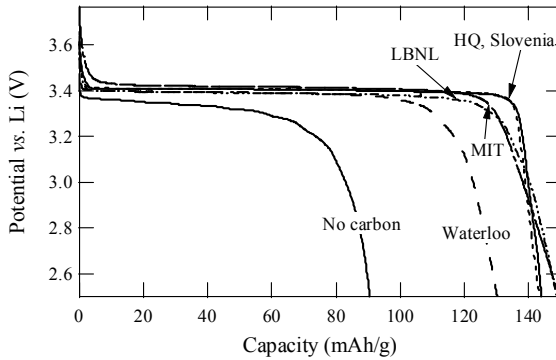| Source/Name	Amount of Carbon		Parameters from the Model Fit	
	Total (%)	In-Situ (%)	Matrix Cond. (S/m)	Particle Size (nm)
HQ	9	1 to 2	50	61 and 144
Slovenian	10	6.1	0.1	58 and 137
Nazar	17.2	15	0.03	21 and 340
LBNL	12.7	0.9	0.01	62 and 608
MIT	10	<1	0.01	64 and 119
no carbon	9	0	0.00035	133 and 288

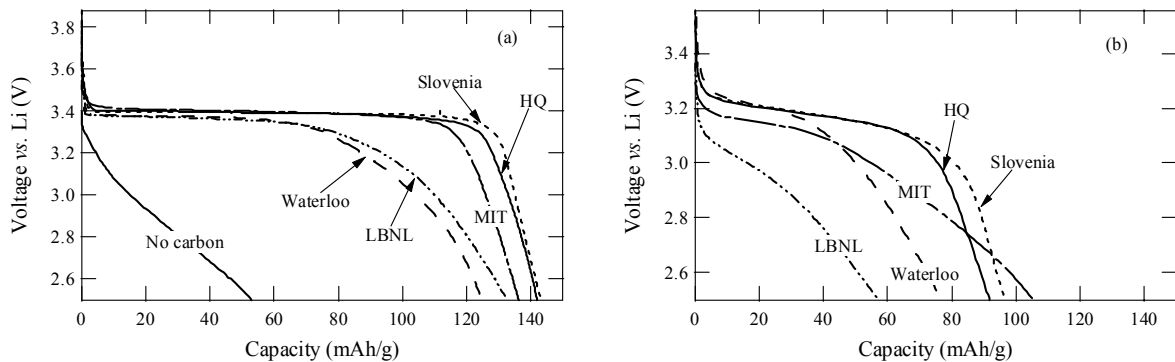Fig 1. Experimentally measured C/25 discharge curves of the six LiFePO$_4$ samples used in this study

Fig 2. Experimental discharge curves at C/5 (a) and 5 C (b) rates for the six samples with the no carbon curve omitted from (b).
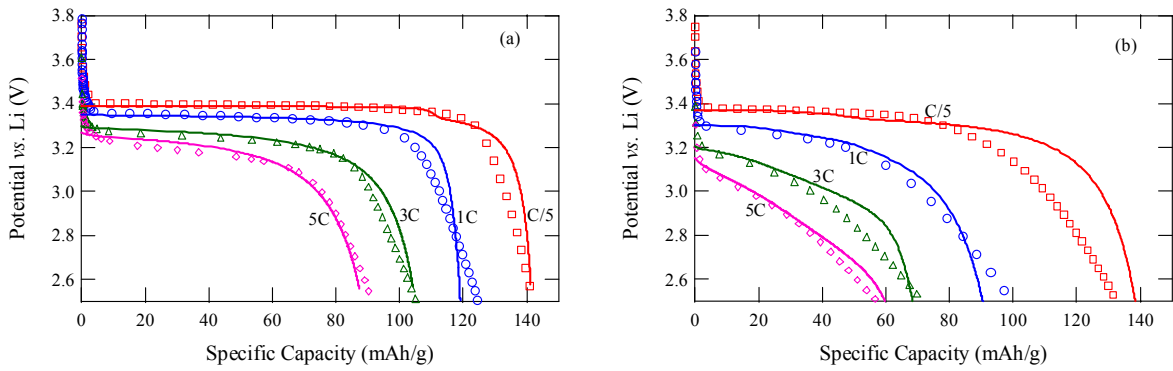
Fig 3. Model experimental comparisons of discharge curves at various rates for the HQ (a) and LBNL (b) material. Note that at 5 C the sample without carbon coating is not shown as there was no useful capacity in the material. See text for details.
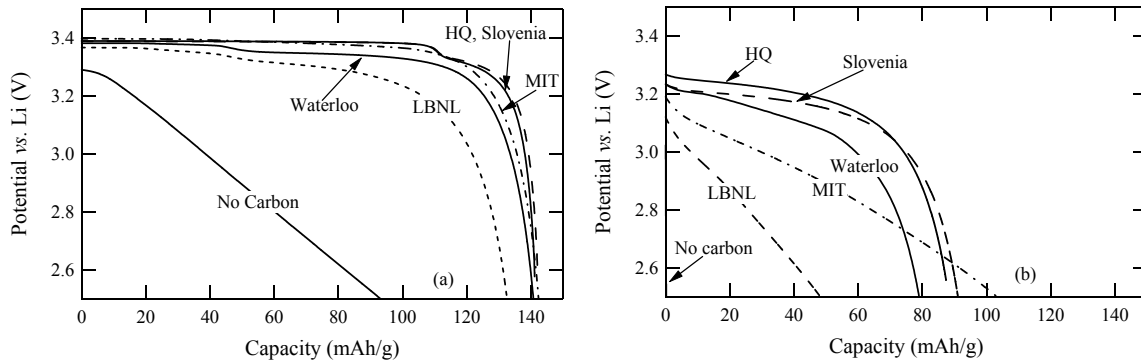

Fig 4. Simulated discharge curves for the six materials used in this study at C/5 (a) and 5C (b) rates. Compare with Fig. 2.
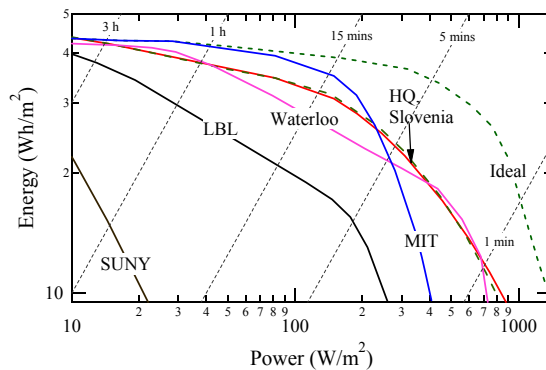

Fig. 5. Simulated Ragone plot for the various materials studied here. The curves were generated using the parameters extracted from the model-experimental fits, as described in the text, and using these values for a constant cell design. The curve marked 'Ideal' represents a hypothetical cell with particle sizes taken from the MIT material and conductivity of the matrix taken from the HQ material.