

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 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 powders and/or electrodes from six different sources and used a combined model-experimental approach to compare the performance. Samples ranged from 0.4% to 15% “in-situ” carbon. In addition, particle sizes varied by as much as an 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 having a distribution in particle sizes, and ideas for making materials in order to maximize the power capability of this chemistry.

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 prospect for a safer cell 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 carbon-coated LiFePO_4 invented at Hydro Quebec [3] and now supplied by PhosTech (Montreal, Canada) in pouch cells prepared with natural graphite anodes and either liquid [7] or gel electrolytes [8]. Huang *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 and/or electron 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 amount of carbon in the structure, either *in-situ* (*i.e.*, either formed during the preparation of the active material, or formed intentionally by adding, for example, sugar solution followed by carbonization) 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 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 sp^2/sp^3 character of the carbon in the $LiFePO_4$ after firing, by Raman spectroscopy.

In another approach to the problem, Chuang *et al.* found that doping (substituting) 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].

There are clearly several approaches to the preparation of a low-electronic-conductivity active material, such as $LiFePO_4$, into a high-performance cathode. The relative intrinsic conductivity as well as the location and quality of the added or *in-situ* carbon will play a role. In addition, poor solid-phase transport means that the utilization of the active material will be a strong function of the particle size. Together, these factors lead to a strong dependence of cathode performance on the loading and thickness of the electrode. This dependence on loading makes it 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 [15] in keeping with XRD evidence of the existence of two phases [11].

EXPERIMENTAL

LiFePO_4 powders with varying amounts of in-situ carbon (carbon resulting from the phosphate preparation) were used as-received from the Institute of Chemistry (Ljubiana, Slovenia), Hydro Quebec (HQ) (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 PVdF (Kureha)/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 pyromelic acid to the precursor mix [12].

The powders were analyzed with X-ray diffraction (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 low rate ($\sim C/25$), and high-rate utilization was measured at discharge rates from $C/5$ to $10C$.

MODEL DEVELOPMENT

The model developed describes the diffusion of lithium and/or electrons in the solid phase and the phase change in the material using the ‘shrinking-core’ approach, with a core of one phase covering a shell of the other phase, as described previously [15]. The model solves for the diffusion 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 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. The carbon coating that this known to exist in this material is not described in the model, and no distinction is made between this carbon and the extra added carbon when electrodes are fabricated. Instead, all conductivity effects are combined into the matrix phase conductivity whose magnitude is thought to capture the impact of both these carbons.

It should be noted that in the solid iron-phosphate particles, the lithium and the electron are envisioned to form a dilute binary electrolyte. This allows us to collapse the diffusion and migration terms into a single Fick’s law-type equation, as shown in Newman [16]. This means that the diffusion coefficient used in this paper is an effective diffusion coefficient which takes the form

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-} \quad [1]$$

Where z represents the charge on the ion, u the mobility, and D the diffusion coefficient. The subscript + represents the Li ion and the – represents the electron. Using the Nernst-Einstein relationship to relate the mobility to the diffusion coefficient and substituting in the charge of the electron and the lithium ion, equation 1 can be rewritten as

$$D = \frac{2D_+D_-}{D_+ + D_-} \quad [2]$$

Therefore the diffusion coefficient used in this paper depends on the relative magnitude of the electron and lithium ion diffusion coefficients. Recently Morgan *et al.* used first-principle calculations to estimate the diffusion coefficient of lithium in LiFePO₄ assuming that the concentration and mobility of electrons are large.[17] The authors concluded that the transport of lithium in the lattice is very large (of the order of 10⁻⁹ cm²/s) thereby suggesting that electron transport is slower than lithium ion transport in this material.[17] Using this result in equation 2 would suggest that the diffusion coefficient used in this paper (8×10⁻¹⁸ m²/s) would be two times the diffusion coefficient of electrons in the LiFePO₄ lattice.

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 electrons in the material was fit using the model to experimental data resulting in a value of 8×10⁻¹⁸ m²/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. A value of 3.14×10⁻⁶ A/m² (at a reference concentration of 1 M and 50% SOC) was used for the simulations. These two values were then maintained for all the simulations reported in this manuscript. All electrolyte properties were same as that used in Reference 15 and correspond to LiPF₆ salt in either EC:EMC or EC:DEC. One cathode used in this study (MIT) was cycled in LiBF₄ electrolyte but due to lack of transport properties for this salt, the simulations were conducted using the properties for LiPF₆. We have previously shown [15] that electrolyte drops

are negligible in cells with thickness and porosities similar to those used in this study. Hence the transport properties used should have little impact on the results presented in this paper.

The comparison of the various materials reported here was performed by first fitting the model to experimental data at various rates to extract the two particle sizes, the matrix conductivity and the contact resistance and then using these numbers to simulate behavior for a fixed cell design. Measuring particle sizes using transmission electron microscopy (TEM) can be difficult due to agglomeration effects. In addition, the technique results in a range of sizes while the model requires the use of two characteristic sizes which give the same overall behavior as the real electrode. Finally, the surface area measurements based on the BET technique, from which particle size can be estimated, can result in areas that can be different from the electrochemical surface area, especially for samples that have a large amount of carbon. For these reasons the particle size was chosen as a fitting parameter. The approach used for the incorporating the particle size involves three additional parameters, namely, the size of the small, size of the large and the size of the average particle. While the size of the small and large particles dictate the transport losses in the system, the size of the average particle is needed for find the total surface area of reaction, which in turn affects the kinetic losses. As the exchange current density is taken to be fairly large, the area has little impact on the simulations, and therefore, the model can be thought to have two unknown parameters that describe the particle size. 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. An average value between these two limits was used for the area calculations. As noted earlier, this quantity has little significance to the results shown in the paper. The slope of the potential-

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 between the current collector and the electrode. The contact resistance was found to negligible for all materials except for the one prepared by the MIT group. 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 in the single phase region and a curve fit to an equation was used in the model. This data 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

LiFePO₄ Materials Properties

The samples were received over a period of a year and do not necessarily represent the best LiFePO₄ from any of the labs. The low-carbon sample from SUNY was included as a baseline material to show the performance of LiFePO₄ with very low carbon content. However, the carbon in this sample was measured to be 0.4% by Luvak Laboratories (Boylston, MA). This amount of carbon resulted from the incomplete combustion of the organic precursors. XRD analysis was carried out for most of the electrodes, as shown in Figure 1. Comparison of the powder pattern for all LiFePO₄ samples shows that they are well crystallized in the orthorhombic (*Pmnb*) structure of LiFePO₄. [18, 19] However, some powders show a few very weak reflections from Fe³⁺-containing impurities such as iron oxide and/or lithiated iron oxide. The

weak reflections are mostly due to the low concentration of material in the powders as well as its lower crystallinity. Crystallite sizes were calculated from these diffraction data by whole-pattern fitting. These are summarized in Table 1, along with the sources of LiFePO_4 , the percentage of in-situ carbon (carbon resulting from the preparation process), and estimates of the primary particle sizes taken from the literature or supplied by the various sources of the LiFePO_4 materials.

Electrochemical Studies

The compositions and loadings for the different cathodes tested are 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 total carbon content the same since the Waterloo active-material powder already contained 15% carbon and the MIT cathode only 10%, as-received. All of the cathodes were tested with two cycles at $C/25$. The second of these discharge cycles is compared in Fig. 2. A specific capacity close to 150 mAh/g was observed for all of the cathodes except for the highest and lowest *in-situ* carbon samples (0.4 and 15%), 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 equilibrium 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, the variable rate discharge data used for the modeling effort were recorded after a C/25 charge. The curves for the C/5 and 5C discharges for the six LiFePO₄ cathodes are compared in Figs 3A and 3B, respectively. It is clear that some treatment of the LiFePO₄, either doping or deliberate *in-situ* carbon, is necessary for adequate performance of LiFePO₄. This is consistent with the early work with uncoated samples [11]. However, further comparison of these data is difficult, since the best discharge curve (for the MIT cathode) is also for the lowest-loading cathode. For this reason, these data were used for fitting purposes in order to enable comparisons between electrodes with the same design.

Model Fits and Predictions

The model described above was run for all six sets of cathode discharge data and the results are presented in Figure 4 to 6. Figure 4(a) shows the model-experimental comparisons for the HQ material. The excellent fits seen in this case are expected considering that this is the baseline used to extract the unknown parameters. The model does not predict the initial sharp drop in potential before the plateau region. We believe that this is caused by a narrow single-phase region in the completely delithiated material. As this single-phase region is not included in the model, no prediction of this behavior is expected. The knee in the low-rate (C/5) curve in Fig. 4a 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. 4 (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.

Figure 5 (a) shows the predictions for the material from MIT. As mentioned previously, this material shows a significantly slopey profile at the end-of-discharge at low-rates as compared to the other materials studied. The remarkable utilization of this material is clear in the figure, where the discharge at the 3C rate shows a potential profile that suggests that decreasing the potential cutoff below 2.5 V would have resulted in the material being completely utilized. This material stands out as having the best high-rate utilization. However, as the rate increases, potential drops occur in this material, suggesting that the preparation conditions have not resulted in an optimum matrix conductivity. In addition, this was the only electrode where a contact resistance was needed to get adequate fits to the data. A value of $0.0017 \Omega\text{-m}^2$ was found to fit the data adequately.

Figure 5 (b) shows the comparison of the Slovenia material. Both the behavior of the material and the extracted parameters are comparable to those from the HQ material. Finally, Figure 6 (a) shows the predictions of the material without carbon and 6(b) the material from the U. of Waterloo. The poor utilization of the material without carbon, even at relatively low rates, is due to the voltage reaching the cut-off potential much before any transport limitations become important. As the electrode is ohmically-limited, extracting transport related quantities (particle size) is not possible.

Table 2 summarizes the particles sizes and matrix conductivities extracted using the model for all the materials. It 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 2). 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. We believe that this feature is the cause for the excellent behavior of the MIT material. The agreement with their particle-size data (from TEM) is remarkable. The particle sizes for the low-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 ohmic drops are minimal.

The fitting parameters from each source of LiFePO_4 were used to calculate the expected performance for a cathode with a thickness of $85 \mu\text{m}$ 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. 7 and

can be compared to the experimental results in Fig. 3. While Fig. 3 shows the experimental data with cell design being different for each material, Fig. 7 shows the simulations for the same cell design. Note that the Waterloo material is seen to have almost *ca.* 140 mAh/g in Fig 7 (a) as the mass of all the materials has been made the same in order to provide a fair basis for the comparison. In addition, to make the comparison of the MIT material fair, no contact resistance was used in these simulations. The excellent utilization of this material is clearly seen in Fig 7 (b), although the potential drops are more significant.

The impact of the decreasing utilization and the drop in potential with current can be captured in one plot by estimating the energy of the cell (area under the voltage-capacity curve) 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 8. As expected, the electrode with the lowest *in-situ* 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, show poor intermediate-rate capability. Of these two, the Waterloo material performs better due to the material's lower average particle size.

Ideal Case

In order to give the reader an estimate of what can be achieved for this material, we performed a hypothetical simulation by using the best features of these different materials and represent it by the line marked 'ideal' in Figure 8. This line was generated by using the particle size of the MIT material and the conductivity of the HQ material. It is clear that as much as a

doubling of the power capability can be achieved by better material-preparation techniques. Each of the materials shown in the figure can be made to achieve this ideal performance, but changes would need to be made to the material properties. In summary, Figure 8 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 8 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 [20]. In addition, smaller particles would require more carbon and binder in order to bind the particles together to form an electrode, thereby resulting in decreased specific energy. This aspect is beyond the scope of this study, and hence no conclusions can be drawn on an optimum particle size to be used in these electrodes.

CONCLUSIONS

Six LiFePO_4 electrodes having different particle sizes, carbon contents, porosities 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, *e.g.*, via doping. However, carbon is still needed to carry the electron from the current collector to the reaction site, and therefore, electrode construction can have a significant

impact on performance. Finally, the utilization of the material can be poor if the particle size is large, or if the distribution of particle size is wide.

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Figure Captions

- Fig. 1. XRD diffraction pattern for five of the LiFePO_4 samples used in this study
- Fig. 2. Slow rate ($C/25$) discharge curves of the six LiFePO_4 electrodes vs. Li reference and counter electrodes measured at 25°C .
- Fig. 3. Experimental discharge curves at $C/5$ (a) and $5 C$ (b) rates for six LiFePO_4 electrodes. Note that at $5 C$ the sample with low-carbon coating is not shown as there was no useful capacity in the material.
- Fig. 4. Model-experimental comparisons of discharge curves at various rates for the (a) HQ and (b) LBNL material. See text for details
- Fig. 5. Model-experimental comparisons of discharge curves for the (a) MIT and (b) Slovenia material. See text for details
- Fig. 6. Model-experimental comparisons of discharge curves for the (a) low carbon and (b) U. of Waterloo material. See text for details.
- Fig. 7. Simulated discharge curves for the six materials used in this study at $C/5$ (a) and $5C$ (b) rates. Compare with Fig. 3. While Fig.3 has different designs, Fig 7 has the same design.
- Fig. 8. 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

Table 1 Properties of LiFePO₄ Powders and Cathodes

Source	<i>In-situ</i> Carbon (%)	Particle Size (nm)	Crystallite Size (nm)	Active Loading (mg/cm ²)	Total Carbon (%)	Electrode Thickness (μ m)	C/25 Capacity (mAh/g)
Low-carbon	0.4%0	NK	43	10.4	9	90	91
LBNL	0.9%	700	200	7.3	12.7	70	149
MIT	<1%	50-100	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%	100-200	81	7.8	17.2	80	130

NK- Not known

Table 2 Model Fits and Comparisons

Source/Name	Crystallite Size (nm)	Amount of Carbon		Parameters from the Model Fit		
		Total (%)	In-Situ (%)	Matrix Cond. (S/m)	Particle Size (nm)	
					Small	Large
HQ	43	9	1-2	50	61	144
Slovenia	200	10	6.1	0.1	58	137
Waterloo	36	17.2	15	0.03	21	340
LBNL	77	12.7	0.9	0.01	62	608
MIT	30	10	<1	0.01	64	119
low carbon	81	9	0.4%	0.00035	133	288

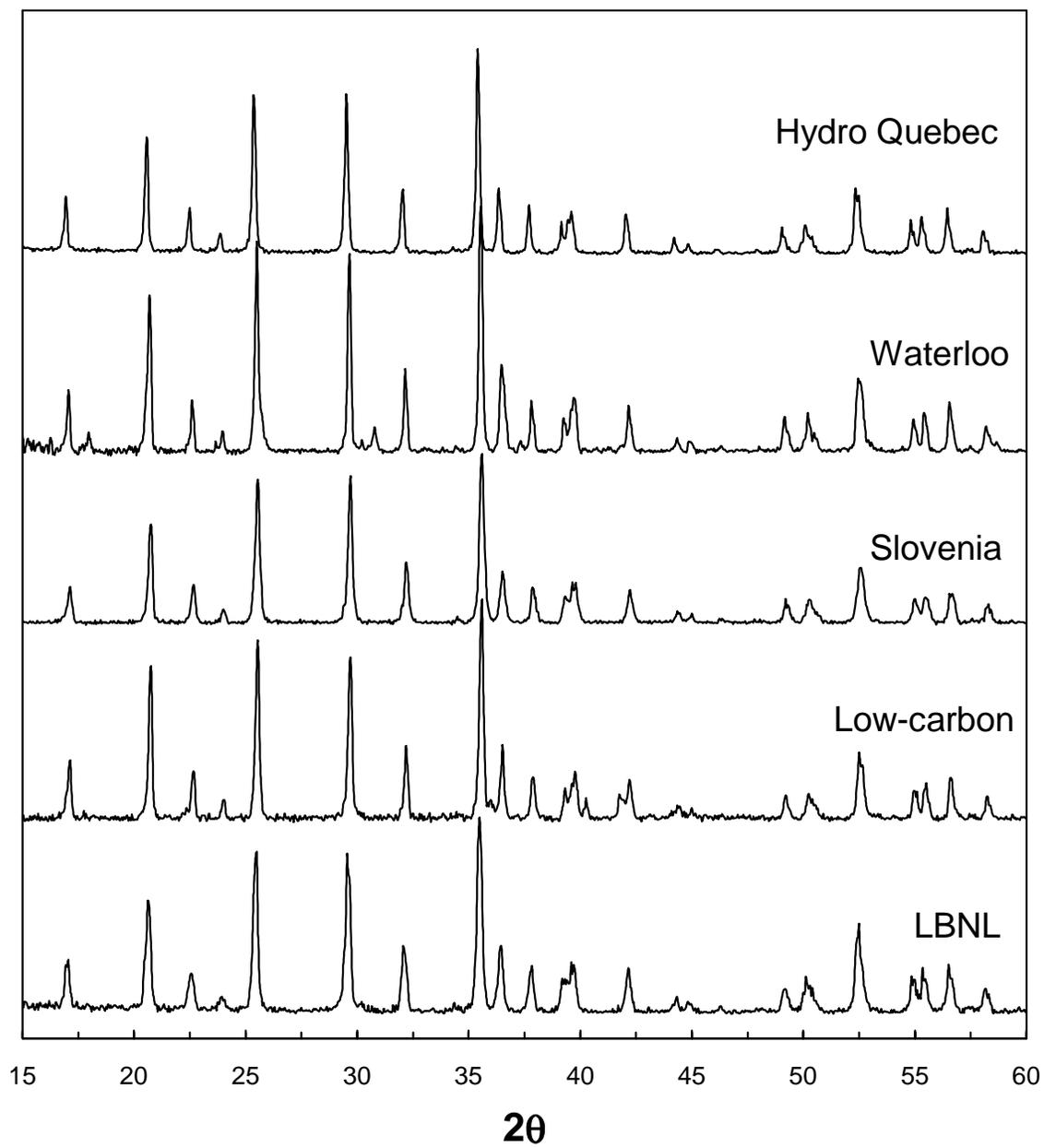


Figure 1

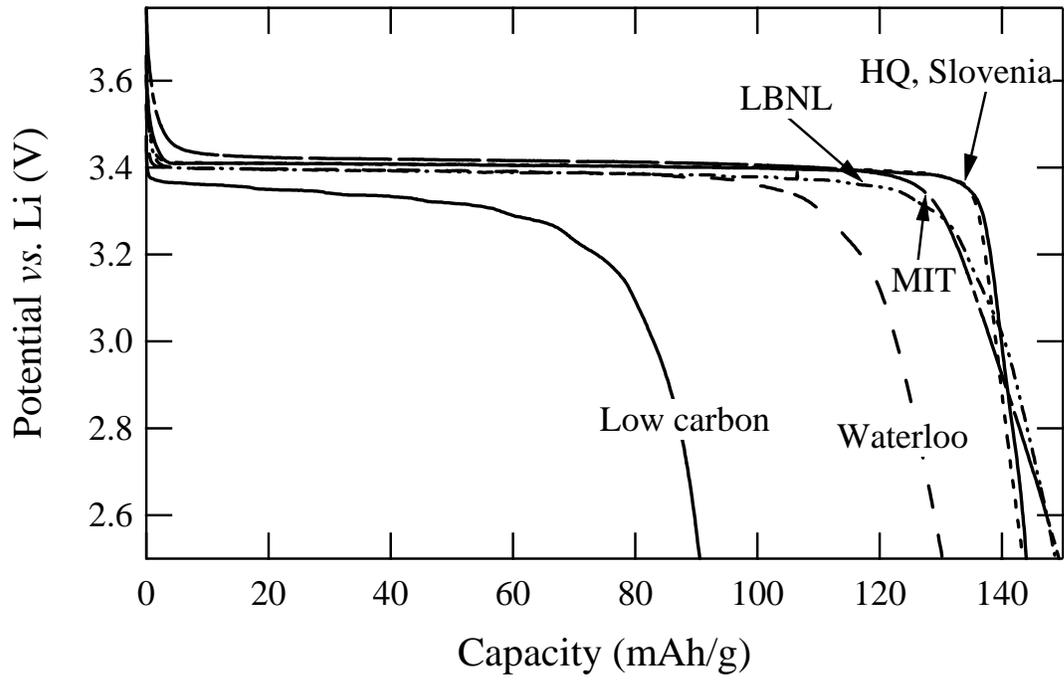


Figure 2

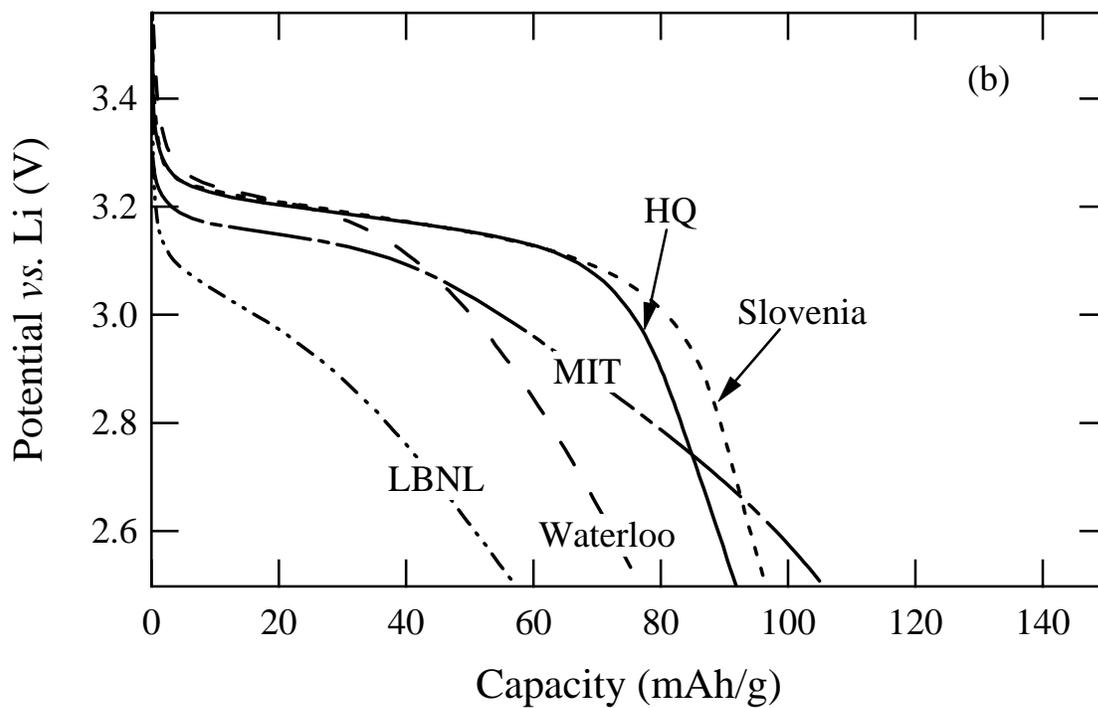
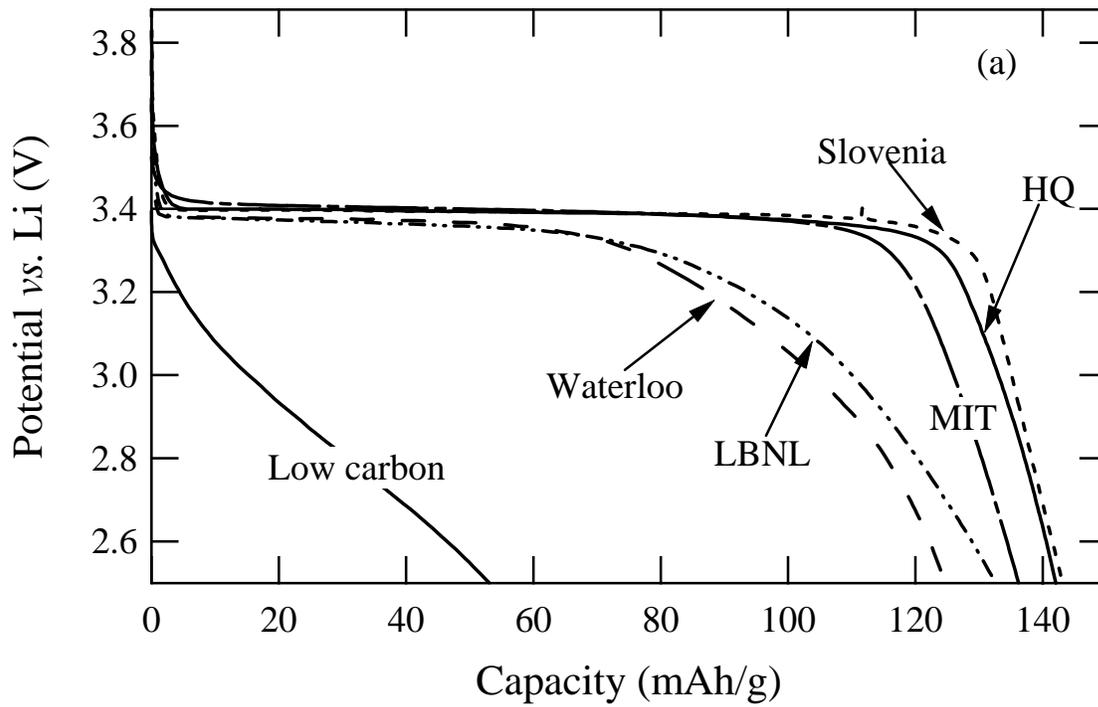


Figure 3

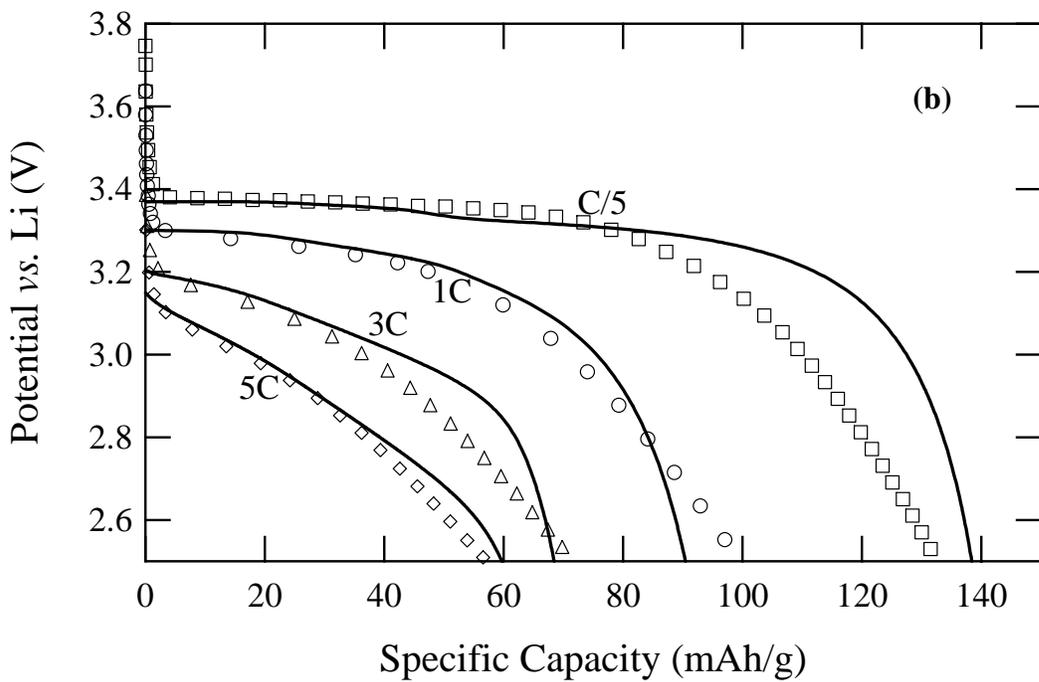
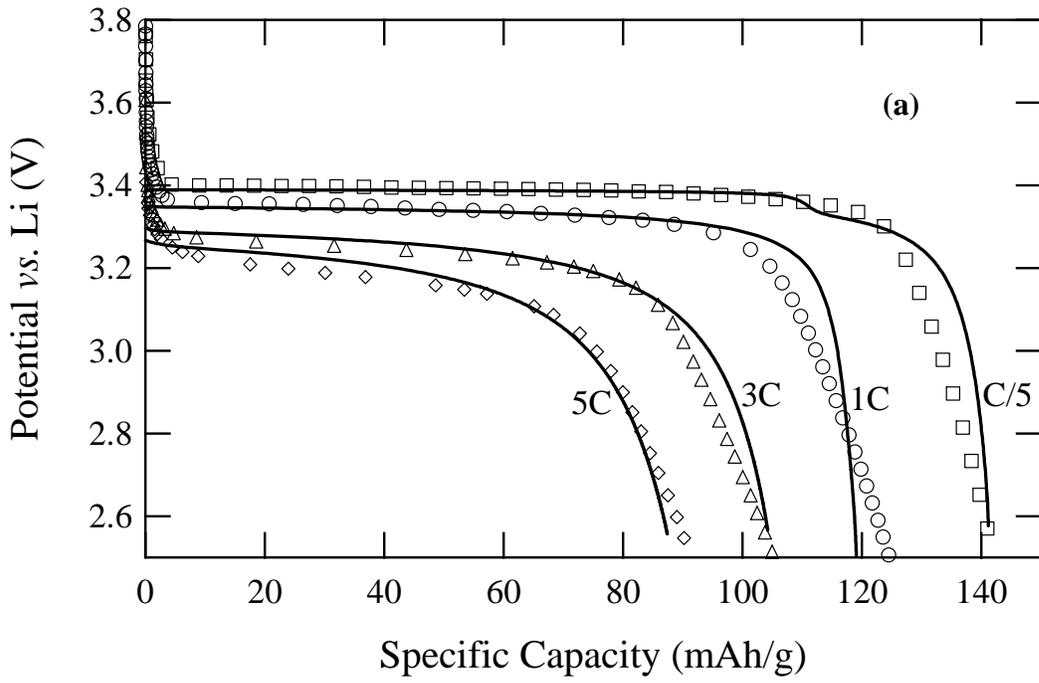


Figure 4

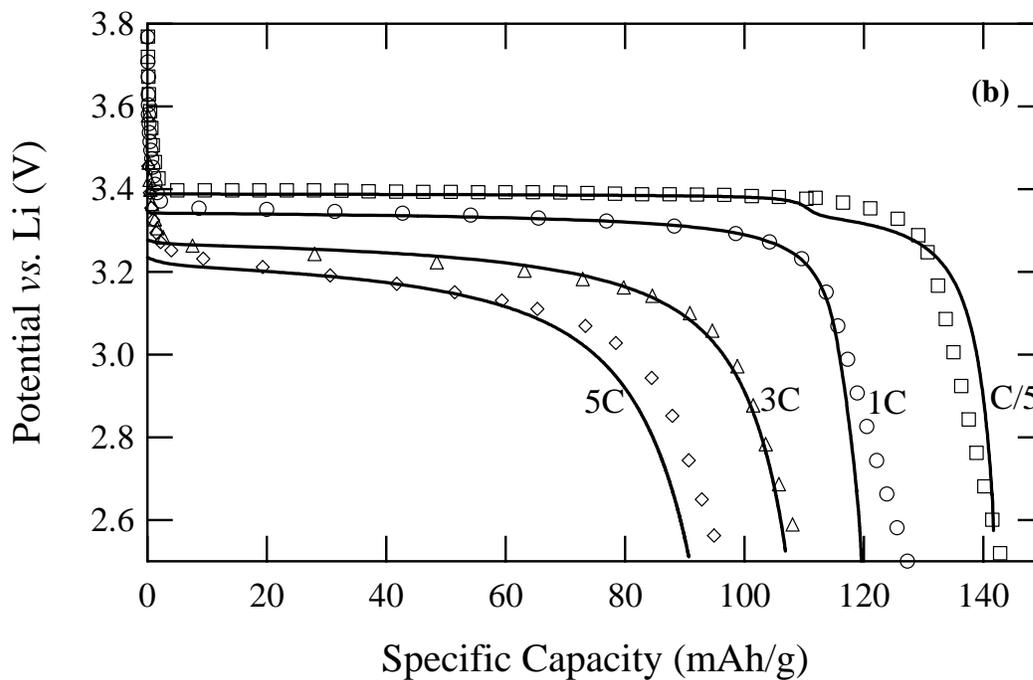
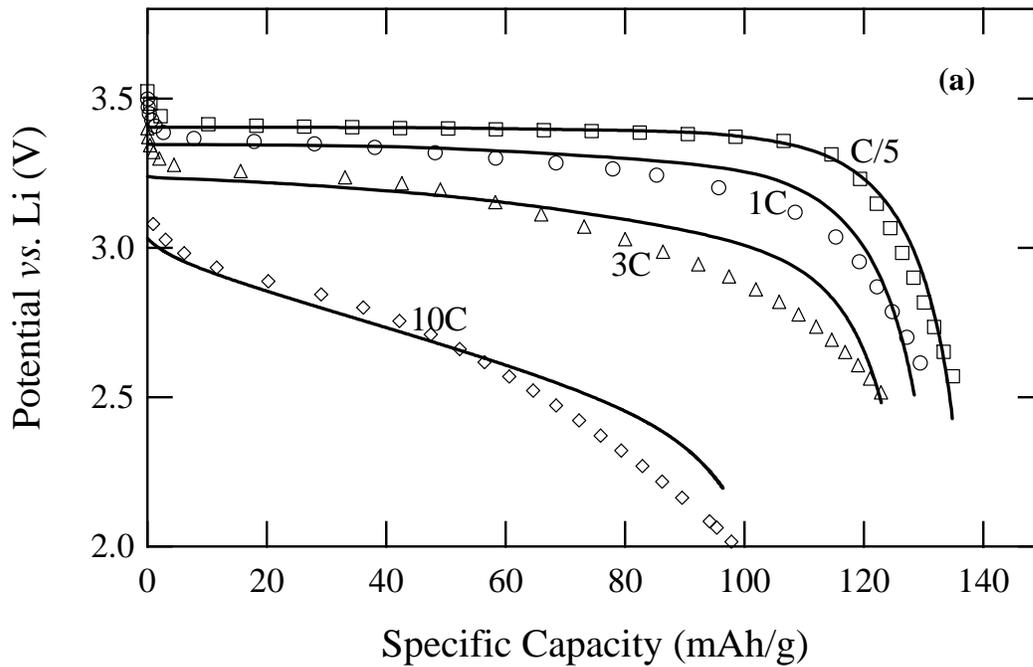


Figure 5

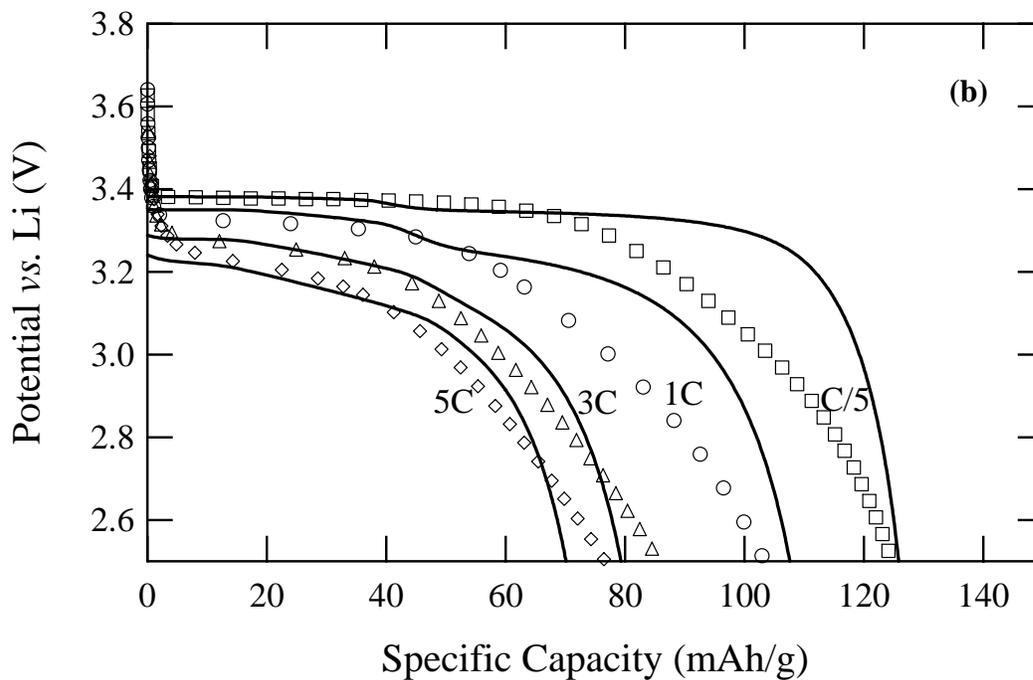
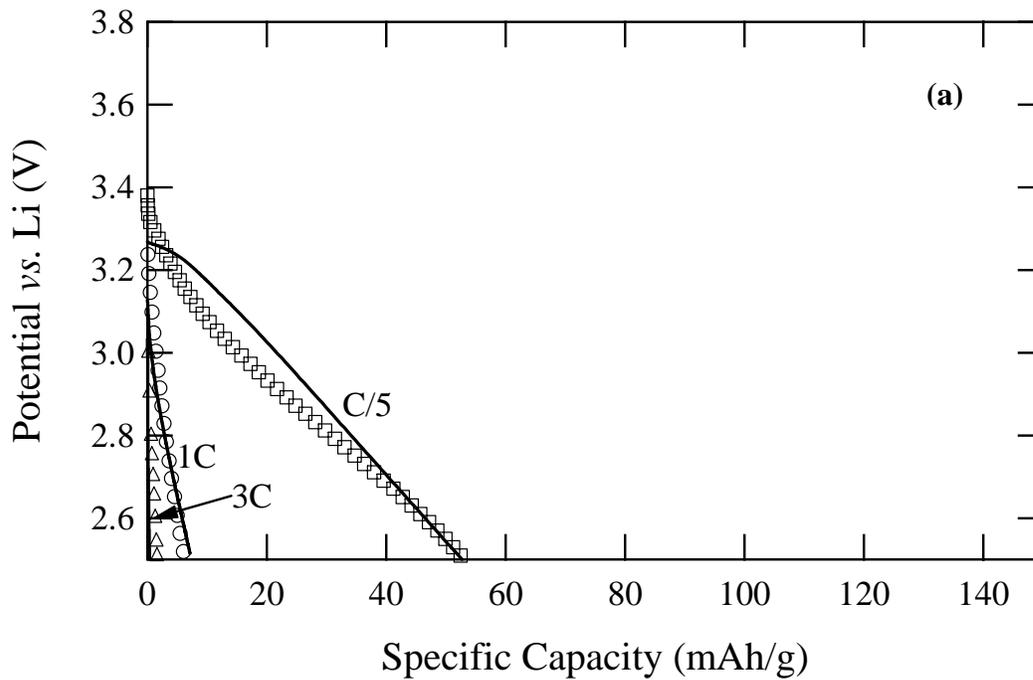


Figure 6

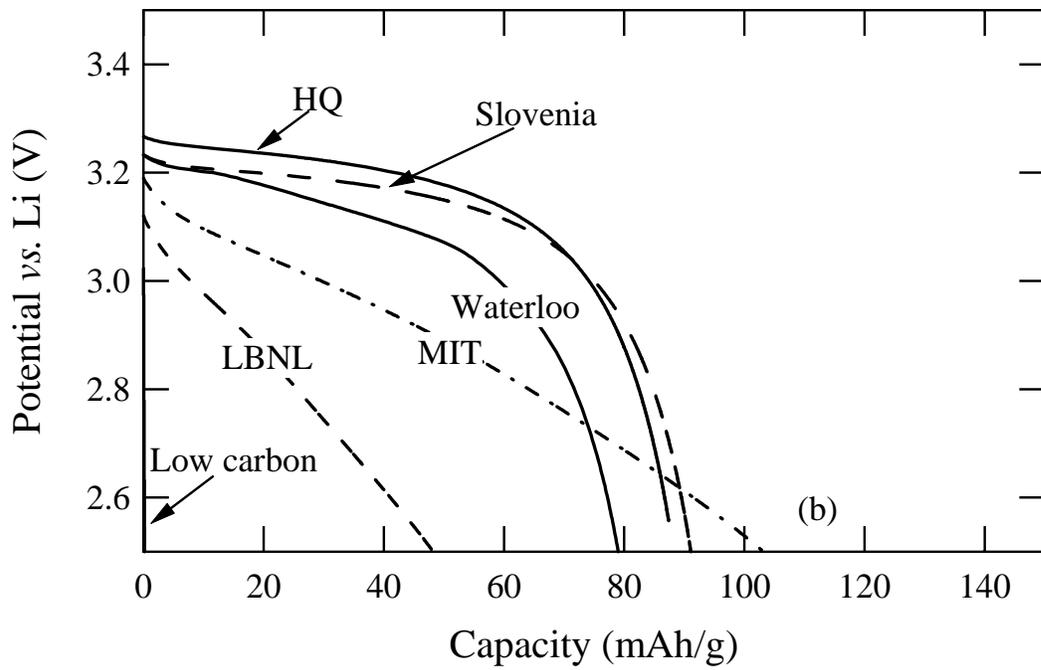
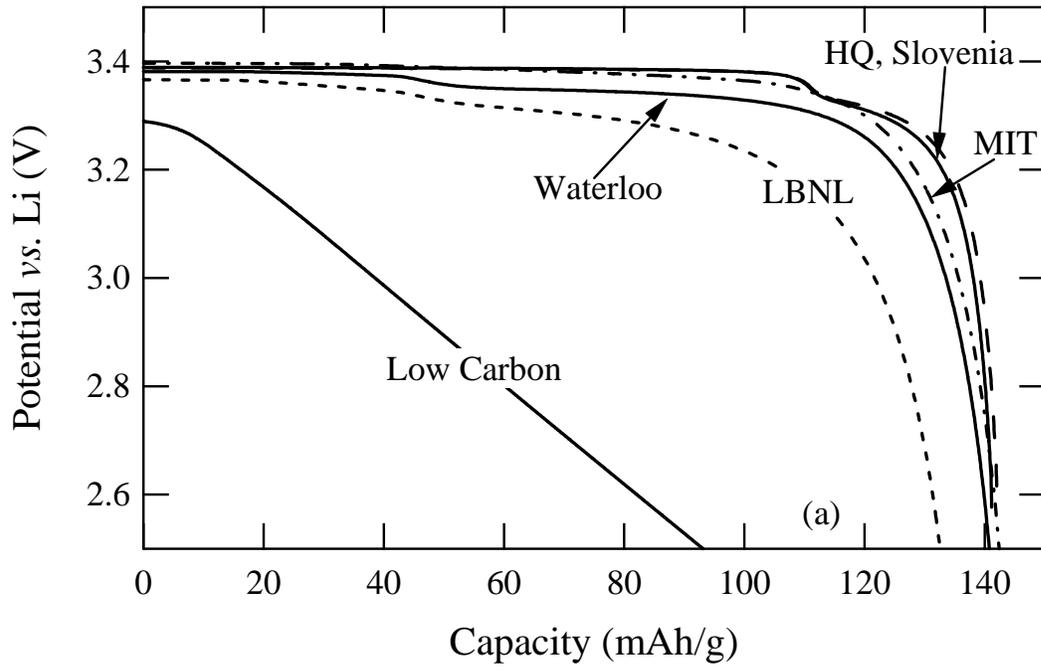


Figure 7

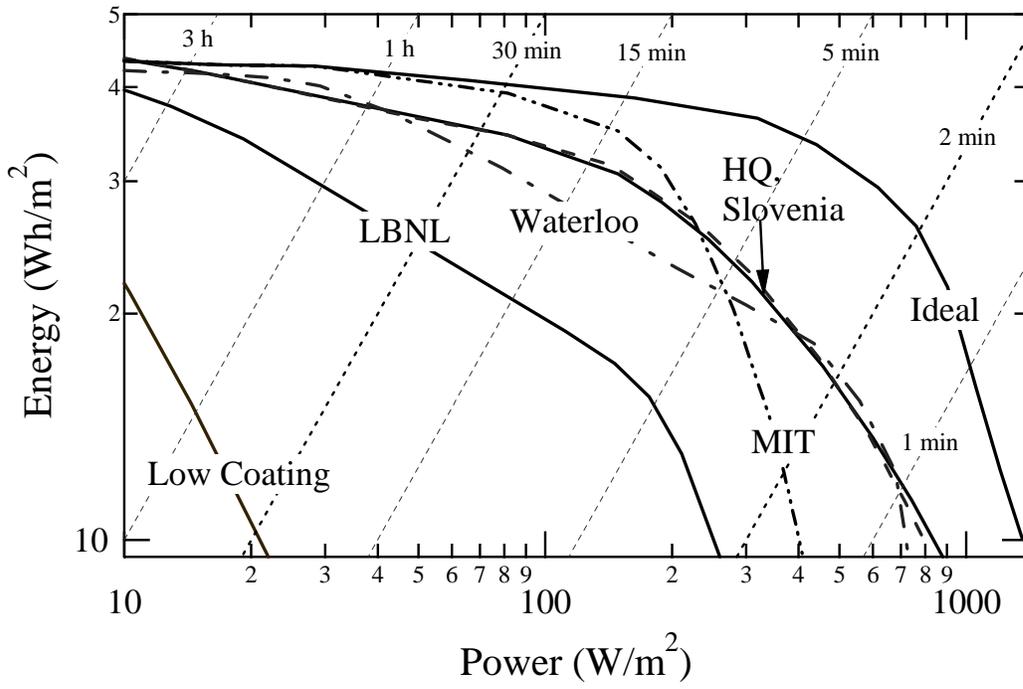


Figure 8