Measurement on Isolated Lithium Iron Phosphate Particles Reveals Heterogeneity in Material Properties Distribution

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Keywords: Li-ion battery, scanning microscopy, micropipette, nanoparticles, electrochemistry.

Abstract

We present herein localized galvanostatic and potentiodynamic measurements on lithium iron phosphate (LFP) particles, using the combination of a scanning micropipette contact method and scanning electron microscopy (SEM). The proposed technique allows small substrate areas (~10 µm in diameter) decorated with LFP particles to be probed within a lithium electrolyte solution in organic carbonate solvents (0.1 M $LiClO_4$ in propylene carbonate in the present study). SEM images of the scanned area allow the correlation of each electrochemical response to the number, and volume of the probed particles. Under favorable conditions, single particles are found within the measurement areas, thus enabling the determination of single particle properties in an anaerobic environment without the additional complications arising from the presence of binders and electronically conductive fillers. The ability to analyze a material with complementary experimental techniques at the single particle level should create new opportunities for fundamental studies and for the quality control of granular materials.

Introduction

Lithium iron phosphate (LFP) is considered an excellent positive electrode material for lithium ion batteries (LIBs), due to its flat potential profile during charging and discharging, high reversibility, excellent rate capability and abuse tolerance.[1–3] Nonetheless, the fundamental electrochemical and physical mechanisms underlying the operation of LFP are still debated, with several proposed reaction pathways.[4–6] Most electrochemical tests for determining intrinsic properties of LIB active materials are performed on porous composite thick film (10 to 100 µm) electrodes. Films consist of 85 to 95 wt% active material particles (*e.g.* LFP, $LiCoO_2$, *etc*., for positive electrodes, and graphite, silicon, *etc*. for negative electrodes) and the balance of 5 to 15 wt% is electronically conductive filler (most often high surface area carbon) and a polymeric binder (*e.g.,* polyvinylidene fluoride, late, styrene-butadiene rubber, *etc.*) in various proportions.[7–9] Data from these tests represent the total response from all active material particles in the electrode, averaged over the size distribution of the active material particles, therefore, such tests only provide average properties for the active material particles. Furthermore, difficulties in the interpretation of test results arise from the heterogeneities within the electrode film under investigation, as well as from the presence of binders and electronically conductive fillers. Additionally, this inhomogeneous structure at the nano- to meso-scale, leads to an inhomogeneous reaction environment, a relatively high resistance of the electrolyte-filled pores in the film, and the finite thickness lead to electrochemical potential gradients across the composite film, which is difficult to predict under dynamic conditions.[10,11] The coating on the surface of active particles is also a significant factor in the overall cell performance.[12,13] Given these complications, it is not surprising that intrinsic properties, such as the diffusion coefficient of Li^+

within an LFP particle have been reported with such widely varying values as 10^{-18} to 10^{-12} cm^2 s^{-1}.[14]

Understanding the structural transformations within LFP provides insights into its reaction mechanism. *Ex-situ* spectroscopy techniques, such as X-Ray diffraction (XRD),[15,16] Raman spectrometry,[17] and transmission scanning electron microscopy,[18] as well as *in-situ* studies by XRD[19–21] and neutron powder diffraction[22] reveal changes in the crystal structure as a function of lithium concentration. However, *in-situ* and *in-operando* studies are typically performed on composite electrodes, which have a heterogeneous distribution of lithium, *i.e.* state-of-charge, among the active particles, due to the non-uniformity of the reaction environment. An alternative to driving the reaction electrochemically and ensuring that the surface of all particle in the sample experiences the same chemical potential is chemical oxidation and reduction, where the driving chemical force is delivered to the particle surface by reactive solution species.[23,24] While these techniques provide high quality kinetic data, the results, like the standard electrochemical analyses convolute the responses from a large ensemble of particles. This makes it exceedingly difficult to determine whether the performance is limited by a general problem affecting the whole particle population, or whether only a subset of the population is the root-cause for a performance below the theoretical level. Clearly, more localized measurement techniques are needed

Recent studies show that lithium ion battery materials can be probed on the micron scale by scanning electrochemical techniques. The influence of the SEI layer on the rate of the redox reactions on a graphite electrode is probed by scanning electrochemical microscopy in one study.[25] In another study, mercury capped microelectrodes detect the variation in the local reactivity of lithium ions at a gold surface, using stripping voltammetry.[26] A scanning micropipette technique is employed to investigate the reduction and oxidation of lithium iron phosphate particles and films in an aqueous electrolyte;[27] however, the oxidation of LFP is obscured by the oxidation of water.[28] Intercalation reactions occurring in lithium manganese oxide particles with a of ~50 µm diameter are studied using simultaneous electrochemistry and RAMAN spectroscopy by mounting the particles onto a microelectrode.[29,30] A platinum wire is brought into contact with a $LiCoO_2$ secondary particle of 8 µm diameter, and an LFP secondary particle with 24 µm diameter, and the particles are investigated by galvanostatic cycling to demonstrate the high rate performance capabilities of these particles.[31,32] However, an electrochemical approach which can inform on particle-to-particle variation of properties in a sample of active material powder has yet to be reported.

We present herein a methodology for probing the electrochemical properties of small numbers of active material particles, down to the single particle level. In the presented proof-of-concept experiments LFP nanoparticles are drop-cast onto a gold substrate, to form a low density dispersion, which is then investigated electrochemically by means of the scanning micropipette contact method (SMCM).[33] The 1 µm diameter micropipette tip is positioned in close enough proximity to the substrate to allow the solution within the micropipette barrel to wet both the particle and the substrate. This forms a stable droplet defining the area of the working electrode. An $Al_{1-x}Li_x$ quasi-reference counter electrode (QRCE) inside the pipette barrel completes the electrochemical circuit. The technique creates a micron-scale localized electrochemical cell, which is used for galvanostatic and potentiodynamic measurements. Subsequent imaging of the measurement area by scanning electron microscopy (SEM) allows correlation of the electrochemical responses with the number and size of probed particles. The data obtained was compared to results from coin cell measurements, to assess the similarities between bulk electrode and individual particle responses and demonstrates the viability of the technique for elucidating key electrochemical properties. The ability to probe individual particles creates new opportunities for fundamental studies of intrinsic material properties, and the ability to detect heterogeneous responses in particles provides a new tool to assist the development of synthesis procedures and for quality control during the manufacture of active materials.

Experimental

A slurry of active material is obtained by mixing carbon coated lithium iron phosphate (ref. 4 from rebuttal) (85 wt.%) with 10 wt.% carbon (Super C5, TimCal) and 5 wt.% binder (PVDF, Kynar) in N-methyl-2-pyrrolidone (99 % Sigma Aldrich). The slurry is cast upon aluminium foil (Exopack) and dried overnight under vacuum at 60°C, to create a 25 µm thick film. Coin cells (CR-2032) are fabricated in an Ar atmosphere using lithium metal as the anode, a Celgard 2500 microporous separator, and the LFP electrode, with 1M $LiPF_6$ in ethylene carbonate (EC) : dimethyl carbonate (DMC) 1:1 (Novolyte) as electrolyte solution, as depicted in Figure 1 (A). Coin cell testing is performed with a Bio-Logic VMP3 potentiostat.

Figure 1 (B) shows the schematic of the SMCM experimental set up. Micropipettes are pulled from quartz capillaries with a 0.3 mm inner diameter of and 1.0 mm outer diameter (Sutter Instruments), using a Model P-2000 laser puller (Sutter Instruments); their tips are made hydrophobic using perfloro-octyl silane (Sigma Aldrich). The $Al_{1-x}Li_x$ QRCE is fabricated by placing an Al wire (4 - 5 cm length, 250 µm diameter, Good Fellows) into a 0.1 M $LiClO_4$ solution in PC as the working electrode, and 2 Li metal strips as counter and reference electrodes. The Li_xAl_{1-x} alloy is formed galvanostatically, and tested for stability by open circuit potential measurements (E = 0.330 V vs. Li/Li$^+$). Gold substrates are fabricated by evaporating 10 nm Cr adhesion layer followed by a 200 nm Au layer onto a borosilicate slide. Lithium iron phosphate particles are drop- cast from an acetonitrile solution (0.1 mg/mL) onto the gold substrate and allowed to dry at room temperature.

SMCM measurements are performed on an ElPro Scan 3 (HEKA Electronics, Germany) instrument operating inside an Ar filled glovebox (MBraun, USA; water and oxygen content < 1 ppm). The ElPro Scan 3 offer a galvanostatic current accuracy of ±30 [U1]fA. This and the zero point was confirmed using a commercial dummy cell provided by the manufacturer. The pipettes are filled with propylene carbonate (99.8% Sigma Aldrich) containing 5 mM $LiClO_4$, and the $Al_{1-x}Li_x$ CE is inserted into the barrel of the pipette. The gold substrate decorated with LFP particles is used as working electrode. The pipette is lowered towards the gold substrate at a 1 µm s^{-1} approach rate whilst a potential of 2.5 V is applied. Upon wetting of the substrate, an electrical circuit between the working electrode and the CE is formed through the electrolyte within the pipette. This created a current spike which is used as a signal to halt the descent of the pipette, ensuring that the pipette does not come in direct contact with the substrate surface or any active material particle dispersed on it. Galvanostatic and potentiometric measurements are performed before retracting the pipette a distance of 100 µm away from the substrate surface. It should be noted that the potential scale is reported with respect to Li/Li^+ throughout this article, for ease of comparison with the existing LFP literature. The pipette is translated after each set of electrochemical measurements to a new location on a 6 x 6 measurement areas grid, with measurement points separated by 20 µm in both the *x* and *y* directions. After completing the scans, the tip was forced into the substrate in a predefined pattern to facilitate alignment in subsequent analysis. Imaging of the 6 x 6 grid was completed through environmental scanning electron microscopy (Hitachi SU3500 VP-SEM). Montage images are captured using the AZtec software package (Oxford). Particle areas are measured using the ImageJ software.

Results and Discussion

The schematics in Figure 1 show the similarities and differences between the coin cell and SMCM geometries. Both electrochemical measurement setups have a conducting substrate supporting the electroactive material; in the case of SMCM a low density dispersion of LFP particles are cast upon a gold substrate, as opposed to a 25 µm thick composite film cast onto aluminum foil in the case of the coin cell. The significant differences between the two electrochemical cells are the absence of the polymeric binder and electronically conductive filler in SMCM, which are required for the proper functioning of a composite thick film electrode in the coin cell. The working electrode areas for the SMCM measurements are defined by the area of the substrate wetted by the electrolyte (~10 µm diameter), whereas the entire electrode is probed in the coin cell. A physical separation between the active material and the QRCE is present in both techniques. In the coin cell this separation is maintained by a porous membrane, while in SMCM it is the tip-to-substrate distance (~0.5 µm) and the distance of the QRCE from the pipet tip. The QRCEs perform the same roles in both setups. However, in the micropipette technique, an $Al_{1-x}Li_x$ alloy is used as the QRCE (E = 0.330 V vs. Li/Li^+), compared to the lithium metal in a coin cell. Both cells provide similar electrochemical environments to investigate the oxidation and reduction of LFP (equation (1)),

$$\mathrm{FePO_4 + Li^+ + e^- \leftrightharpoons LiFePO_4} \tag{1}$$

with two significant differences, namely that (i) SMCM allows for active material particles to be probed in the absence of any binder or conductive carbon filler and (ii) is capable of measuring single particles.

Figure 2 compares galvanostatic cycling data obtained with a SMCM setup and with a coin cell. The measurement by SMCM is performed in a 5 mM $LiClO_4$ solution in propylene carbonate (PC), with an $Al_{1-x}Li_x$ QRCE, and a galvanic current of 1 pA and -1 pA for oxidation and reduction of the LFP respectively. The potential vs. time response during oxidation (Figure 2 (A)) exhibits a sharp rise in potential for $t < 1$ s and peaks at $t = 2.8$ s, before decreasing slightly until $t = 20$ s. Note that a similar trend is observed in data from coin cell measurements for rates of 5C and higher (Figure 2 (B)). Several explanations are proposed for the occurrence of the peak at the start of the charging half-cycle, including transport limitations in the solution or particle, and phase separation between sites saturated with and those without lithium.[4–6] For times 20 s < t < 50 s, a gradual increase in potential is observed as lithium concentration gradients develop. For times $t > 50$ s, a fast increase in potential is observed, indicating that it is no longer possible to remove lithium ions from the material during this charging half-cycle.

Charging/discharging curves recorded at different rates for a coin cell are shown in Figure 2 (B). One hour is required to fully charge or discharge the cell at 1C rate; at 60C rate the charging or discharging is completed within one minute. Note that the experimentally accessible capacity decreases with increasing rate. Additionally, there exists a significant potential polarization between charging and discharging at the faster rates, consistent with mass transport limitation. Scanning electron microscopy images of the area measured by the SMCM technique (Figure 2 (C)) and an area typical for a cast thick film electrode (Figure 2 (D)) show the morphology of the two surfaces. In the case of the SMCM measurement, small agglomerates of particles are present within the probed area, with the bulk of the electrode surface being Au, which does not support the oxidation and reduction of lithium ions within the measured potential range. In contrast, the thick film electrode coating is a mixture of active LFP particles, conductive carbon filler, and PVDF binder. The active material particles are approximately cylindrical in shape, with diameters of 100 nm. Assuming that the length of the particles observed by SEM lay flat upon the substrate, the theoretical capacity is calculated to be 2.97 x 10^{-11} mA h (using a $LiFePO_4$ density of 3.6 g cm^{-3} and a theoretical capacity of 170 mAh·g^{-1}). A charging capacity of 1.67 x 10^{-11} mA h is measured by SMCM, *i.e*. 56% of the theoretical value, for currents of 1 pA, which requires 60 s per measurement (corresponding to a ~60C rate). The coin cell measurements at 60C and 30C discharge rates show that, respectively, 35% and 53% of the theoretical capacity is available from the film (Figure 2 (B)), which indicates a decrease in capacity at high discharging rates for both the coin cell and SMCM measurements. Additionally, the SMCM measurement has a much smaller separation between potentials recorded during charging and discharging, due to the low current applied in SMCM. Importantly, the electrochemical measurements for both systems have a very similar mid-point between the charging and discharging operating potentials and qualitatively similar potential-time responses, indicating the applicability of SMCM as a tool for investigating individual active material particles for LIB positive electrodes.

Figure 3 (A) displays cyclic voltammograms with scan rates of 50, 20, 10, 5, and 1 mV·s^{-1}. The 5th consecutive wave is reported for each scan rate, except for 1 mV s^{-1} where the 3rd wave is reported. The oxidation peak for the deintercalation of lithium from the LFP particles occurs at *ca*. 3.65 V vs. Li/Li^+ and the reduction peak (intercalation) occurs at *ca*. 3.15 V vs. Li/Li^+. These peak potentials are in agreement with the values reported by CV measurements on coin cells for LFP oxidation and reduction reactions at 3.7 V and 3.1 V vs Li respectively.[28,34,35] Importantly, at comparable rates, the potential splitting of the oxidation and reduction peak for different particles is similar, which shows that the Au-substrate-LFP particle contact is not limiting. As the scan rate increases, the peak potential for the oxidation increases and the reduction peak potential decreases. Additionally, the peak width increases with scan rate, which is similar to the behavior of a thin layer of adsorbed species.[36] An increase in the magnitude of the oxidation and reduction peak currents is observed as the scan rate increases from 1 to 50 mV s^{-1} (Figure 3 (C)) with a linear dependence on scan rate, this is in agreement with adsorbed species and thin layer systems.[36,37] At potential scan rates greater than 50 mV s^{-1} waves were no longer reproducible. At scan rates of 20 mV s^{-1} or less, the oxidation peak of the CV returns to a background current value, and the integral of the charge for the oxidation and reduction waves yields 170 pC (4.7×10^{-11} mA h) for 5, and 10 mV s^{-1}, indicating complete reaction at these scan rates. Note, a scan rate of 5 mV s^{-1} takes approximately 2 minutes to oxidize the particles. Most importantly, the larger peak heights for the oxidation compared to the reduction of LFP show that the governing properties of the reaction are different, supporting previous findings[23,24] for chemical reduction and oxidation.

CV measurements are performed on multiple areas of the gold substrate decorated with LFP particles, in order to obtain information about the electrochemistry of individual particles. 36 measurements are performed on a 6 by 6 grid, with 20 µm separation between the center of the measurement areas in both the x and y directions, in order to completely separate the areas wet by the meniscus. From these experiments (*vide supra*), a CV sweep rate of 5 mV s^{-1} is chosen to investigate the complete oxidation and reduction of the LFP particles (Figure 3 (A)), with 5 CVs recorded at each measurement point. After the SMCM measurements, the scan area is visualized by SEM, in order to determine the area of the particles present on the substrate at each location probed by the pipette.

Figures 4 (A) and 4 (B) display the forward peak current (i_{pf}) and forward peak potential (E_{pf}) recorded for each micro-drop cells during the 5th CV cycle, as a function of their location (x and y coordinates) on the substrate surface. The peak current varies across the substrate from 0 to 36 pA (Figure 4 (A)). For the majority of the locations the current response is greater than 0 pA and a forward peak potential between 3.62 and 3.68 V vs. Li/Li$^+$ was observed. A similar narrow peak potential range (3.09 - 3.19 V vs. Li/Li$^+$) was observed for the reduction waves at currents below 0 pA (Supporting Information, Figure SI1).

The SEM image from Figure 5 (A) is a montage of multiple images at a 6000x magnification, providing a microscopic map of the substrate areas where the electrochemical measurements are performed. The image shows that the drop-cast deposition creates a surface dispersion, consisting of areas where no LFP particles are present, areas with individual particles, and areas with particle agglomerates. The colored circles indicates the area wet by the meniscus on the substrate, while the color of the outline indicates the peak current during a forward potential scan as presented in Figure 4 (A). The particle cross section areas obtained from SEM are compared to the forward (oxidation) peak current and the integrated charge in Figure 5 (B). Typically, a larger cross section area of particles within the wetting area correlates to both a higher peak current and increased charge. The measurement areas with no LFP signal are not plotted. The theoretical maximum charge, based on a capacity of 170 mAh g^{-1} and a density of 3.6 g cm^{-3} for LFP is plotted for two limiting cases, a sphere with diameter determined by the cross section area, and for a 100 nm diameter cylindrical particle with the length in the plane of the substrate surface. The majority of areas probed have a capacity below the theoretical maximum for a 100 nm diameter particle, with the remaining areas close to the theoretical value for a sphere. For the data below the maximum capacity for a cylinder there is a linear trend with the visible area of the particle, however, the data has a wide spread. This variation has been reported previously for aqueous pipet measurements[27] and could be due to spreading of the meniscus to wet particles close to the perimeter, due to the high wettability of the particles to propylene carbonate, or to variations in the reactivity of the active material (*vide infra*) which could be attributed to crystal properties (e.g. morphology[38] and phase[39]) for primary and secondary particles,[13] or variations in the surface coating.[12,40] Control measurements are performed to demonstrate that the particles are not displaced during the measurements, these are detailed in the supporting information.

The 36 individual measurement areas from the SMCM map reveal significant differences in electrochemical performance between particles. For example, some CVs display a more complex response than a single peak (Figure 6 (A)). An area where no LFP particles are present provides the background response (blue line, Figure 6 (A)). 67% of CV measurements provide a single peak when active LFP particles are present within the wetted area (green line, Figure 6 (A) and corresponding SEM image in Figure 6 (B)). In other areas (27% of cases) with LFP particles present, the CV has a double peak or a shoulder in the oxidation and the reduction peaks (red line Figure 6A and corresponding SEM image in Figure 6 (D)). For another set of measurement areas a large shift (+150 mV) in the oxidation and reduction peak potentials is observed (black line Figure 6 (A)). In such cases, the reduction peak is much broader, suggesting a slower than normal discharge of the particles wet by the meniscus. The corresponding SEM image (Figure 6 (C)) show several particles on the perimeter of the wetted area. A poor wetting or resistive contact would result in an increased separation between the oxidation and reduction peaks. Similarly, variations in the carbon coating of the particle,[40–42] and hindered mass transport within the solid, due to the particle geometry or to defects in the lattice structure[45,46] would lead to an increase in peak separation, while the origin of a change in the average oxidation-reduction potential could be chemical impurities (ref 6 rebuttal), structural defects (ref x) or a combination of the two. Whatever the cause for the difference in response, these data show that SEM measurements can be directly linked to the electrochemical response, thus yielding a combined methodology by which the quality in the electrochemical performance of a material can be addressed down to the single particle level.

Conclusions

Isolated LFP particles are probed electrochemically using a carbonate solution in an inert environment, and subsequently identified using SEM. The oxidation and reduction of LFP is performed by galvanostatic and cyclic voltammetry experiments. In both cases, the potentials for the reactions are in good agreement with the reported values for macroscopic films measured in coin cells.

CV measurements at potential scan rates greater than 10 mV s^{-1} showed that the capacity of LFP particles is scan rate dependent. For rates below 10 mV s^{-1} there was no change in capacity. Note, at a scan rate of 5 mV s^{-1} oxidation of the particle takes ~2 minutes. Furthermore, the oxidation waves show higher peak currents than the corresponding reduction peak currents. These findings are in agreement with cyclic voltammetry data reported in the literature.[28,34,35]

Electrochemical maps obtained by measuring CVs at a scan rate of 5 mV s^{-1} show that the majority of particles display a single oxidation and reduction peak at *ca*. 3.65 V and *ca*. 3.14 V vs.

Li/Li$^+$. However, heterogeneity between particles can be observed as a shift in the oxidation and reduction potentials, and importantly, particles can be further studied by complementary techniques. As such, the SMCM technique can be highly relevant for probing electrochemical properties of battery materials at the single particle level, and identifying variations in particle consistency. Therefore, the SMCM and SEM technique may become highly relevant for probing intrinsic properties of battery materials at the single particle level over distributions of active material particles and as a quality control tool for active material fabrication, to monitor batch-to-batch variations in particle properties

Supporting Information

Maps for the reduction peak potential and peak current, and experiments showing that the particles are not displaced by the pipette measurements are provided in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

This work is supported by Natural Sciences and Engineering Research Council of Canada (NSERC) and General Motors Canada (Grant: NSERC/McMaster/APCPJ 412488-11). We thank F. Wang and C. Heinemann for experimental advice and discussion, and I. Halalay and M. Jiang for scientific discussion.

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