



Atom Probe Tomography of Lithium Iron Phosphate (LiFePO₄) Battery Electrode Material

Abdul Wahab Qurashi¹, Guido Schmitz¹, Muhammad Farhab²

¹Department of Material Sciences, University of Stuttgart, Germany

²College of Veterinary Medicine, Yangzhou University China

Corresponding Author: farhab.dvm@gmail.com

Abstract

We have measured the Lithium iron phosphate battery electrode system by using Atom probe tomography and also reconstruct the measured data. The systematic study of laser-assisted APT for LiFePO₄ provides an insight into the problems associated with APT analysis of lithium iron phosphate by using UV laser. Different material classes have been investigated by this measurement. In this study, some trials have been performed on APT of Lithium iron phosphate.

Keywords: Lithium iron phosphate, battery electrode system, laser-assisted APT, LiFePO₄, UV laser.

1. Introduction

In Human Civilization science and technology play an important role. Human desires force the scientists to develop the equipment small, portable, efficient and cheap. These small portable devices need energy for working and this energy is stored in the batteries. In 1791 Alessandro Volta published an article on the batteries after that people started to find the efficient electrode material for batteries. Alessandro Volta was the first man who described the basic phenomena of storing current in batteries. Since then different materials start to synthesis on the nanoscale to increase the performance of the batteries. In order to produce efficient battery electrodes, the material properties need to be varified on nanoscale. So far the Atom Probe Tomography (APT) is one of the characterization technique which is used for characterizing the materials near atomic resolution [1]. The most recent development in APT is the introduction of a local electrode which reduces the potential needed for evaporation [2]. The commercially used APT has a local electrode along with voltage and laser pulsing to increase the reliability of the APT [2]. APT techniques already have a great contribution and hold even great promise as enabling tools for chemical analysis and crystal structural investigation [3]. APT measurement is very sensitive to the sample preparation method and machine parameters *i.e* temperature of the tip, laser power [4]. In combination with the work of Dhamodaran *et al* [6] this work mainly focus on finding the parameters of atom probe tomography (ATP) for measuring Lithium iron phosphate (LFP). Previously Daniel et al investigated the Lithium Iron Phosphate system. Additionally, he tried to investigate the effect of laser

energy during measuring the Lithium Iron Phosphate in Atom Probe Tomography [42].

2. Materials and Methods

The rapid growth of interest in the field of batteries increases also the studies on electrode material, which provide high efficiency and reliability like LiFePO_4 . In this study, LiFePO_4 was measured with APT. As introduced early, APT is the sophisticated technique for microstructural analysis of materials. LiFePO_4 is environmentally non-toxic and inexpensive material [27].

Delacourt *et al.* investigated the thermal behavior of different $x\text{LiFePO}_4$, $0 \leq x \leq 1$ and discovered two phase mixture with an intermediate solid solution phase [28]. Neutron diffraction studies show the disordering of lithium is present in the solid solution of LiFePO_4 in [100] and [010] direction [29]. At ambient temperatures LiFePO_4 shows a better capacity retention characteristics than LiMn_2O_4 in LiPF_6 based electrolytes, perhaps owing to a lower *Fe* dissolution compared to *Mn* dissolution [31]. So it has been observed that the LiFePO_4 electrode material works efficiently at 60°C under electrochemical conditions, and may have a slight dissolution tendency in the electrolytes at this operating temperature [32]. This capacity fade at operating temperature is due to the impurities in an electrolyte of the electrochemical cell. Iron dissolution in the electrolyte can be an issue at elevated temperature in the presence of water and other acidic contaminants [33]. Due to the high mobility of Lithium ions in LiFePO_4 , it is difficult to measure lithium and lithium compounds in APT [42].

As measured directly from the FIM image the distance between (011) and (112) pole is 23.18nm and the specimen to screen distance account to 50mm [37]. The number of rings counted between lattice planes (011) and (112) direction are $n = 16 \pm 1$. The Lattice parameter of Tungsten is $a = 0.316\text{nm}$. The evaporation of tungsten takes place at 52Vnm^{-1} [5], and the tip was developed up to up to 10 kV . Small diameter wires, fibers, whiskers, nanowires or roughly polished needles can be prepared by a FIB for characterization in APT. In these cases, the annular milling method (Larson *et al.*, 1998, 1999a) is most suitable one. Annual milling may also apply directly to multiple tips and *post procedure* by the Bosh etching process (Larson *et al.*, 2001; Thompson *et al.*, 2004). Several different methods have been designed for atom probe specimens (Miller *et al.*, 2005; Cairnet *et al.*). The choice of the method depends on milling time as well as the geometry of interest (Miller *et al.*, 2005). Samples were checked by transmission electron microscope, regarding the quality of the interface between two layers, layer thickness and shape of the tip. METAP was employed for the LFP measurement [35]. Oppositely, the counter electrode of METAP is kept at zero potential during the whole measurement [36].

3. Results and Discussion

The field of view analyzed by Atom probe tomography is limited to an aperture angle of 34 ± 1 . One of the obvious featured to measure lithium iron phosphate under APT is to get the complex phases and their positions in the mass spectrum. The measurement demonstrated in were performed with the laser power of 15mW and 3.2 million of atoms were detected. Different elements, with hydrides of Phosphorus, Oxide of iron and Chromium are observed in the mass spectrum, which lies at 1-2, 6-7, 15-18, 23-27, 27-28.5, 32-34, 42-47, 52-54, 54-58, 63-68, 71-73 and 83-84 Da. This amount of peaks during APT measurement of Lithium iron phosphate makes the identification of peaks difficult. Unfortunately, controversy is present in an identification of one isotope of chromium 54 and iron 54, due to overlapping of their

corresponding peaks. However, hydride of Phosphorus are located at 33 Da, 34 Da and 71-73 Da describe as PH_2 , PH_3 and LiP_2H_3 . The peak of maximum intensity lies from 6-7 Da, which is the representation of pure Lithium. However, the identification of these peaks performed with great precision. On one side of this, commonly adsorption of impurities, gas molecules and other atoms may contribute more and less to these peaks. A further complication arises during measurement of Lithium iron phosphate was the evaporation of Lithium, its evaporation started at ≈ 12.5 μm and suddenly drop after $0.6 - 0.7$ μm and again started after $1 - 1.5$ μm . This fluctuation in evaporation shows that Lithium is mobile in the sample or maybe it is due to the rupture of layers. This measurement is a rare measurement from the batch of un-anneal samples because it's hard to measure Lithium iron phosphate in APT due to field drift ion migration of lithium or may be due to brittle nature of LFP at low temperature. Moreover, it is clear in the reconstruction that Lithium is just present on the surface of the tip. In addition to this, the detector was not homogeneous in the whole measurement and position of the atoms on detector were changing. The inhomogeneous distribution of atoms on detector is maybe due to the bad quality of sputter layer or may be defocusing of the laser on tip apex or may be due to field drift ion migration of lithium. This arises the inhomogeneity in this experiment and unfortunately due to the limitation of time, reliable measurements are not available. Elements and compounds, which are identified in the measurement of un-anneal sample are listed in table under below:

Table 1: Mass spectrum peaks of un-annealed sample.

m/z[Da]	Identity	m/z[Da]	Identity	m/z[Da]	Identity
1	H^{+1}	33-34	PH_3^{+1}	71.8-72.2	$\text{LiP}_2\text{H}_3^{+1}$
6-7	Li^{+1}	43.8-44.2	FeO_2^{+1}	84-86	CrO_2^{+1}
16-16.2	O^{+1}	46.9-47.2	PO^{+1}		
17-17.2	OH^{+1}	52-54	Cr^{+1}		
18-18.2	H_2O^{+1}	56-58.5	Fe^{+1}		
25-27	Cr^{+2}	62.8-63.2	P_2H^{+1}		
27.5-28.5	Fe^{+2}	64	$\text{P}_2\text{H}_2^{+1}$		
31	P^{+1}	65	$\text{P}_2\text{H}_3^{+1}$		
31.5-32	O_2^{+1}	66	$\text{P}_2\text{H}_4^{+1}$		
33	PH_2^{+1}	68	FePO_4^{+1}		

The initial radius R and shaft angle α are the major requirements. However, it is not possible to measure these data during APT measurement. Despite this, the reconstruction of the tip is done by fixing the evaporation field corresponding to the literature by adjusting both the tip radius r and shaft angle α . The evaporation field of Lithium is 14 Vnm^{-1} and for iron is 33 Vnm^{-1} from this it can be says that the evaporation field of Lithium iron phosphate is lies between $14-33 \text{ Vnm}^{-1}$ [38]. The vaporization field of LFP on 4nm of chromium along with the thickness of the layer. Just in the beginning of the measurement, the voltage applied to the specimen is

constantly increasing; which result in the increasing electric field. Subsequently, homogeneous evaporation has been achieved and the plateau appears in the evaporation plot, which shows the constant evaporation from surface.

In the beginning of measurement the evaporation field is fluctuating up to 10nm but after that it becomes constant. This fluctuation is due to change of radius curvature with field strength, irregularity on tip surface, non-spherical tip apex and break or rupture of sputtered layer. The voltage on the tip is increased to achieve the constant evaporation of LFP. However, the constant evaporation for LFP in METAP is more severe as compared to other metallic materials. Therefore, Lithium is just measured at the beginning of the experiment because its evaporation field strength is low as compared to other components of LFP (e.g O, Fe and P). Oppositely, the measurement of pure Tungsten confirms the termination of the experiment. But there is no measurement of pure tungsten atoms in this experiment because the tip broke before the evaporation of tungsten.

Irregularity on the surface can be minimized by controlling the parameters during electrochemical etching, sputtering and FIM development. The drastic turbulence of the evaporation rate and the rupture of LFP layer have been encountered during this work rapidly. This problem has a negative influence on the reconstruction because it causes distortions and loss of atoms. For the optimal atom probe measurement of LFP, some attention must be paid during measurement. First of all, standard quality of sputter layer on the tip is the precondition for stable evaporation and good APT measurement. Secondary the suitable measuring temperature of the specimen is also the precondition of good measurement. Lower temperature (60-65K) makes LFP brittle, which causes the rupture of a layer during evaporation. High temperature (73-93K) supports the evaporation but there will be a compromise for the resolution. However, it is clear that all the lithium is coming from the surface and it is located just from one portion of the tip. Because the 28% of lithium atoms diffuse from part □ to part □ Moreover, this one side evaporation of lithium atoms are due to Field drift ion migration of *Li* to the surface or may be due to the bad quality of sputtered layer on the tip. Nevertheless, as a matter of fact, the position of the laser cannot be Performed very precisely. Furthermore, a significant change in intensity of atoms is affected by slight drift or a shrink of the tip during measurement. The solution of this problem is to change the laser spot position on the tip apex, which may cause different effective intensity and also effects the reconstruction result.

Moreover, it can clearly identify that the band region is located at one side of the cylindrical (left top side of Cylinder) which is enriched with 40 % of pure lithium, 22 % of iron, 15% chromium, 5 % of phosphorus and 8% (at zero distance from the tip). The corresponding composition profile indicates that *Li* is diffusing to the surface (28% of lithium) and remaining other elements *Cr*, *Fe* and *P* are spread in the whole tip. Oppositely, the amount of Chromium is maximum at the end corner of measured tip because it's the intermediate layer between LFP and tungsten.

Table 2: Composition of Li, Fe, P, Cr and O of un-annealed

	Li	Fe	P	Cr	O
Absolute quantity	1298849	1194274	3910	190558	404391
Relative percentage	42.00	38.62	0.126	13.07	6.16

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