Applied Surface Science 322 (2014) 85–94

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Chemical and microstructural transformations in lithium iron phosphate battery electrodes following pulsed laser exposure

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ARTICLE INFO

Article history:
Received 27 June 2014
Received in revised form 9 September 2014
Accepted 14 October 2014
Available online 24 October 2014

Keywords:
Laser cutting
Raman spectroscopy
Lithium ion
$LiFePO_4$
Graphite

ABSTRACT

Multi-layer lithium iron phosphate (LFP) battery electrodes are exposed to nanosecond pulsed laser radiation of wavelength 1064 nm. Test parameters are chosen to achieve characteristic interaction types ranging from partial incision of the active coating layers only to complete penetration of the electrodes with high visual cut quality. Raman spectroscopy is performed on unexposed regions and at points approaching each incision, highlighting changes in chemical composition and microstructure in the heat affected zone (HAZ). Thermogravimetric analysis is performed on the unexposed electrode active materials to distinguish the development of compositional changes under conditions of slow heating below the melting and sublimation temperatures. A brief theoretical description of the physical phenomena taking place during laser exposure is provided in terms of direct ablation during each laser pulse and vaporization or thermal degradation due to conductive heat transfer on a much longer time-scale, with characteristics of the HAZ reported in terms of these changes. For all laser exposures carried out in the study, chemical and microstructural changes are limited to the visible HAZ. Some degree of oxidation and LFP olivine phase degradation is observed in the cathode, while the polycrystalline graphite structure becomes less ordered in the anode. Where complete penetration is achieved, melting of the cathode active layer and combustion of the anode active layer take place near the cut edge due to thermal conduction from the metallic conductive layers. The presented results provide insight into the effects of laser processing on LFP electrode integrity.

1. Introduction

Lithium iron phosphate (LFP) battery technology [1] is emerging as a major player for energy storage in hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to its potential for high energy density, long service life, improved safety and superior environmental compatibility compared to other lithium cell types [2–8]. A large body of research has recently been dedicated to improving the performance of this battery type and overcoming its low electronic conductivity [9,10]. Though the raw materials of LFP batteries are abundant and cheap [11,12], production costs remain high due to the use of expensive tooling for electrode cutting operations that requires regular servicing and replacement [13]. The use of laser sources in place of mechanical cutting devices, though necessitating large initial outlay, provides long-term cost savings due to lower maintenance requirements and improved process flexibility [14–17]. Laser sources also present opportunities for additional processes such as electrode microstructuring and annealing [18,19]. For cutting, nanosecond pulsed laser sources yield high process efficiency and visual cut quality for electrode sizing applications [20]; however, the thermal nature of laser–material interactions with nanosecond laser pulses presents a situation in which the chemical and microstructural integrity of the electrode active layers near the cut edge is placed under question. Resolution of chemical and microstructural changes in the heat-affected zone (HAZ) facilitates a more complete understanding of laser processing in the field.

LFP battery electrodes typically consist of graphite coated copper anodes and $LiFePO_4$ coated aluminum cathodes, both of approximately 100 μm in total thickness. Complete battery cells comprise alternating anode and cathode films separated by porous layers that allow the passage of electrolyte. The active LFP layer of the cathode has an ordered olivine structure that allows intercalation and deintercalation of lithium ions during discharge and charge cycles via a first-order transition between $FePO_4$ and $LiFePO_4$ [21]. To overcome the low electronic conductivity of both

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http://dx.doi.org/10.1016/j.apsusc.2014.10.069
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Table 1
Tested electrode layer compositions and thicknesses.

Film	Layer 1	Layer 2	Layer 3
Cathode	$LiFePO_4$ (45 μm)	Aluminum (20 μm)	$LiFePO_4$ (45 μm)
Anode	Graphite (47 μm)	Copper (10 μm)	Graphite (47 μm)

Table 2
Parameter groups under test conditions.

Parameter group	1	2	3	4a[a]	4b[a]
Wavelength (nm)	1064	1064	1064	1064	1064
Pulse duration (ns)	4	4	4	30	200
Repetition rate (kHz)	500	500	500	100	20
Beam quality (M^2)	1.5	1.5	1.5	1.5	1.5
Lens focal length (mm)	100	100	100	100	100
Spot diameter (μm)	25	25	25	25	25
Rayleigh range (μm)	320	320	320	320	320
Average power[b] (W)	19	9.6	15.1	15.1	9.5
Pulse energy[b] (μJ)	38	19	30	151	475
Fluence[b] ($J\,cm^{-2}$)	15	8	12	60	187
Exposure velocity (mm/s)	1000	100	100	100	100

[a] Group 4a was applied to the cathode and 4b to the anode.
[b] Values at sample surface calculated from power meter measurements.

phases, the particle size is minimized and a carbon coating applied [22,23]. The active graphite layer of the anode allows penetration of lithium ions via a reversible reaction forming Li_xC_n, with the lithium storage capacity dependent on the graphite microstructure and crystallinity [11]. The sensitivity of both cathode and anode active layers to microstructural and chemical changes necessitates investigation into potential effects of this nature resulting from laser exposure.

A number of studies have investigated laser cutting of LFP and lithium metal oxide battery electrodes experimentally in terms maximum cutting speed and defect size [13–17]. The cutting efficiency, coating layer delamination width and defect size of LFP electrodes have been shown to be functions of the wavelength, pulse duration, fluence, repetition rate and cutting velocity [20]. Good cut quality has been demonstrated with nanosecond laser pulses, leading to delamination widths of less than 30 μm and defect dimensions of less than 5 μm [20]. Though providing insight into process feasibility, the aforementioned studies do not consider chemical or microstructural changes in the HAZ.

The present work sees Raman analysis of LFP battery electrodes before and after nanosecond pulsed laser exposure with parameters similar to those utilized in Ref. [20]. Thermogravimetric analysis (TGA) is undertaken on unexposed electrode active materials to provide insight into phenomena taking place upon slow heating below the melting and sublimation temperatures. Material transformations are described in terms of existing theory for short-pulse laser exposure of thin multi-layer films, with characteristics of the HAZ reported in terms of these changes. The presented results establish the influence of laser processing on LFP electrode active layer integrity.

2. Experimental setup

2.1. Tested electrodes and experimental parameters

LFP battery electrode films were used for the experiments, with layer thicknesses and compositions as given in Table 1. Four experimental parameter groups, the details of which are given in Table 2, were selected to achieve the following characteristic material responses observed in Ref. [20]:

1. Partial incision of upper coating layers only, invoking minimal or no visual defects.
2. Removal of coating layers and partial removal of metallic layers, invoking large visual defects (∼25 μm) in the cathode.[1]
3. Complete cut of electrodes, invoking large visual defects (∼25 μm) in the cathode and large delamination widths (∼50 μm) in the anode.[2]
4. Complete cut of electrodes, invoking smaller visual defects (<5 μm) in the cathode and smaller delamination widths (∼20 μm) in both electrodes.

Comparison of incisions and cuts with these characteristics allowed investigation into the correlation between visual cut quality and chemical and microstructural changes in the electrode active layers.

2.2. Procedure

2.2.1. Laser exposures

Single line laser exposures were performed on both electrodes with an IPG YLPM-1-4 200-20-20 fiber laser utilizing the parameter groups in Table 2. Electrode films were held horizontally under the focused laser beam on a mounting that consisted of a series of holes connected to a vacuum source. Cutouts were present on the mounting to avoid contact between the electrode film and mounting for at least 3 mm to either side of the exposed areas. Laser beam translation was achieved via a galvanometric scanning head.

2.2.2. Raman analysis

Raman spectra were acquired for the electrode active materials before and after laser exposure. Line map spectra were performed across the HAZ of all exposed electrodes so as to determine the dependence of chemical and microstructural changes on the distance from the laser axis. For each electrode and parameter group, several line map spectra were acquired at different cross-sections so as to confirm the consistency of results. Spectra were also taken at specific points on the cathode where visible defects were present. All spectra were measured using a Thermo Fisher DXR Raman microscope with a 532 nm He–Ne laser. The device was equipped with 10× and 50× long working distance (LWD) objectives and a 20× focal plane objective. A 25 μm pinhole aperture was used for all experiments, with the diameter of the laser spot at the sample surface in the range 1.2–2.4 μm. Preliminary tests were carried out at various microscope laser power levels to establish the optimum parameters for the materials in question. A laser power of 1 mW was then utilized for all measurements to avoid oxidative decomposition of the electrode materials [24]. Acquisition of Raman spectra was undertaken with three exposures of maximum total duration 90 s. Acquisitions were terminated prior to the maximum duration where a signal-to-noise ratio of 500 was attained for the most intense peak in the examined region.

2.2.3. Thermogravimetric analysis

Thermogravimetric analysis was performed on the unexposed electrode active materials with a Perkin Elmer TGA7 analyzer. Fine powder samples were obtained by scraping the active materials from the electrode conductor films with a spatula. Approximately 5–6 mg of electrode active material was placed in the Pt crucible of the analyzer for each measurement and heated under a constant airflow of 30 mL/min to simulate oxidative conditions during laser exposure in air. Two different thermal programs were employed. In the first, material samples were heated from 50 °C to 900 °C at a constant rate of 20 °C/min. In the second, isothermal and heating

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[1] Visual defects were not observed in the anode under any of the tested conditions.
[2] Delamination widths were smaller for the cathode than for the anode under all tested conditions.