



Effect of particle-size distribution on LiFePO_4 cathode electrochemical performance in Li-ion cells

Efecto de la distribución del tamaño de partícula en el rendimiento electroquímico de un cátodo LiFePO_4 en celdas de ion litio

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Abstract

LiFePO_4 has structural and electrochemical advantages that make it an important candidate as a cathodic material due to its low cost, structural stability and low toxicity. These features make it a good option for energy backup systems. However, it is necessary to address the problem of low capability to operate at high cycling speeds due to low electrical conductivity and a low diffusion coefficient. In this work, LiFePO_4 powders were treated with ultrasound for different periods of time to study the effect of reducing agglomerated particles in wet mixture during manufacturing stage. Samples were characterized by a scanning electron microscope, particle-size analysis and electrochemical methods. Results revealed that ultrasonic treatment reduced particle size of both active material and conductive additive improving overall electrochemical behavior and specific capacity of samples treated for longer periods of time.

Keywords: LiFePO_4 , Battery, Cathode, Particle size.

Resumen

El LiFePO_4 tiene ventajas estructurales y electroquímicas que lo convierten en un importante candidato como material catódico. Su bajo costo de producción, estabilidad estructural y baja toxicidad lo convierten en una buena opción para sistemas de respaldo energético. Sin embargo, es necesario trabajar en soluciones que permitan mejorar su baja capacidad para operar a altas velocidades de ciclado, su baja conductividad eléctrica y bajo coeficiente de difusión. En este trabajo, se ha tratado polvo de LiFePO_4 con ultrasonido durante diferentes períodos de tiempo durante la etapa de fabricación del electrodo con el objetivo de estudiar el efecto electroquímico producido por la reducción del tamaño de las partículas en la mezcla. Las muestras se caracterizaron por medio de microscopía electrónica de barrido, análisis del tamaño de partículas y métodos electroquímicos. Los resultados revelaron que el tratamiento ultrasónico redujo el tamaño de partícula tanto del material activo como del aditivo conductor mejorando el comportamiento electroquímico y la capacidad específica de las muestras que fueron tratadas por períodos de tiempo más prolongados.

Palabras clave: LiFePO_4 , batería, cátodo, tamaño de partícula.

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1 Introduction

During the last decades, different cathode materials have been studied by various researchers in order to improve their electrochemical properties (Tan *et al.*, 2018), safety parameters (Finegan *et al.*, 2021) and develop new ways to reduce environmental impacts during their life cycle (Pinna, Martínez, Tunes, Drajlín Gordón, & Rodríguez, 2019). Nevertheless, most rechargeable batteries used in mobile electrical devices still employ lithium-ion batteries based on cobalt oxides (LCO, NMC, NCA), due to their lightweight and suitable working voltage. Additionally, a number of methods, such as "greener" materials application, particle size reduction, carbonaceous conductive coatings and super valent metal ions doping or development of new synthesis methods have been used to achieve improvements in cyclability and active materials specific capacity (Fergus, 2010; García-Limón, Salazar-Gastelum, Lin, Calva-Yañez, & Pérez-Sicairos, 2019; Li, Erickson, & Manthiram, 2020; Llusco, Grageda, & Ushak, 2020).

Polyanionic transition compounds with olivine structure in the form of LiMPO_4 ($M = \text{Co, Fe, Mn, Ni or V}$) have been the center of numerous studies (Bensalah & Dawood, 2016), since they present options for lower production cost and lower environmental impact during final disposal (L. Wang, Wu, Hu, Yu, & Huang, 2019). Among these, LiFePO_4 (LFP) created by J. B. Goodenough (Padhi, Nanjundaswamy, & Goodenough, 1997) has been one of the most investigated because it shows relevant physical and electrochemical characteristics, such as suitable working voltage, higher than 2000 cycles of useful life, high specific capacity (150 mAhg⁻¹) and good thermal stability. Nevertheless, its commercial implementation has been limited due to its low electronic conductivity and ionic diffusivity. Both characteristics have direct impact on material charging and discharging speeds during cycling (Julien, Zaghbi, Mauger, & Groult, 2012).

From a physical point of view, the time it takes for a particle of active material to be charged or discharged is limited by lithium-ion diffusion coefficient in the material and path length that ion must travel. These two parameters define the time it takes for a lithium ion to diffuse through electrode material (equivalent time, t_{eq}). According to Equation 1, t_{eq} is equal to squared length of diffusive path

(l), divided by the diffusion coefficient (D). Thus, increasing diffusion coefficient D of material through synthesis of more conductive materials or reducing diffusive path length that ion must travel through nanometric materials use, reduces Li^+ diffusion time. Among these two options, the second one does not require any additives or modifications in active material crystalline structure and can be achieved by controlling operational parameters during synthesis of powder or by granulometric control while cathode preparation takes place (Levi & Aurbach, 1997):

$$t_{eq} \approx l^2/D \quad (1)$$

Since active material redox reaction occurs from particle surface towards its interior, use of powders with greater surface area accelerates the process and reduces activation energy required by charging transfer reaction of active material. Smaller particles are also less prone to fractures and have shorter diffusive paths, preventing active material internal isolation (Chung, Ebner, Ely, Wood, & García, 2013). They also improve interaction between active material, conductive additive and electrolyte, increasing mono dispersity and mixture homogeneity allowing a better porosity control inside of electrode body (Ramadesigan, Methekar, Latinwo, Braatz, & Subramanian, 2010; Satyavani, Ramya Kiran, Rajesh Kumar, Srinivas Kumar, & Naidu, 2016). Unfortunately, as surface is increased, more reactive material is exposed and it is prone to react irreversibly with electrolyte.

A lithium-ion battery works due to a protective layer formed on electrode surface delaying future reactions with electrolyte, but it also affects cell capacity and life cycle. As resistance increases, conductive grid produced by conductive powder degrades and isolates active material (Liu *et al.*, 2005; Zhu, Park, & Sastry, 2012). For this reason, control of physical parameters, such as granulometry and electrode porosity can also have a positive impact on cells electrochemical characteristics. However, due to difficulty in standardizing parameters for each active material and mixture composition, most studies do not consider their control during electrodes elaboration on a laboratory scale (Zhao *et al.*, 2016).

Several studies have been conducted to study particle size reduction effects to improve high-rate capacity and cycling stability of LiFePO_4 materials, however; all previous studies (Chung, 2013, Zhao, H 2016, Zahn J. 2021) on cathode powders size effects are performed by wet or dry ball-milled before the slurry mix or during the synthesis process. In this

work, sonification was applied to cathode powders suspensions in the cathodic slurry during the cathode elaboration step to determine particle size reduction and agglomeration reduction of cathode material impact on battery electrochemical performance.

2 Method

In order to study powder size reduction effects in lithium coin cell electrochemical performance, a wet cathode mixture composed of active material, conductive additive and binder was subjected to different periods of ultrasonic treatments and evaluated for electrochemical performance in coin cells batteries.

2.1 Physical characterization

First, active material powder and conductive additive particle size and surface area prior to slurry elaboration were determined by means of laser diffraction (LD) using a Microtrac S3500. LD analysis method is based on laser beam deflection by an ensemble of particles dispersed in liquid. Diffraction or scattering angles are characteristic for a specific particle size. A particle diameter obtained by laser diffraction method (LDM) is equivalent to that of a sphere giving the same diffraction as particles.

To study size and dispersion of active material particles, a field emission scanning electron microscope FE-SEM, Hitachi SU5000 operated at 15kV was used.

2.2 Slurry and cathode elaboration

Cathode slurry was elaborated from a mixture of industrial LFP/C (Argonne National Laboratory), TIMCAL C45 (Xiamen Top New Energy) as conductive additive and polyvinylidene fluoride (PVdF 4%, Xiamen Top New Energy) as binder solution, in a ratio of 80:10:10, respectively. Slurry was mixed for 1hr to 300 rpm in a vacuum mixer (MSK- SFM-7) to improve mono dispersity.

Mixture was divided in four samples and subjected to ultrasound treatment (40 kHz ultrasonic bath) for different periods of time: 0 min (control), 30 min, 120 min and 240 min. Samples were spread on aluminum foil using a doctor blade to a total thickness of 100 μm and dried in an oven at 80 °C overnight to obtain four different electrodes (C0, C30, C120,

C240). A calendaring step was used to homogenize dried electrodes surface and control their porosity to 34%.

2.3 Electrochemical characterization

Dry cathodes were sized to be used in CR2032 coin cells type to perform electrochemical tests. Cells were assembled using a porous polymeric separator made of polypropylene (Celgard 2325), lithium hexafluoride (LiPF₆ 1M) as electrolyte, metallic lithium as anode and C0, C30, C120 and C240 electrodes as cathodes. Cells activation was carried out at a C/10 rate, operating cycles were carried out at C/3, between 2.5V - 3.6V (V vs Li+ / Li) (Miao, Bai, Jiang, Sun, & Wang, 2014).

Electrochemical impedance spectroscopy (EIS) was used for insertion reactions characterization to gain a deeper insight into electro-chemical system. EIS was performed with a potentiostat-galvanostat in a frequency range of 0.01Hz-1kHz with a signal of 10mVs⁻¹ for a 100% state of charge (SOC).

3 Results

3.1 Physical characterization

Untreated LFP powder presented a dispersed granulometric distribution, with P80 of 258 μm in diameter and a specific surface area of 1.136 m²/cm³. In comparison, use of ultrasound reduced particles size (P80) to 18 μm and increased their specific surface area to 2.499 m²/cm³. Conductive additive presented a particle size distribution for P80 of 37.1 μm and a specific surface area of 10.18 m²/cm³. While the treated sample reduced its particle size to 22.4 μm and increased its surface area to 16.62 m²/cm³ as shown in Figure 1.

Figure 2 shows scanning electron microscope (SEM) images of a sample without ultrasonic treatment (a) and a sample that was subjected to ultrasound for 15 min (b). Comparing both samples, a significant decrease in grains size, as well as increase in homogeneity of granulometry for the sample subjected to ultrasound can be observed.

Wang *et al.* (Z. Wang, Zhao, & Takei, 2017) observed a similar phenomenon in structural change in particles suspended in a cathode slurry that was agitated during a certain period of time. Wang, claimed that change in granulometry and associated

electrochemical performance was due to dispersity of additive conductive in the mixture. Considering the above, a granulometry change in both active material and conductive additive could have a greater effect on electrochemical performance of a LIB.

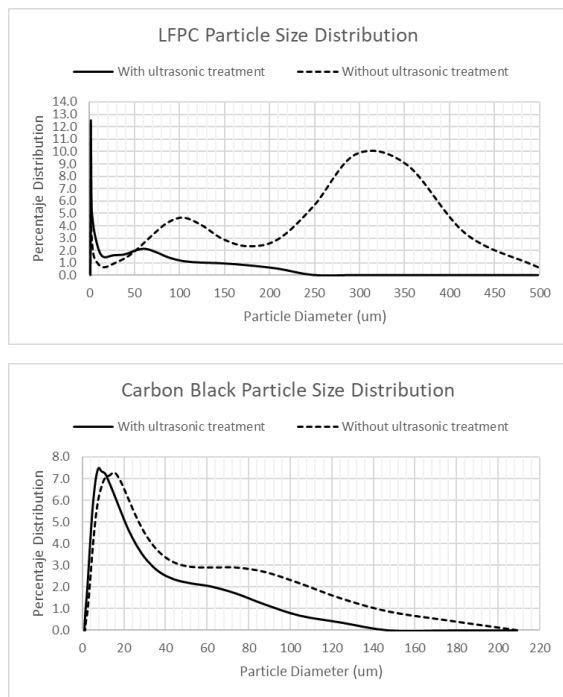


Figure 1: Granulometric analysis of LFPC (upper) and TIMCAL C35 (lower).

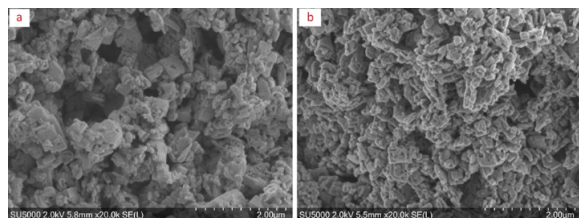


Figure 2: SEM image of LiFePO_4/C . (a) Before ultrasonic treatment and (b) after 15 min of ultrasonic treatment.

3.2 Electrochemical characterization

Control cathode C0 reported the lowest capacity during first activation cycle reaching 121.63 mAhg^{-1} , while cells C30, C120 and C240 cathodes, reported 136.03 mAhg^{-1} , 126.56 mAhg^{-1} and 146.73 mAhg^{-1} , respectively (Fig. 3). Also, during cycling process, all treated cathodes reported a better stability with a more extended discharge plateau and less of capacity

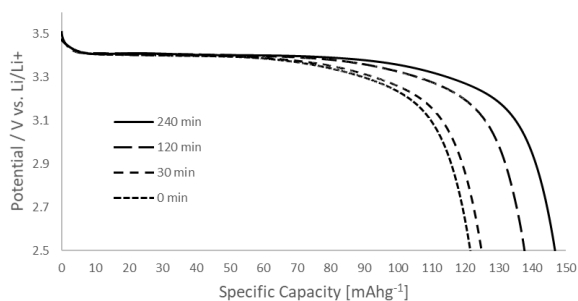


Figure 3: Initial capacity profiles for cathodes with different ultrasonic treatment times.

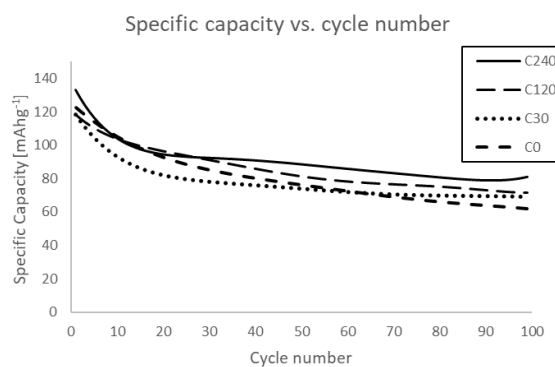


Figure 4: Cathodes cycling performance with different ultra-sonic treatment times.

Table 1. Specific capacities (mAhg^{-1}) according to mixing time.

Cycles	C0	C30	C120	C240
Activation	121.63	136.03	126.56	146.73
	105.84	119.91	116.84	134.87
	107.18	113.67	115.12	126.23
1st	104.2	107.63	116.87	117.32
100th	68.76	61.99	70.27	79.43

loss at end of 100th cycle than C0 cathode, as shown in Figure 4. Some authors have attributed this phenomenon to particles fracture during the Li^+ insertion processes, which causes deterioration of conductive matrix or encapsulation of active material due to passivating layer formation at a high discharge rate (Hu, Zhao, & Suo, 2010; Zhu *et al.*, 2012). As particle size decreases, surface area and kinetics of surface reaction increase, improving active material performance, which has also been reported in other studies (Churikov *et al.*, 2010). Ultrasonic treatment effect of on specific discharge capacity throughout 100 operating cycles is shown in Table 1.

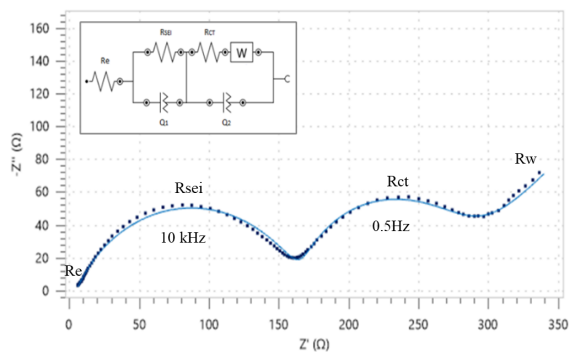


Figure 5: Nyquist plot for cathodes with 240 min of ultrasonic treatment (points) and equivalent circuit fit (line).

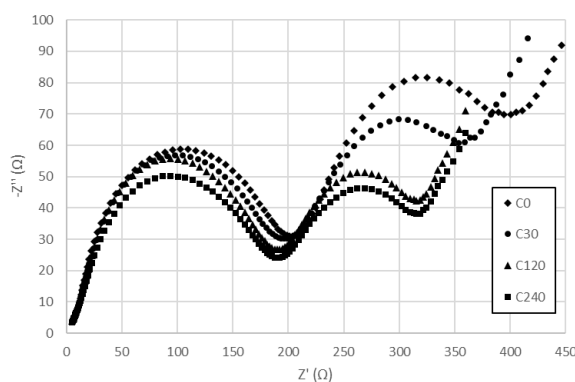


Figure 6: Impedance response for different ultrasonic treatment times.

3.3 Electrochemical impedance spectroscopy

Figure 5 shows a Nyquist plot with ultrasound treatment effect on C0, C30, C120 and C240 cells. All reported spectra have an initial point in high frequency area (Re), corresponding to ohmic resistance (electrolyte), followed by a semicircular curve in medium-high frequency region (Rsei) attributed to solid-electrolyte interface, another semicircular curve in the mid-frequency region (Rct) corresponding to charge transfer, and an inclined line in low-frequency area (Rw), corresponding to lithium ions diffusion in the active material particles (impedance of Warburg) (Gao & Tang, 2008). A simplified equivalent circuit model was developed to analyze impedance spectra. In order to study particle size effect on cell electrochemical processes, charge elements (Q) were used to represent double layer and passivation film capacitances in electrode porous structure (Zhai, Li, Wang, Zhang, & Xu, 2006).

Table 2. Electrode kinetic parameters obtained from equivalent circuit fitting of experimental data after 100 cycles.

Sample	Rsei	Rct	σ
C0	279	251	21.04
C30	188	237	19.7
C120	175	162	16.03
C240	164	122	15.64

The semi-circular curve in mid-frequency zone, corresponding to Rsei, was similar for all treatment times, a possible indication that although granulometry effect in impedance reduction related to surface area increase exists, it is limited and it may be related to contact area increase between particles, PDVF and current collector (Zahnaw *et al.*, 2021).

On the other hand, the half circle in mid-frequency zone corresponding to Rct showed a significant reduction with increase of ultrasonic treatment time. Other authors (Gaberscek, Moskon, Erjavec, Dominko, & Jamnik, 2008; Satyavani *et al.*, 2016) have reported that since smaller particles have a lower diffusion coefficient and shorter diffusive paths, they have better electrical conductivity. Satyavani has attributed this phenomenon to a decrease in reaction activation energy due to surface area increases in active material particles. Adjusted parameters for the equivalent circuit are shown in Table 2.

Cells exhibited a progressive decrease in their general resistance as treatment time increased. The most significant change was observed in medium frequency zone (Rct), which presented resistance reduction up to 52% that could be attributed to activation energy decrement for redox reactions. Low-frequency zone also had a significant reduction of resistance, reporting 42% less resistance than the C0 cathode, which could be associated with an increase in the solid-electrolyte interface.

Warburg coefficient (σ), that considers a barrier for lithium ions diffusion, also decreased as treatment time and surface area increased. Since this coefficient corresponds to the entire cathode and not to isolated LFP material, it is possible to assume that particle size reduction decreased material diffusive paths, facilitating Li^+ ions transport as other authors have observed (Xi *et al.*, 2012).

Conclusions

In this work, a study was carried to evaluate reduction of granulometry of active material and conductive additive effect during electrode slurry manufacture on final electrochemical performance of a LIB. Active material (LFP) and conductive additive (TIMCAL C45) powders were subjected to an ultrasonic treatment while suspended in PVDF. A laser diffraction and scanning electron microscope analysis determined changes in granulometric dispersion and surface area of particles of active material and conductive additive when they were exposed to ultrasonic frequency treatment. As a result, LFP grain size reduced from 258 μm to 18 μm and specific surface area increased from 1.136 m^2/cm^3 to 2.499 m^2/cm^3 .

Effect on electrochemical performance was evaluated through study of specific capacity of coin-cell type batteries assembled with treated cathodes. Experimental data reported a more stable behavior during activation cycles and a higher specific capacity after 100 cycles as treatment time increased from 0 to 240 min. C240 cell reported 20.63% more capacity than C0 reference cell during first activation cycle and 15.51% after the 100th cycle. Hence, a direct correlation between time samples were subjected to treatment and the reported capacity was observed.

Electrochemical impedance spectroscopy showed that half circle in the mid-frequency zone corresponding to charge transfer reaction was significantly reduced as ultrasound exposure time increased from 251 Ω for C0 to 122 for C240. Results show that cells decrease in capacity and increase in impedance are strongly related to material granulometry as reported for cell C0.

In general, granulometry control of mixtures helped reduce powders agglomeration during battery elaboration process, allowing to improve electrodes performance for their use in lithium-ion cells.

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