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Lattice Microstructure Design for Cathode Electrodes for High-Performance Lithium-Ion Batteries

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Abstract. The electrode geometry is an essential parameter affecting the cycling performance of batteries. In this work, the effect of lattice geometry of the cathode electrode on battery performance was studied by theoretical simulations keeping its volume constant. It was observed that the variation of the lattice geometry improves the cycling performance when compared to conventional planar geometry. The improvement of thr cycling performance in the lattice geometry is related to variations in the electrolyte current density. It was demonstrated that the lattice geometry allows to improve the discharge performance in lithium-ion batteries at higher discharge rates.

Keywords: Electrode, lattice, simulation, capacity, lithium ion battery.
PACS: 88.80.F-, 88.80.ff, 88.05.-b

INTRODUCTION

Lithium-ion batteries are one of the most widely used energy storage systems in electronic devices, mainly based on their autonomy. Advances in electronic miniaturization require batteries increasingly smaller and lighter, safer and with higher performance [1]. Lithium-ion batteries present high energy density, low self-discharge, no memory effect, high number of charge/discharge cycles, and low weight, being thus advantageous with respect to other battery technologies [1]. Lithium-ion batteries consist of two electrodes (negative: anode and positive: cathode) and a porous separator with electrolyte solution. The electrodes affect the voltage range and the battery capacity value [2].

Recently, the trend in this area is to manufacture of three-dimensional (3D) batteries, as 3D geometry allows short ion diffusion distances, regardless of the electrode thickness with high energy and power compared to the 2D geometry [3]. Several 3D geometries have been proposed, such as, interdigitated, concentric, and aperiodic porous

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structures. A geometry that requires special attention is the lattice structure, once it allows an increase in surface-to-volume ratio and the free surface also reduces lithiation stress during the electrochemical processes [4]. This geometry is composed of a unit cell with an open octahedral structure, the unit cell determining the cell porosity and surface-to volume ratio [4]. Lattice geometry is typically produced by 3D printing with a sintering process to create porosity [4]. One of the main advantages of this geometry is the strain tolerance to deformation during the electrochemical processes.

Taking into account that the lattice geometry for electrodes in lithium-ion batteries allow to increase battery performance, the aim of this work is to evaluate the influence of the lattice structure, while maintaining the same volume, through theoretical simulation, as shown in Figure 1. The battery performance of this structure is compared to a conventional planar structure.

METHODOLOGY

The theoretical simulation was performed by the Finite Element Method, applying the Doyle/Fuller/Newman model that describes the battery operation [5].

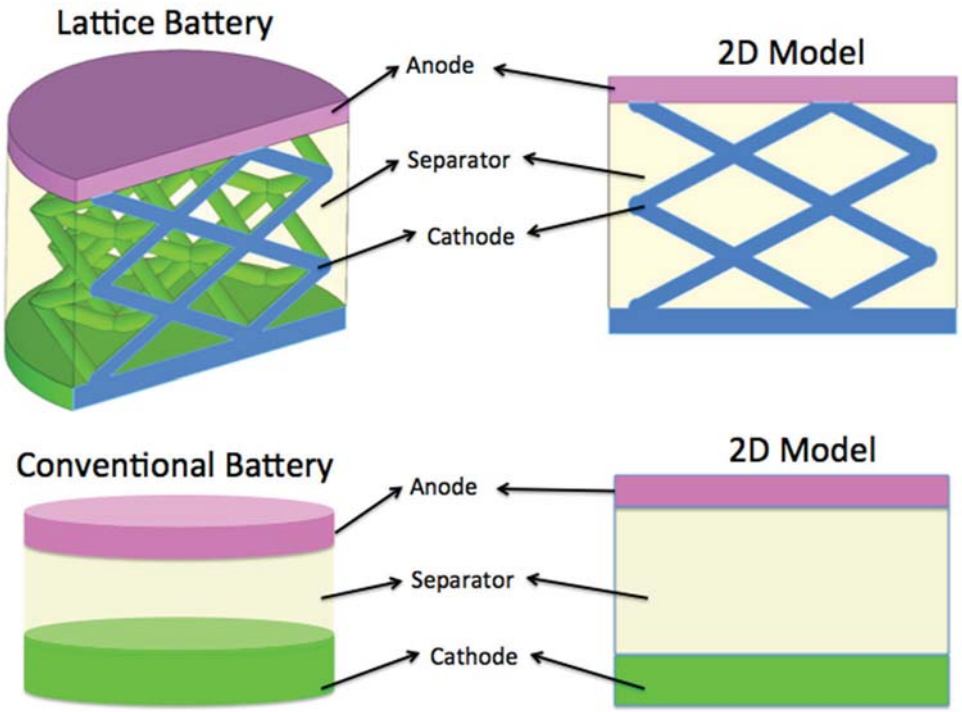

FIGURE 1. Schematic representation of the lattice and conventional geometries applied in the simulated batteries.

Table 1 presents the main values of the different parameters used in the simulations for the separator and the cathode in Li/Li_xFePO_4 half cells. The complete mathematical formulation for the simulations can be found in [5].

TABLE 1. Parameters used in the simulations.

Electrochemical parameters of the battery components			
Parameter	**Unit**	**Separator**	**Cathode** (Li_xFePO_4)
$C_{E,i,0}$	$mol.m^{-3}$		3900
$C_{E,i,max}$	$mol.m^{-3}$		21190
C_L	$mol.m^{-3}$	1000	
L_i	m	150×10^{-6}	20×10^{-6}
$k_i(T)$	$S.m^{-1}$	a)	a)
$D_i(T)$	$m^2.s^{-1}$	b)	b)
$D_{ef,i}$	$m^2.s^{-1}$	$D_i(T)\times4.84\times10^{-2}$	$D_i(T)\times0.444^{1,5}$
D_{LI}	$m^2.s^{-1}$		3.2×10^{-13}
$D_{LI}(T)$			c)
ε_i		0.70	0.444
σ_i	$S.m^{-1}$		11.8
i_{1C}	$A.m^{-2}$	17.5	
$E_{ad,i}$	$J.mol^{-1}$		39×10^3
$E_{ak,i}$	$J.mol^{-1}$		29×10^3
T	K	298.15	298.15

a) Model Fits: Ionic conductivity as a function of salt concentration in the $LiPF_6$ in EC:DMC mixture [6]:

$$ki(T) = c\times(-10.5+(0.0740\times T)-((6.9610^{-5})\times(T^2))+(0.668\times c)-(0.0178\times c\times T)$$
$$+((2.8\times10^{-5})\times c\times(T^2))+(0.4949\times c^2)-((8.86\times10^{-4})\times(c^2)\times(T^2)))^2$$

b) Diffusion coefficient as a function of temperature [5]

$$D_i(T) = 10^{\left(-(0.22c)-4.43-\left(\left(\frac{54}{T-229-5c}\right)\right)\right)}$$

c) Diffusion coefficient of Li ions [5]

$$D_{Li}(T) = D_{t298,15i}e^{-E_{ad,i}/R}\left(\frac{1}{T}-\frac{1}{298.15}\right)$$

RESULTS AND DISCUSSION

Li/Li_xFePO_4 half-cell lithium-ion batteries with conventional and lattice geometric configurations (Figure 1) were simulated at low, medium and high discharge rates with the same volume of its components. The results are represented in Figure 2.

Figure 2 shows that at low discharge rates up to 200 C, the discharge value is very similar for both geometries due to the low effective ion mobility at this discharge rate. Therefore, up this discharge rate, the different geometries does not affect the battery performance.

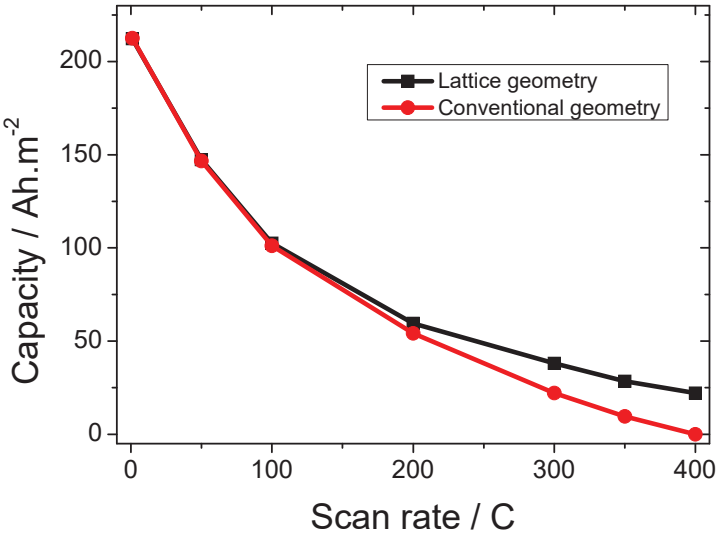

FIGURE 2. Delivered discharge capacity as a function of scan rate for the different electrode geometries.

For discharge rates above 200C, different discharge capacity values are observed for the lattice geometry compared to the conventional geometry, the latter geometry facilitating ion transport though a shorter diffusion paths with an enhanced electrochemical reaction due to the larger interface area between separator and cathode.

At higher discharge rates, the conventional geometry limits the transport of ions and electrons, resulting in a very poor battery performance. On the contrary, comparing both samples, the lattice structure shows a better discharge capacity.

To assess the differences in the discharge capacity value in both geometries, Figure 3 shows the electrolyte current density in the different regions of the battery. These figures show the battery discharge process, where the ions move from the anode to the cathode.

Figure 3a) shows the electrolyte current density for the lattice structure. In this structure there is a larger density of ionic current in the cathode region, changing the direction of movement of the ions to reach the cathode. The fact that the ions reach the cathode material earlier, allows a high percentage of ions to take part in the intercalation process as they travel shorter distances within the separator.

In the conventional geometry, Figure 3b) shows that the electrolyte current density is uniform in all battery regions.

The main advantage of the lattice structure can be observed in Figure 3a): the cathode is dispersed and embedded in the separator, shortening the travel of the ions in the separator until they reach the cathode, implying less resistance caused in the ion's mobility.

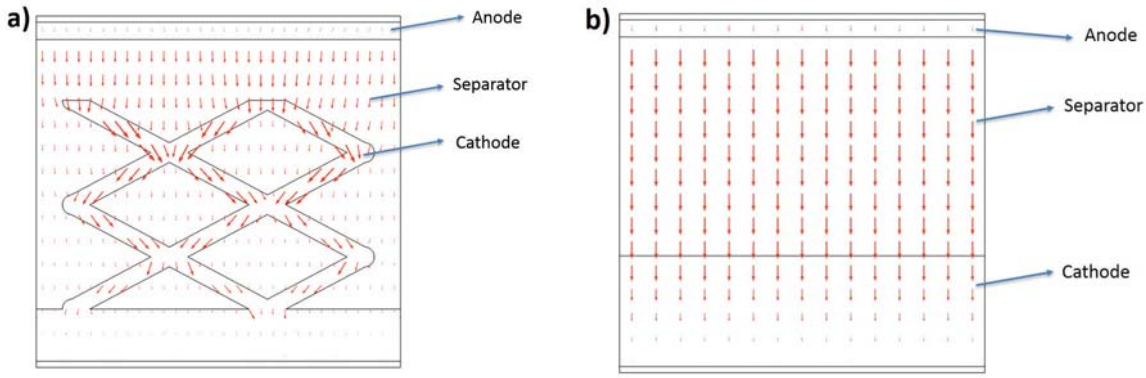

FIGURE 3. Electrolyte Current Density at the battery for 350 C: a) lattice and b) conventional structure

Furthermore, in the lattice structure (Figure 3a) it is shown that in the cathode region closest to the current collector, the ionic current density is lower compared to the conventional structure (Figure 3b), which proves that a high percentage of ions take part in the intercalation process earlier, due to the larger contact area between the cathode and the separator. The cycling behavior of this geometry can be further optimized through the evaluation of other parameters, such as electrode mass or pore structure, among others.

CONCLUSION

Electrode geometry affects battery performance, and, in this work, a lattice geometry was theoretically evaluated for Li/Li_xFePO_4 half-cell lithium-ion batteries and compared with conventional geometry, with the same volume of the components. Lattice geometry has been shown to improve cycling performance compared to conventional geometry at high discharge rates. The discharge capacity value is affected by the geometry, being observed different electrolyte current densities in all battery regions. It has been shown that the lattice geometry facilitates ions transport via a shorter diffusion path originated by a larger interface area between separator and cathode. Thus, the lattice geometry enhances the cycling performance and is adequate for the next generation of additive manufactured high-performance lithium-ion batteries.

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