Study of Fractal Dimension and Porosity of Li$_2$TiO$_3$ Used as a Battery

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ABSTRACT

Lithium ion batteries are becoming more important because of their high energy density and design flexibility. The capacity of these batteries is usually cathode limited; so, it follows that increasing the capacity of the cathode is essential to raise the performance of such batteries. In this work, fractal dimension study is used to understand the behavior of a Li$_2$TiO$_3$ made by mechanical milling as a way to improve their uses in energy storage. Digital image analysis allows the study of fractal dimension; X-ray, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis were used to analyze changes on the surface of samples from the current results the distinctive characteristics of the surfaces for each sample may be obtained, making it possible to predict a future behavior of the samples. MATLAB software FRACLAB 2.03 developed by INRIA was used as a tool.

INTRODUCTION

Rechargeable lithium-ion batteries are widely used today as the main power sources for portable electronics and have a promising application in future transportation and large-scale energy storage.

 Particularly, to meet demands the high energy density, long cycle life, and environmental friendliness for electric vehicles (EVs) and hybrid electric vehicles (HEVs), various electro-active materials have been explored as alternatives to replace current carbonaceous anode in which has these materials have a limited theoretical capacity of 372 mAh g$^{-1}$. In the past two decades, many researchers focused on metallic or semi-metallic elements which can alloy with lithium reversibly and release a high Li-storage capacity [1-2].
Seemingly, one of the best solutions for these systems is the Li ion battery (LIB) that exhibits great potential for outstanding performance. The high energy density of LIBs has been produced commercially, but the low rate capability of LIBs has limited its use in important applications such as hybrid electric vehicles (HEVs) and portable power tools that require fast charging and discharging [2].

Since the isolation of graphene in 2004, excitement has been widespread among scientists due to its exceptional properties. Graphene is ideally suited for implementation in electrochemical applications due to its large electrical conductivity, vast surface area, and unique heterogeneous electron transfer.

During the second half of the twentieth century, metal matrix composites (MMCs) have been considered as one of the important materials. Graphitic structured materials like carbon nanotubes (CNTs), graphite, and graphene have been among the most widely researched materials due to their exceptional mechanical. The Graphene is favored by excellent mechanical properties and high electrical and thermal conductivities. Not much research, however, has been found on synthesis of metal–graphene composites and on the understanding of graphene dispersion on mechanical properties [3-4]. In this research, graphene was used as an alternative to dope the lithium.

**EXPERIMENT**

Pure materials (Sigma), Lithium Titanate, Titanium Oxide powders and Graphene oxide, were prepared by milling the corresponding quantity of metal powder in a high energy SPEX 8000M connected to a hardened steel container with 13mm(O) balls as milling media, under inert Ar atmospheres.

Pressed samples were mounted, polished and etched; using standard metallographic techniques in order to carry out the microstructural observations by using a scanning electron microscope (SEM) JEOL-5800-LV, without sintering process. The structural changes of powders during the milling process were determined by X-ray diffraction (XRD). A Panalytical X’Pert PRO diffractometer (40 kV, 35mA) with Cu Kα radiation (λ = 0.15406 nm) was used for the measurements.

SEM images were taken for their analysis by fractal dimension; the feasibility of the two-dimensional R/S analysis was tested with synthetic matrices representing fractional surfaces. In this work, the MATLAB software FRACLAB 2.03 developed by INRIA (http://www.irccyn.ec-nantes.fr/hebergement/FracLab) was used to understand the fractal behavior of the samples. This process is shown in figure 1.
The dimension of pores changed because of the time involved during the process of compacting and milling: the fractal theory is a very useful tool to analyze a complicated system. Fractal dimension (D) can be detected from the slop of $\lg N$ and $\lg \varepsilon$. The microstructure feature is related to fractal dimension. The number of grid $N$ multiplied by $\varepsilon$ is approximate the length of the grid $L(\varepsilon)$. A pore area, when $\varepsilon$ becomes smaller when time is increased. The relationship relating the length estimate $L(\varepsilon)$ with $\varepsilon$ given by:

$$L(\varepsilon) = M\varepsilon^{(1-D)}$$

(1)

Figure 1. FracLab image during fractal dimension analysis.

The images obtained from SEM were charged on Matlab software, using the third party FracLab. This tool has the necessary elements to calculate the fractal dimension once image process is made.
DISCUSSION

Fractal dimension describes some part of the samples behavior. It is noted that the intensity of Ti and O observed, and these elements have been viewed in SEM, but lithium and graphene is impossible to see it in SEM analysis. When ball milling was longer that 6 h contamination in sample was observed. It demonstrates that Ti will be re-oxided under long ball milling time which is in agreement with XRD results. Other investigations demonstrated that 10 h are the limit time for milling [5-6].

**Table 1.** Densities of nanometric samples and milling time with fractal dimension.

<table>
<thead>
<tr>
<th>Milling intensity [h]</th>
<th>Density</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.3364 ± 0.2610 g/cc</td>
<td>0.86</td>
</tr>
<tr>
<td>4</td>
<td>3.2516 ± 0.0790 g/cc</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Some studies show that the structure, surface chemistry, and electrochemical behaviors of Li2TiO3 reduced graphene oxides [7-8]. These findings may be beneficial to the material design of graphene-based anode materials with high energy density.

**X-ray Diffraction**

The diffraction profiles in XRD pattern of the composite indicate that the structure of Ti and O keeps unchanged during ball-milling. The principal problem in x-ray analysis is the capability to observe Lithium. In figure 1., it is possible to see the Ti and O, but to understand the behavior of Lithium in this research the IEES (Electron Energy Loss Microscopy) study in TEM was made.
Figure 2. X-ray diffraction of TiO$_2$ and Li$_2$TiO$_3$.

**SEM Images analysis**

Figure 3. SEM image of Li$_2$TiO$_3$ samples milling with TiO$_2$ and doped with graphene.
Figure 4, shows the IEES. The peaks of lithium can be compared with the references observed in EELS Atlas made by R.P Burgner [9-10].

![Graph showing IEES study where Lithium is shown](image)

**Figure 4.** IEES study where Lithium is shown.

**CONCLUSIONS**

The results of fractal dimension are shown in table 1. The samples of higher fractal dimension were observed at 4h. The XRD were listed in figure 2. In this graphics, it was possible to see that Ti and O define the structure. Figure 3 shows that there were changes in surface, which were cased made by graphene. Samples were made by green powders of materials with 5 grams of weight, and compacted in 5 seconds with 10 tons. In general, the fractal dimension of the samples reflects the changes in surface observed by SEM analysis. For future work, more studies about graphene reaction with lithium will be required.

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