Characterization of Advanced Nanomaterials for Lithium Ion Batteries Cathodes

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Nowadays, the high and fluctuating oil prizes combined with the urgent need for clean transport technologies have pushed the leaders in the energy storage industry to develop high capacity batteries to sustain a driving autonomy that could competition oil-based vehicles. For this purpose, safe and efficient materials regarding the charge/discharge cycling as well as the storage capacity need to be developed for each electrode of the battery.

At this time, the more promising materials for the positive (cathode) electrode of lithium ion batteries (LIB) in terms of electrochemical properties and safety has been the lithium iron phosphate, $LiFePO_4$ (LPF), powders. However, the bulk electronic conductivity of lithium iron phosphate is quite low, and carbon is generally added in the LPF matrix or at the LPF particles surface to enhance their electrical conductivity [1]. Recently, orthosilicate materials were investigated for cathode electrodes due to the SiO^{4-} polyanion potential in reducing the M^{2+}/M^{3+} redox potential in Li_2MSiO_4 nanomaterials (M = Mn, Fe, Co or Ni), thus improving the charge/discharge behavior of the cell [2].

Since the last two decades, scanning electron microscopy has faced a revolution in the development of field-emission microscopes with the most powerful in terms of versatility and spatial resolution being the cold-field emission scanning electron microscope (CFE-SEM). This type of SEM provides low voltage surface-sensitive imaging as well as low voltage STEM imaging with transmitted electrons detectors combined with high efficiency x-ray detectors and transmitted diffraction capabilities that permitted to obtain high quality results on a wide range of materials science topics [3, 4]. Figure 1 is a comparison of a LFP powder in pristine condition (Fig.1a, b) and with a carbon layer at the particles surface (Fig.1c, d) where the visibility of the carbon layer is obvious when considering the loss of contrast from the facets of the particles in Figure 1c, d. Micrographs and an x-ray map obtained at low voltage in deceleration mode as well as in STEM mode from a Li_2CoSiO_4 orthosilicate are shown in Figure 2. The high spatial resolution achieved in these micrographs is striking and demonstrate the high capability of this type of new CFE-SEMs to characterize and assist the development of new potential nanomaterials for LIB.

References:

[1] K. Zaghib *et al*, Positive electrode: lithium iron phosphate, In *Encyclopedia of electrochemical power sources* (2009), p. 264-296: Elsevier.
[2] K. Zaghib *et al*, Journal of Power Sources, **160** (2006), pp. 1381-1386.
[3] M. Guinel *et al*, Journal of Microscopy, **252** (2013), pp. 49-57.
[4] N. Brodusch, H. Demers, and R. Gauvin, Journal of Microscopy, **250** (2013), pp. 1-14.
[5] N. Brodusch *et al*, Surface and Interface Analysis, **46** (2014), pp. 1286-1290.
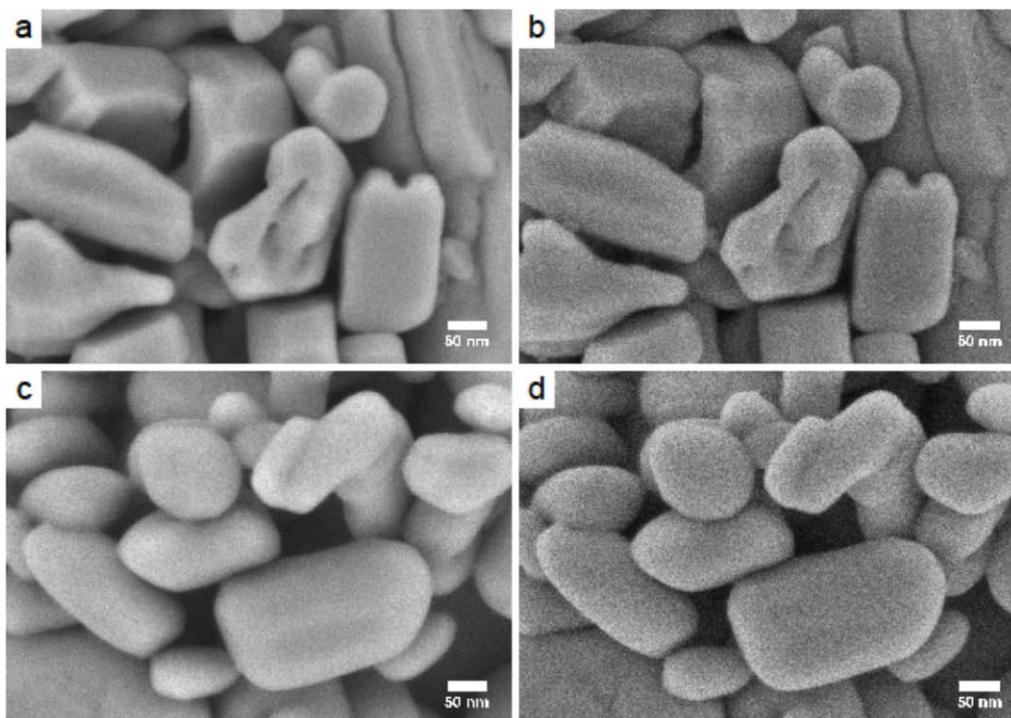
Figure 1. Secondary electron micrographs of a pristine LPF powder (a, b) and the same LPF powder with a surface carbon layer (c, d) recorded at $E_0 = 2$ kV with a stage bias of 10 V (landing energy of 1.9 kV). (a, c) Upper in-lens detector, (b, d) top in-lens detector without energy filtration.
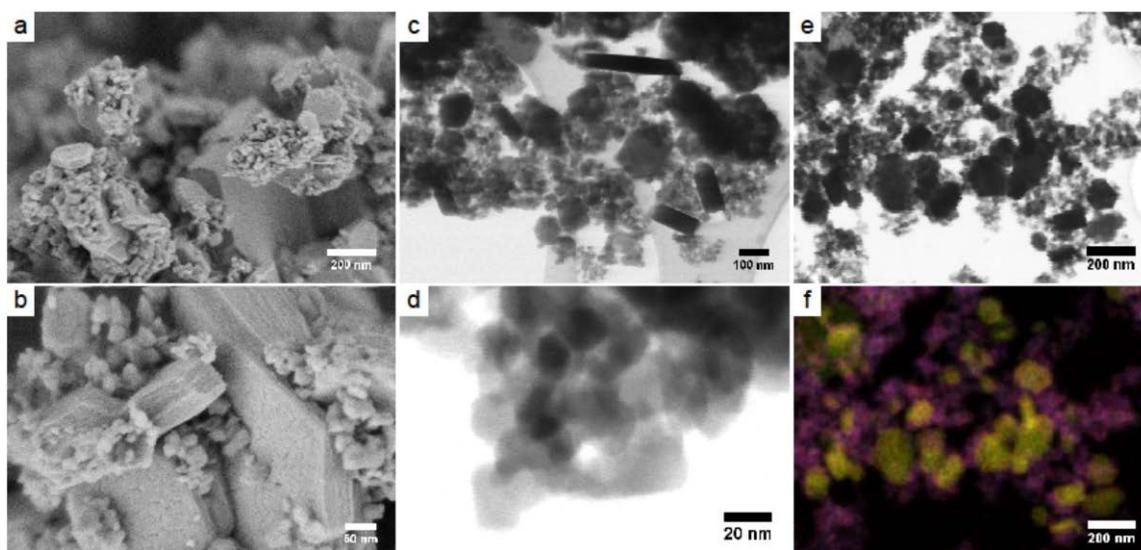

Figure 2. (a, b) Secondary electron micrographs with landing voltage of 1 kV in deceleration mode with the upper detector, (c, d) bright-field STEM micrographs at $E_0 = 30$ kV and (e, f) bright-field STEM micrograph and its corresponding EDS-x-ray map showing the Li_2CoSiO_4 nanoparticles in pink and the CoO by-product particles in yellow. All micrographs were from a Li_2CoSiO_4 nanopowder used as a cathode material for LIB.