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Short communication

$LiCoO_2$ particle size distribution as a function of the state of health of discarded cell phone batteries

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ABSTRACT

The size of $LiCoO_2$ cathode particles have fundamental importance on the electrochemical performances of corresponding lithium-ion batteries, especially on their charge capacity and retention upon charge-discharge cycling. Battery cycling and storage are known to promote changes in the crystalline structure of $LiCoO_2$ cathodes as well as cracks, fractures and dissolution of their particles. However, up to now there are no measurements reporting systematic changes in cathode particle sizes, as described in this study, in which the sizes of $LiCoO_2$ particles extracted from cathodes of discarded batteries decrease with the battery's state of health (SOH).

1. Introduction

The performance of lithium-ion batteries is greatly influenced by the size, morphology, shape and crystalline structure of the electroactive particles of their electrodes [1–5]. In particular, the size of active particles from which the electrodes are manufactured correlates with important electrodes and battery parameters such as cyclability, charge density and capacity, rate capability, charge capacity retention, intercalation kinetics and power capacity [1,4].

A correlation between the electrochemical and kinetic properties of lithium-ion battery cathodes with particle sizes ranging from nano to tens of micrometer have been reported [1]. Nanoparticles-mounted cathodes present large surface area and short diffusion length, resulting in fast intercalation–deintercalation kinetics of Li^+ ions, which favors high-rate discharges [6,7,8]. On the other hand, some drawbacks such as formation of passivation layer on the cathode particles are observed due to large particle surface area in contact with the electrolyte, resulting in lower retention capacity and cycle life. $LiCoO_2$ and $LiMn_2O_4$ cathodes with particles sized in the micrometer range presented better cyclability and charge capacities for the electrodes manufactures with the smaller particles [9,10].

In what concerns nano and micro electroactive particle sizes, it seems that there are intermediate particle sizes whose electrodes present better electrochemical performances. At high-rates discharges (1C and 9C) $LiCoO_2$ cathodes manufactured with 50 nm, 100 nm, 300 nm and 1 μm medium particle sizes showed the highest charge capacity and better cyclability for the 300 nm sized particles [6]. Likewise, among $LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$ electrodes manufactured with eight mean particle sizes ranging from 55 nm to 3210 nm the highest discharge capacities and cyclability were found for those with particles larger than 700 nm [11]. Electrodes of porous nanostructured $LiFePO_4$ particles presented better charge capacities when manufactured under average particle size of 170 nm compared with that of 600 nm [12]. All these characterizations were performed on particles of fresh electrodes.

Moreover, several phenomena have been identified to occur in the cathode particles as a consequence of the electrode/battery cycling and storage, such as the formation of a solid organic-inorganic surface layers over the cathode particles due to electrolyte decomposition reaction, dissolution/migration of cathode transition metals (Co, Mn) to electrolyte and anode surface, structural disorder with exchange between transition metal and Li atomic positions, particle cracks and fractures caused by lattice expansion and contraction of electrode particles during lithium-ion extraction and insertion into the crystalline structure of these compounds [13–16].

However, measurements of cathode particle size after battery cycling or storage for long time are very scarcely reported. Post-mortem analysis on aged battery does not report changes in the $Li[NiMnCo]O_2$ particle sizes of a commercial battery [15]. $LiCoO_2$ particle SEM images taken from an electrode submitted to 150 cycles do not show visible change

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in the particle sizes [17]. Only few papers show SEM images with smaller and more irregular $LiCoO_2$ particles in spent and cycled cathodes, compared with the particles of fresh cathodes [18,19].

Filling the lack of information about this subject, in this work we present size distribution measurements of $LiCoO_2$ particles extracted from cathodes of spent batteries with different states of health (SOH), considering that the value of this parameter is closely related to the numbers of charge-discharge cycles undergone by a battery. The lower the SOH is, the greater the number of charge and discharge cycles that the battery was subjected to.

Cathode particle size distributions were obtained for eight discarded commercial cell phone batteries and for a fresh one. Nine batteries with SOH values from 100% to 25% were analyzed, showing a decrease in the $LiCoO_2$ particle sizes from 5.30–7.80 μm range for a fresh battery (SOH = 100%) to 1.50–2.80 μm range for a discarded battery with SOH = 25%, indicating that the battery cathodes suffered physical, chemical or mechanical processes throughout successive battery charge-discharge cycles or during their storage, which led to a decrease in the $LiCoO_2$ particle sizes.

2. Experimental details

Eight batteries from the same manufacturer and the same model (780 mAh nominal charge capacity, $LiCoO_2$ cathode) with state of health (SOH) values ranging from 25% to 86% were selected among tens of discarded commercial cell phone batteries, collected and stored by a local cell phone service company. A fresh battery (SOH = 100%) was added into the sample set. According to company information, after collected, the spent batteries stayed storage for three to five months before be sent to recycling. The battery SOH was measured at a 0.2C discharge rate as the ratio between the charge measured at discharge and the battery nominal charge capacity. Table 1 shows the SOH values for the selected batteries.

After manual dismantling, the electrodes and separators were heated in a balloon under vacuum for electrolyte extraction by the evaporation-condensation method. In order to detach the $LiCoO_2$ powder strongly adhered to the aluminum collector strip, the cathode was treated in *N*-methyl-2-pyrrolidone (NMP) solvent at 80 °C for 60 min under stirring, resulting in a fine grained powder in suspension into NMP solvent, which was further decanted after three days under resting. By removing the supernatant NMP, the obtained $LiCoO_2$ powder was warmed to evaporate residual NMP. The resulting $LiCoO_2$ powder was three times rinsed with distilled water and dried in a hot plate. The dried $LiCoO_2$ powders were gently crushed in a mortar and pestle and sieved in a 170 mesh (90 μm) vibratory sieving unity in order to separate the larger particle agglomerates whenever present.

To survey the sizes of the particles present in the cathodes, cathode powders from a few batteries were scanned under a wide range (0.3 nm to 10.0 μm) by using the Zetasizer Nano ZS90 particle sizer, that operates under light scattering principle. After identify the $LiCoO_2$ particle size range, the acoustic attenuation spectroscopy (AAS) and scanning electron microscopy (SEM) techniques were employed to measure the particle size distribution (PSD) of the $LiCoO_2$ powders extracted from the nine battery cathodes described in Table 1. PSDs were obtained directly from the AAS equipment, while a graphical procedure was employed to obtain the particle size distribution from the powder SEM images.

In the AAS technique, the attenuation of ultrasound waves traveling through a liquid medium with $LiCoO_2$ in suspension is measured as a function of the ultrasound wave frequencies (MHz). The decrease in the wave intensities is functionally related to the sizes of $LiCoO_2$ particles dispersed in water (at 0.2% in concentration) [20]. The measurements were performed in a Zeta-APS equipment (Matec Applied Sciences), under the 10 nm to 10 μm set-up particle range and in the 1 to 100 MHz ultrasound frequency range.

The $LiCoO_2$ particle size distribution from the powder SEM images were obtained from the linear intercept method [21,22], by drawing lines on $LiCoO_2$ SEM micrographies magnified by 4,000×, in images of 2048 × 1886 pixel at 7.92 pixel·mm^{-1} resolution (FEI QUANTA 200 electron microscope). The size of each $LiCoO_2$ particle was measured as for the length of the segment line crossing the particle border image. The free ImageJ software, calibrated over the SEM scale, was employed to obtain the segment values. The measurements were performed only on those particles in which the border images were clearly visible after digital amplification (zoom). Care was taken to distinguish $LiCoO_2$ particles from the PVDF binder and particle agglomerates. The sizes of 60 to 100 particles were measured in each SEM image to determine the corresponding particle size distribution.

Due to the small number of particles sized from SEM images, their distributions were presented as histograms, whereas continuous curves were employed to describe the distributions obtained from the AAS technique. The PSDs correlate the normalized relative particle number (particle frequency) weighted by the inverse of bin width, with the particle sizes.

Table 1
Battery SOH values and particle size data extracted from the AAS and SEM particle size distributions, Figs. 2 and 4, respectively. The standard deviations σ were obtained from Gaussian fits on Fig. 2 distributions.

Battery	SOH (%)	Smallest size (μm)		Largest size (μm)		Mean size (peak) (μm)		σ (μm)
		AAS	SEM	AAS	SEM	AAS	SEM	–
Batt1	25	1.53	1.50	2.30	2.80	1.88	1.84	0.14
Batt2	32	1.62	1.41	3.97	4.19	2.73	2.69	0.32
Batt3	39	3.07	2.59	4.73	4.99	3.84	3.79	0.30
Batt4	52	2.45	2.20	3.98	4.18	3.12	3.09	0.26
Batt5	55	3.06	2.97	4.68	4.79	3.73	3.70	0.30
Batt6	72	3.28	2.99	4.96	5.59	4.04	3.92	0.31
Batt7	75	4.04	3.98	6.81	6.62	5.16	5.05	0.43
Batt8	86	3.58	3.60	5.96	6.22	4.63	4.52	0.41
Fresh	100	5.34	5.20	7.76	7.80	6.17	6.29	0.48

3. Results and discussion

Fig. 1 shows the PSDs obtained for cathode powders of three batteries from particle size measurements in the 0.3 nm to 10.0 μm extended range, by light scattering. Two kinds of distributions are clearly distinguishable: one with particles sizing from 1 to 4 nm and other with sizes from 1 to 6 μm. The distributions with smaller particles were attributed to C-graphite, added to the cathode material to improve its conductivity and the distributions encompassing the larger sizes were ascribed to $LiCoO_2$ particles. On the purpose to correlate the sizes of $LiCoO_2$ cathode particles with the battery SOH, all results to follow were obtained from measurements carried out by the AAS technique.

The AAS particle size distributions for $LiCoO_2$ powders extracted from the nine battery cathodes as a function of battery SOH are showed in Fig. 2. Clearly, the $LiCoO_2$ particle size distributions change with the battery SOH. The largest $LiCoO_2$ particles were found in the fresh battery cathode (SOH = 100%) ranging from 5.30 to 7.80 μm in sizes, while cathode powder of battery with SOH = 25% presented the smallest particles, sizing from 1.50 to 2.5 μm.

SEM images of $LiCoO_2$ powders detached from cathodes of batteries with three different SOH values (100, 52 and 25%) are displayed on Fig. 3 under a 10,000× magnification (particle size measurements from SEM micrographs were performed on images magnified by 4,000×, as described in the Experimental section). $LiCoO_2$ crystalline particles and foam-like PVDF agglomerate binder are identified and well distinguished in the SEM images. The PVDF is added to the $LiCoO_2$ powder during the cathode manufacture process.

Although present in the powders extracted from the cathodes, carbon particles will not be counted in the AAS measurements, since their sizes between 1 and 4 nm (Fig. 1) are out of resolution of this equipment.