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Operando monitoring the nanometric morphological evolution of TiO₂ nanoparticles in a Na-ion battery

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Abstract

Na-ion batteries are nowadays receiving renewed attention because of its propitiousness for large-scale stationary applications. Although the Na storage mechanism is still not completely understood, TiO₂ nanoparticles are very promising active anode materials in Na-ion batteries provided that a correct dispersion is achieved within the battery electrode. Whilst the structural changes, either in crystallinity or crystalline phase, that occur during operation are receiving much recent attention, the nanometric morphological evolution of the TiO₂ nanoparticles within the electrode is yet to be thoroughly addressed, despite its implication in battery efficiency. In the present work, *operando* small-angle x-ray scattering studies on TiO₂/Na-ion batteries show that whereas the nanoparticle size is preserved during the discharge-charge cycles, the mean distance between nanoparticles increases. The observed morphological changes are consistent with electrode swelling and nanoparticle aggregation during operation, being one phenomenon dominant over the other depending on the applied density current; thus, depending on the differences in ion diffusion within the electrode.

Keywords

operando studies; x-ray scattering; batteries; morphology; titania nanoparticles

1 Introduction

Nowadays, Na-ion batteries are considered as convenient energy storage devices for large-scale grid applications due to the wide availability and low cost of Na in comparison to Li compounds [1–4]. Nevertheless, for the successful implementation of Na-ion batteries, high efficiency electrode active materials are needed and much effort is being currently invested to find suitable, low intercalation potential anode materials. In this respect, TiO₂ nanoparticles (NPs) have emerged as a promising candidate, being currently under thorough investigation despite the remarkable irreversibility of the first discharge-charge cycle [5–9]. Moreover, although the Na storage mechanism remains elusive, much effort is being

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

invested to elucidate the structural changes that TiO_2 undergo during battery operation [10–14]. Additionally, very recently some authors have reported crystalline and crystallinity changes during device operation [15–19], crucial for the development of optimized strategies to improve the performance of these devices.

On the other hand, despite its importance for optimizing battery performance, little attention has been paid to the sub-micrometric morphology of the electrode. Moreover, the nanometric morphological changes that the electrode experiences during operation, to our knowledge, has not previously been addressed, albeit of utmost importance since Na-ion batteries are very complex devices comprised of several materials with different length scale structures.

A solid composite electrode for Na-ion batteries with an active material in the form of NPs dispersed within, can be regarded as a solid-solid colloidal system. Thus, NPs are allowed to move to some extent within the electrode provoking a change in the morphology of the system. Therefore, in addition to the structural changes that occur in the crystalline form and/or the crystallinity, and the formation of new chemical compounds, the morphological rearrangement of the NPs have an impact on battery efficiency [20, 21].

In the last decade, *in-situ* and *operando* Small-Angle X-Ray Scattering (SAXS), either in transmission or grazing incidence geometries, has become a very powerful tool for the characterization of nanoscale phenomena during material preparation and processing as well as on working devices [22, 23] with a time resolution in the millisecond regime [24]. These experiments have facilitated a deeper understanding of, e.g., the underlying kinetics of drying colloidal droplets [25, 26] and nanoparticle formation [27, 28], the morphological evolution during thin film preparation and processing [29–32] or the correlation between polymer solar cell efficiencies and morphology [33]. However, despite the valuable information provided by *operando* SAXS it has not been previously applied to investigate Na-ion batteries during discharge-charge cycles. This work presents an *operando* investigation on the morphological evolution of the TiO_2 NPs employed as the active anode material in Na-ion batteries and demonstrate that continuous irreversible morphological changes in the nanoscale occur during operation.

2 Materials and methods

2.1 Electrode preparation

TiO_2 nanoparticles were prepared as described in [5, 34]. The TiO_2 NPs were then dispersed in 1-methyl-2-pyrrolidinone (Sigma Aldrich) along with conductive carbon (TIMREX Super-P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1, respectively. The obtained slurry was stirred during 24 h and cast on a 7 μm thick copper foil using blade coating. The prepared film electrodes were dried at 70 $^\circ\text{C}$ for 1.5 h and subsequently overnight at 120 $^\circ\text{C}$ under vacuum.

2.2 Coin-cell assembly

CR 2032 coin-cell batteries were assembled in an argon glove box (H_2O content < 1 ppm). Film electrodes were cut to 12 mm diameter, providing an active material mass loading of

ca. 1.3 mg per battery. A sheet of Whatman BSF-80 glass fiber was used as a separator, drenched with 1M solution of NaClO_4 - PC electrolyte. Sodium metal (pure sticks, PanReac AppliChem) was used as counter and reference electrodes. Modified battery casing and current collectors were manufactured to enable enough X-ray transmission for SAXS measurements (see appendix A).

2.3 Electrochemical measurements

Several electrochemical measurements were performed: (a) Rate capability test was carried out in an Arbin-BT4 battery system using specific currents 0.2, 0.5, 1, 2, 3, 4 and 5C for discharge and a constant charge of 0.2C. (b) Cyclic voltammetry was performed employing a VMP3 Potentiostat (BIOLOGIC). Five cycles were measured at each of the following scan rates: 0.1, 0.2, 0.3, 0.4 and 0.5 mV s^{-1} . In both cases, the cells were kept at 30°C for 12 h before the electrochemical measurement and a working temperature of 30°C was set.

2.4 Morphological characterization

X-ray diffraction patterns (XRD) were recorded using a Bruker D8 Advance instrument ($\text{Cu K}\alpha$, 40 kV, 30 mA) in an angular range of $2\theta = 15^\circ - 80^\circ$. FE-SEM measurements were performed in a Hitachi SU 8000 microscope with 1 kV accelerating voltage and 2.6 mm working distance.

2.5 Operando SAXS measurements

Concurrent electrochemical studies and SAXS were measured at the NCD beamline of the ALBA synchrotron (Cerdanyola del Vallès, Barcelona, Spain) employing a photon energy of 10 keV ($\lambda = 1.24 \text{ \AA}$). The X-ray beam was collimated to a beam size of $500 \times 500 \mu\text{m}^2$ (Horiz. $\times$ Vert.). The sample to detector distance was $6480 \pm 5 \text{ mm}$ and was calibrated using silver behenate. The detector employed was a Pilatus 1M (Dectris, Switzerland) with a pixel size of $172 \times 172 \mu\text{m}^2$. Two different *operando* experiments were performed using an IM6 Zahner Scientific Instruments galvanostat/potentiostat at 24°C and 40 % relative humidity: (a) Slow discharge-charge cycle performed at a current density of C/12. Simultaneously, SAXS patterns were recorded with an exposure time of 0.6 s and 30 repetitions, which were subsequently averaged for analysis. This acquisition procedure was repeated with a period of 240 s during the whole discharge-charge battery cycle; (b) Galvanostatic cycling measurement of 8 discharge-charge cycles at a 1C rate. Simultaneous SAXS pattern acquisition was identical to that of the previous experiment, except that the repetition period was set to 120 s. A K-type thermocouple was used to monitor the temperature of the battery casing during the experiments, observing a stable temperature of $24.0 \pm 0.5^\circ\text{C}$ throughout the experiments. All electrochemical studies were performed with a cell voltage window between 2.5 and 0.1 V vs. Na / Na^+ . An applied current rate of 1C corresponds to a theoretical capacity of 336 mA g^{-1} [13, 35]. The batteries were transported to the synchrotron facility in hermetically sealed plastic bags filled with the glove box atmosphere. They were opened immediately prior to the SAXS experiments. See appendix A for the details of SAXS data analysis. All experiments have been repeated and showed a very high repeatability for both the electrochemical response and the evolution of the SAXS patterns. We have also verified that the high intensity X-ray beam did not induce modifications of the material by cycling a battery without the X-ray beam traversing the battery and the

subsequent recording the SAXS pattern. The results obtained (not shown) were within experimental error.

3 Results and discussion

Figure 1a shows a SEM microphotograph of the TiO_2 NPs employed as the active material. These are spherical NPs with a mean diameter of ca. 43 nm and log-normal size distribution (see appendix A). Their crystal structure corresponds to the anatase phase with mean crystalline domains of 6.7 nm (Figure 1b), as determined from the Scherrer equation for the (101) peak. Due to the process employed for the chemical synthesis of the NPs, the anatase domains correspond to the primary synthesized NPs, which were subsequently thermally treated to form larger polycrystalline NPs (secondary NPs), as described in [5, 34]. Figure 1c shows the specific capacity of a battery assembled as described in the experimental section and employing the synthesized anatase TiO_2 NPs as active material. The electrode provided a capacity of 460 mA h g^{-1} during the first discharge, which is larger than the theoretical capacity of TiO_2 (336 mA h g^{-1}) [13, 35]. The cell showed a charge capacity of 211 mA h g^{-1} and a coulombic efficiency of 46%, a value comparable to those reported in the literature for untreated TiO_2 nanostructured electrodes employing organic electrolytes [6, 36]. Moreover, the electrode can deliver reversible capacities of 201 (5th cycle), 171, 153, 139, 132, 126 and 121 mA h g^{-1} at density currents of 0.2, 0.5, 1, 2, 3, 4 and 5 C, respectively. Additionally, when the current reverts to 0.2 C, the electrode recovers a capacity of 178 mA h g^{-1} (see the value for 5th cycle).

To be able to perform *operando* SAXS of the assembled coin-cell, a modification of the cell casing and collectors was performed to ensure sufficient X-ray transmission through the battery. Briefly, the modifications consisted in drilling holes in the stainless steel collectors and installing polyimide windows in the battery casing (full details can be found in appendix A). Very recently, a similar coin cell modification has been reported and used to *operando* study the strain evolution of microparticulate Ge anodes in Li-ion batteries using synchrotron X-ray diffraction [37].

Figure 2 shows the analysis of the SAXS patterns acquired at the NCD beamline of ALBA synchrotron (Cerdanyola del Vallès, Barcelona, Spain) during a discharge-charge cell cycle performed at a rate of C/12. The corresponding profiles are shown in Figure 2e. The low initial voltage value was related to the relaxation of the materials associated with cell storage time, an unavoidable consequence of the time needed for transporting the samples to the synchrotron facility, and not due to the modifications carried out on the coin-cell (see appendix A).

The radially averaged differential SAXS patterns (Figure 2a) were fitted using the SASFit software [38], considering spherical NPs with a bimodal log-normal size distribution and a Sticky-Hard-Sphere interaction within the Local Monodispersed Approximation and a fractal term for the low- q region (see appendix A). The evolution of the fitted parameters (Figure 2b-d) showed that the diameters of both the primary and secondary NPs remained constant throughout the discharge-charge cycle, which shows the good stability of these hierarchical nanostructures upon battery cycling. However, the mean secondary NP center-

to-center distance increased following a sigmoidal temporal profile. These results are consistent with either NP aggregate formation and/or electrode swelling. If NP aggregates with low size-polydispersity are forming, the mean diameter of the aggregates must be larger than 300 nm, which corresponds to the minimum q-range accessible with the experimental SAXS setup installed, since maxima in the SAXS curves are not visible for the low-q region. However, the exponent of the fractal term (see appendix A) did not show an accelerated decrease until saturation sets in, as would be expected for the formation of large NP aggregates [39, 40]. On the contrary, after a rapid fall, the fractal exponent slowly increased again. Thus, in this case, swelling of the electrode is a more likely explanation. Nevertheless, to correctly interpret the changes in the fractal exponent, access to lower q-range is needed. These experiments will be programmed in the near future to provide a more detailed description of the morphological evolution of the electrode over several length scales, from the crystalline structure of the NPs to the micrometer level.

To investigate the battery response on cycling we also followed the evolution of the SAXS patterns during 8 discharge-charge cycles. In addition, for the cycling experiments the applied density current was increased to 1C in order to increase the contribution of the capacitive term of the electrode to the battery performance (see appendix A). Figure 3 correlates the evolution of the SAXS fitting parameters with the simultaneously measured coin-cell electrochemical response. Similar results to those at a rate of C/12 were obtained, i.e., no changes in the primary and secondary NP mean diameter were observed even after the performed 8 cycles, but a monotone increase in the center-to-center secondary NP distance took place. In this case the increment followed a linear trend and did not reach saturation. Furthermore, the exponent of the fractal term followed an accelerated decrease until saturation was reached, pointing towards the promotion of NP aggregate formation.

Our results suggest that two different physical phenomena occur simultaneously. First, electrode swelling implies an increase in the mobility of the NPs within the electrode. Second, NP aggregates form while the cell is cycled, which reduces the exposed surface area of the secondary NPs, thus diminishing the battery electrochemical response in addition to, e.g., the loss of crystallinity of TiO_2 (see appendix A).

Depending on the density current, one phenomenon dominates over the other. When a low current is employed (C/12 experiment), the behavior of the TiO_2 NP composite electrode is approximately half-capacitive and half-diffusive, as revealed by cyclic voltammetry (see appendix A). On the other hand, when cycling is performed at high current (1C experiment), the capacitive contribution represents around two-thirds.

Therefore, although the data suggests that both electrode swelling and aggregate formation occurs simultaneously, the increase of the capacitive term increases the aggregation probability due to an increase in the NP-NP interaction (it is the SAXS structure factor which experiences changes and not the SAXS form factor). Thus, the change in NP-NP interaction results in the aggregation of NPs becoming the dominant phenomenon over electrode swelling.

On the contrary, when the diffusive battery term is high enough, swelling dominates over aggregation, due to the absence of a strong change in the NP-NP interaction that could promote aggregation; thus, instead of a monotone increase of the NP center-to-center mean distance, a sigmoidal curve is obtained. Both phenomena are schematically depicted in Figure 4.

4 Conclusions

Through the concurrent measurement of the electrochemical response of Na-ion cells employing TiO₂ hierarchical NPs as the active anode material and *operando* SAXS experiments, we have observed an increment in the secondary NP mean center-to-center distance, whereas both the primary and the secondary NP mean diameter remained constant irrespective of the density current applied to the battery. Moreover, evidence for secondary NP aggregation during battery operation has been obtained. Our results suggest that both electrode swelling and secondary NP aggregation occur during the battery cycling, revealing that irreversible changes at the nanoscale takes place in the electrode material, which might have an impact on the battery capacity loss during cycling. These results are of utmost importance for the optimization of the new generation of forthcoming electrodes for Na-ion batteries and establish *operando* SAXS as a powerful tool to address nanoscale phenomena in Metal-ion batteries.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Highlights

- Morphological changes at the nanoscale of TiO_2 nanoparticles are monitored during Na-ion battery operation.
- During the discharge-charge battery cycles, the nanoparticle center-to-center mean distance increases.
- Aggregation and swelling phenomena are identified as being responsible for the observed experimental result

Figure 1.

(a) SEM image and (b) X-ray diffraction of the TiO_2 NPs used as active material. (c) Rate capability test at various current densities from 0.2 to 5C in a potential window of 2.5 – 0.1 V vs. Na / Na^+ .

Figure 2.

(a) Experimental (black) and simulated (red) SAXS patterns during the C/12 cell discharge-charge experiment. The curves are shifted for clarity. (b) Primary particle mean diameter, (c) secondary particle mean diameter and (d) mean NP center-to-center distance as extracted from the fitting of the SAXS profiles. The red lines correspond to constant fittings in (c) and (d) and to a sigmoidal profile fitting in (d). (e) First discharge-charge voltage profile at a specific current of C/12 in a potential window of 2.5 – 0.1 V vs. Na / Na⁺.

Figure 3.

(a) Primary particle mean diameter, (b) secondary particle mean diameter and (c) mean NP center-to-center distance as extracted from the SAXS profile fittings for the 1C battery cycling. The red lines correspond to constant fittings in (a) and (b) and to a linear fitting in (c). (d) Discharge and charge voltage profiles for eight cycles at a specific current of 1C in a potential window of 2.5 – 0.1 V vs. Na / Na⁺.

Figure 4.

Sketch of the phenomena observed during the operando experiments. When a C/12 rate is employed, swelling of the electrode dominates, which is represented as a system expansion (left), leading to an increase in the NP mean distance. On the other hand, for the 1C rate experiments, NP aggregation is promoted over swelling, which is represented by maintaining the initial system size and grouping the sketched NPs.