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The peculiar redox mechanism of copper nitroprusside disclosed by a multi-technique approach

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Abstract

We report the structural analysis on copper nitroprusside (CuNP) used as cathode material in a Li-ion battery during the first lithiation process. The investigation involved a multi-technique approach, where multiple edge Extended X-ray Absorption Fine Structure (EXAFS) refinement has been coupled with Density Functional Theory (DFT) calculations. The reduction occurring at the Cu site involves structural distortion, which is believed to be the main reason for the capacity fading in the first cycles.

Keywords

Copper nitroprusside, Li-ion battery, EXAFS, multiple edge refinement, DFT

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1. Introduction

The need for large scale energy storage on the electrical power grid is growing rapidly, and new battery technology is currently being developed to power an increasingly diverse range of application, from cars to microchips. In this context, active material electrodes that allow the rapid insertion and extraction of lithium ions with generally little lattice strain are of great interest. Prussian blue analogues (PBAs), in particular metal hexacyanoferrates, have gained considerable attention among insertion materials due to the ease of synthesis and purification, and wide versatility towards several ions.[1–3] due to the three-dimensional porous network of repeating -Fe-CN-M-NC- units, where Fe and M sites are typically octahedrally coordinated. Copper hexacyanoferrate (CuHCF) has shown considerable performance at high rate as cathodic material,[4] with negligible lattice strain in the (de)lithiation process.[5] In the previous work,[6] we suggested the substitution of one cyano ligand in the octahedral environment of iron in CuHCF with the nitrosyl ligand (NO) to give copper nitroprusside (CuNP), Cu[Fe(CN)₅(NO)]. Briefly, the advantages of such strategy were proven to be: a) the NO does not act as bridging ligand, enhancing the porosity of the structure, which in turn may favour the ion intercalation process; b) the NO takes part in the redox processes concomitant with the (de)insertion of ions as third redox centre together with Fe and Cu, hence extending the specific capacity. However, we experienced a capacity loss during the first 20 cycles and a reversible behaviour in the next cycles that was ascribed only to a fraction of available electroactive species. To reach a deeper understanding of the reaction mechanism and the decay in specific capacity, we focus here on the structural modifications that occur during the first discharge process. In this work, an X-ray Absorption Fine Structure (XAFS) data treatment performed in *operando* mode is presented and combined with computational quantum mechanical modelling to extract structural information on the system dynamics.

2. Materials and methods

The synthesis of CuNP was based on a co-precipitation method, while suitable PTFE-based electrodes were obtained for electrochemical cycling.[6] Galvanostatic cycling with potential limitation (GCPL) was conducted by considering 1C rate equals to the current needed to insert one Li-ion per Fe in one hour, thus a theoretical specific capacity of 114 mAh g⁻¹. Cycling started at C/31 current rate after a rest time at OCP (open circuit potential) conditions (E = 3 V) with a negative imposed current up to 2.0 V vs. Li⁺/Li. X-ray absorption spectroscopy experiments were performed at the XAFS beamline of Elettra Sincrotrone in Basovizza (Italy).[7] The storage ring operated at 2.0 GeV in top up mode with a typical current of 300 mA. The beam was monochromatized using a fixed exit monochromator equipped with a pair of Si(111) crystals. The data were recorded in transmission mode at Fe and Cu K-edges. The energies were defined by assigning the first inflection point of the spectra of the metallic iron and copper to 7112 eV and 8979 eV, respectively. An internal reference of iron and copper foil was used for energy calibration in each scan. The Extended X-ray Absorption Fine Structure (EXAFS) analysis was performed by using the GNXAS package[8,9] that takes into account the multiple scattering (MS) theory. The theoretical signal is calculated *ab initio* and contains the relevant two-body $\gamma^{(2)}$, three-body $\gamma^{(3)}$, and four-body $\gamma^{(4)}$ MS terms,[10]. A typical structure of hexacyanoferrates [11] was used as a structural model for the MS signal calculation.

Total energy calculations were performed within the Density Functional Theory (DFT) framework using the VASP package.[12] The electron wave functions were expanded on a plane-waves basis set

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with an energy cut-off of 850 eV, while the integrations in the Brillouin zone were performed on a grid of $2 \times 2 \times 2$. Geometry optimizations were carried out by means of the conjugate gradient technique using the exact Hellman-Feynman forces acting on the ions. The structure was considered as optimized when the forces acting on the atoms were smaller than $0.03 \text{ eV } \text{\AA}^{-1}$ and the energies variation between successive geometries was below 1 meV. Lithiated structures during discharge were simulated by inserting consecutive atoms of lithium in the model structure, obtained from the literature.[13] Frequency calculations on the stable geometry have been carried out by numerical differentiation of the force matrix. All the optimized degrees of freedom are used in the frequency calculation.

3. Results and discussion

The previous X-ray absorption near edge structure (XANES) analysis[6] evidenced a progressive decrease of the edge energy position of both metals during lithiation, consistent with the reduction of both metallic sites. Indeed, the pre-edge feature at Cu K-edge located at $\sim 8983 \text{ eV}$, related to the well-known $1s-4p$ transition, arose from lithiation deriving from the reduction of Cu^{II} to Cu^{I} . This was accompanied by a partial reduction of $\text{Fe}^{\text{II}+\delta}$ to Fe^{II} . Complementary structural information regarding both metallic sites was acquired with the EXAFS analysis. First, the pristine electrode was inspected to check reliability of the structural model as well as to set the relevant parameters for the minimization. For an accurate extraction of the structural information, both Fe and Cu edges were analyzed by multiple edge approach,[11] *i.e.*, a simultaneous fitting procedure at both metal edges. Details of this fitting approach are available in the references [11,14]. Figure 1 displays the details of the EXAFS analysis for the pristine electrode at Fe (left panel) and Cu (right panel) K-edges. Few relevant EXAFS contributions were necessary to simulate the overall EXAFS signal, including also the three- and the four-body MS terms.

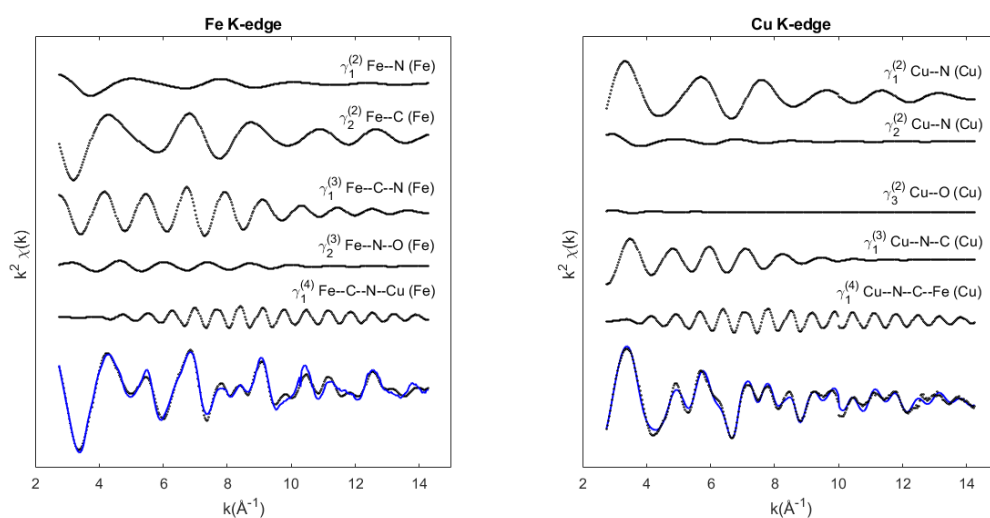


Figure 1. Details of the EXAFS fit of the pristine electrode. The figure displays the MS contributions to the EXAFS signal for both Fe (left) and Cu (right) K-edge. At the bottom the experimental curve (blue line) is compared to the calculated

The main results of the fitting procedure applied to the *operando* dataset are available in Figure 2, where relevant bond length distances (left) and corresponding EXAFS Debye-Waller factors (right) for few selected spectra are included. While bond lengths were not significantly altered during lithiation, an increase of the structural disorder at the Cu site was revealed by the corresponding EXAFS Debye-Waller factors, with a four-fold increase along lithiation. To reinforce this result, an example of DFT-derived structures is graphically reported in Figure 3, and it highlights as the lithiation is associated to growing distortion and structural

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disorder around the copper environment, with a decrease in the chains linearity. This represents a key point in understanding the electrochemical performance of CuNP and the non- fully reversibility of the system.

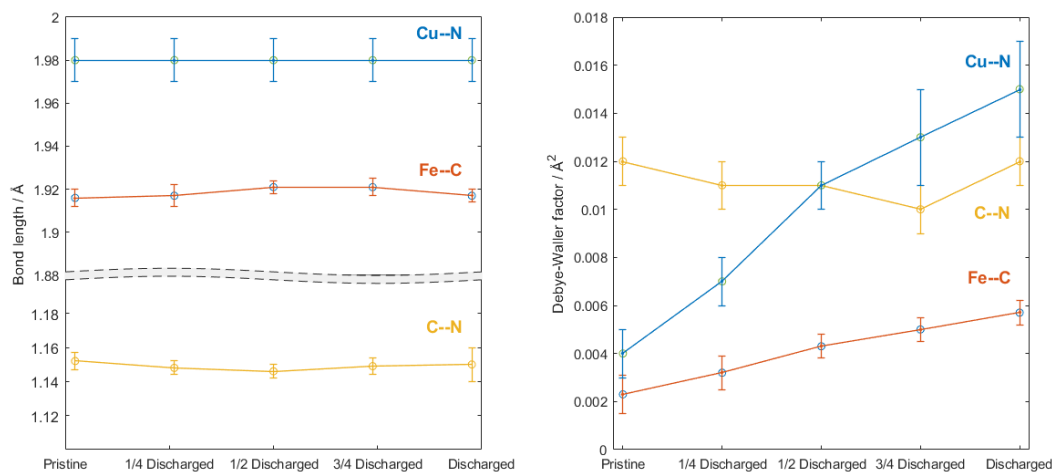


Figure 2. Trends of bond lengths (left) and respective Debye-Waller factors (right) during lithiation

According to the magnetization values, calculated as the integral over local spin densities in the atomic sphere, the reduction of the NO energetically occurs after the Cu sites and is detectable also with a change in the Fe-N-O angle geometry which drops from 178° to 142°, denoting a partial shift from a sp to a sp^2 hybridization. The respective computed vibrational frequencies (Figure 3) are influenced as well, dropping in the case of the NO of roughly 200 cm^{-1} . This outcome is in agreement and complements the *operando* FT-IR experiment carried out in the previous study.[6]

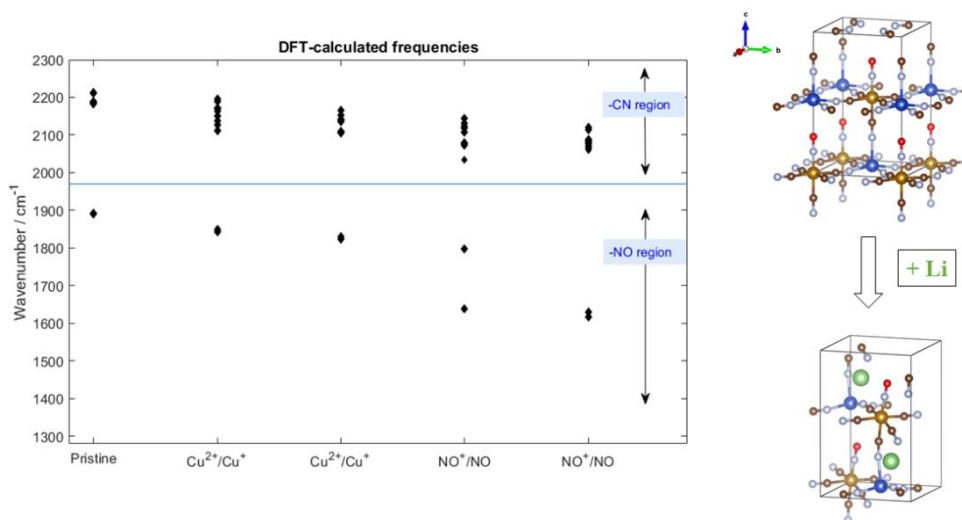


Figure 3. DFT-computed vibrational frequencies and an example of derived geometries. Note that one lattice cell is made of two-unit formulae

4. Conclusions

A multi-technique approach has been employed to thoroughly investigate the lithiation process of CuNP adopted as cathodic material. According to XANES, copper and iron reductions occur during

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lithiation, and are accompanied by a structural distortion at the Cu site, observed by both EXAFS analysis and DFT calculations. The lattice deformation caused by the insertion of Li is ascribed to be the main reason for the capacity fading in the first cycles.

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