

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

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Electrochemical energy storage plays a major societal role due to its widespread technological applications. Active insertion electrode materials have a crystal structure with insertion sites, channels and/or interlayer spacings allowing the rapid insertion and extraction of lithium ions with generally little lattice strain. A typical class of such active electrode materials is represented by Prussian blue analogues (PBAs). Copper nitroprusside $\text{Cu}[\text{Fe}(\text{CN})_5(\text{NO})]$, a Prussian blue analogue, has been investigated for its potentially interesting performances as cathodic active material [1], since the nitrosyl group is a *non-innocent* ligand and may act as third redox centre, beyond metals' ones.

A scalable and reproducible synthesis of copper nitroprusside has been successfully carried out. Electrochemical tests have been performed on formulated electrodes in a coin cell geometry, defining different redox processes in the selected potential window.

Operando characterization [2] has been achieved through different techniques (above all, XAFS, XRD, FTIR) and focused mainly on the first discharge process, since the material clearly undergoes a deep modification during the very first insertion of Li-ions.

Computational quantum mechanical modelling has been accomplished by means of density functional theory (DFT) calculations within the VASP package. Vibrational frequencies have been computed on resulting optimized structures, which have been employed to obtain crystallographic positions as well.

Both Cu and Fe are electroactive at the beginning of cycling, as corroborated by *operando* XAFS measurements. A close inspection of the Cu K-edge XANES evidences a progressively decrease of the edge energy position and reveals a pre-edge peak increasing during lithium-insertion, which is well known fingerprint of the occurrence of reduction to Cu(I). Moreover, a partial reduction of $\text{Fe}(\text{II}+\delta)$ to Fe(II) also occurs. EXAFS calculations show an increment of the Debye-Waller factor for Cu-N bonds and a decrease trend of the Cu-NC-Fe linear chains seen from the Cu site: this indicates an increase of disorder in the system and a possible distortion provoked by lithium insertion. A contraction in the (*xy*) plane and an elongation along the *z* direction is observed by means of *operando* XRD and attributed to the insertion of ions in the tetragonal (*I4mm*) lattice, further verified by DFT calculations on lithiated optimized structures. Interestingly, nitrosyl ligand takes part in the first discharge process, as highlighted by *operando* FTIR and DFT-calculations, evidencing an additional reduction during Li-insertion due to the nitrosyl ligand.

Overall, a very good agreement with experimental data is reached throughout all calculations, making DFT-structures a good approximation of the system under study. The reduction of the nitrosyl group is responsible for an extra-capacity during the first discharge, giving rise to a remarkable specific capacity fairly above the average among PBAs, even though formulation has still to be optimized. Outstandingly, it represents a unique case in PBA materials where a ligand is electrochemically active, beyond the metals' redox centres.

XAFS and XRD measurements at ELETTRA have been done through the 20140337 and 20155185 projects, respectively. MG acknowledges the RFO funding of the University of Bologna.

- [1] A. Mullaliu, M.-T. Sougrati, N. Louvain, G. Aquilanti, M.-L. Doublet, L. Stievano, M. Giorgetti, The electrochemical activity of the nitrosyl ligand in copper nitroprusside: a new possible redox mechanism for lithium battery electrode materials?, *Electrochim. Acta.* 257 (2017) 10.1016/j.electacta.2017.10.107. doi:10.1016/j.electacta.2017.10.107.
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