

Detailing the self-discharge of a cathode based on a Prussian Blue analogue

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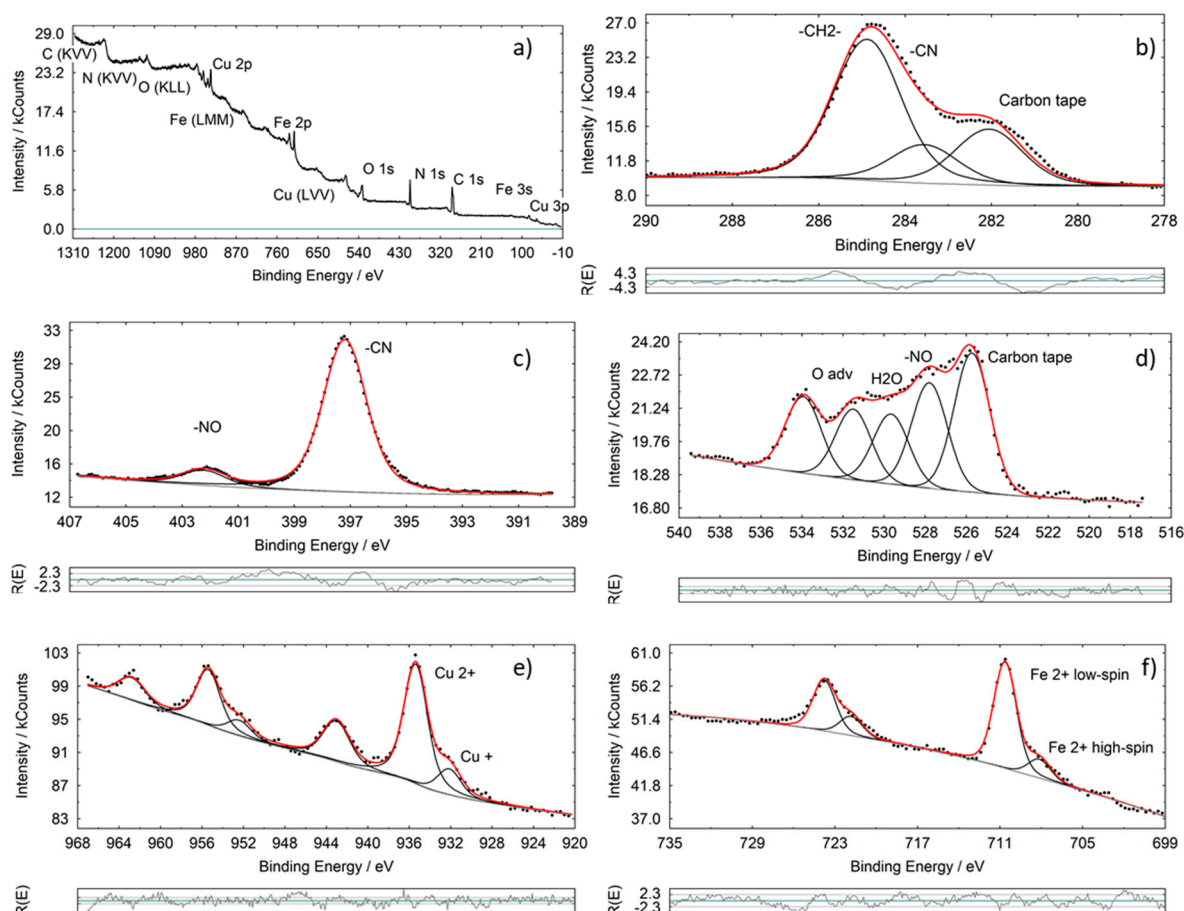


Figure S1: XPS fitted data of copper nitroprusside II. The detailed spectra reported are a) survey b) C 1s c) N 1s d) O 1s e) Cu 2p and f) Fe 2p. The signals denoted as sample holder/carbon tape arise from accidental measurement of the steel sample holder. The analyzer defined measurement spot then covers more than the sample itself. Consequently, the strong contamination layer of adventitious hydrocarbons on the sample holder gives rise to C 1s and O 1s signals, that are shifted to lower binding energies compared to similar species on the sample. This “artificial” shift is due to the charge correction derived from the actual sample, which would be actually not applicable to a species directly on the conducting sample holder.

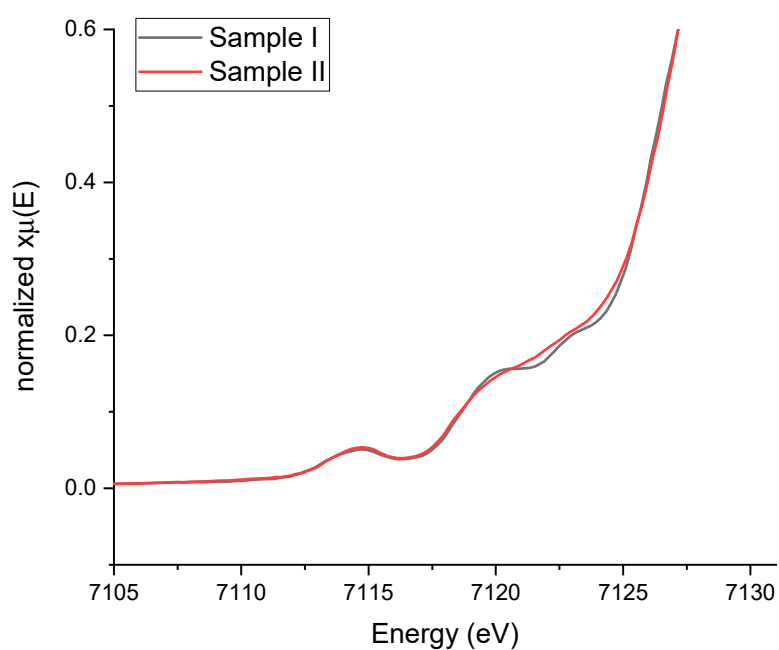


Figure S2: Pre-edge structure at the Fe K-edge for sample I and II (pristine sample). Peak at about 7114-7115 eV is due to the 1s-3d transition, whereas contributions at higher energies (7120 and 2134 eV) are due to edge transition where long range order effect causes the break-down of the local octahedral symmetry (Kuniko Hayakawa et al. J Am Chem Soc 2004, 126, 15618-15623)

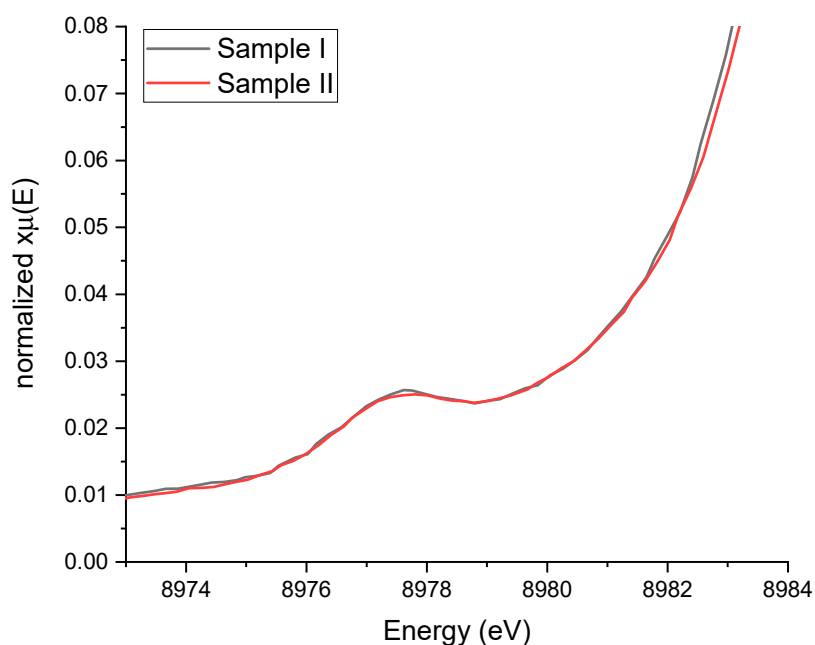


Figure S3. Zoom of the Pre-edge structure at the Cu K-edge for sample I and II (pristine sample). The pre-edge peak at about 8977 eV and the absence of a corresponding peak at 8981 eV indicates the presence of Cu(II) in the bulk of the material.

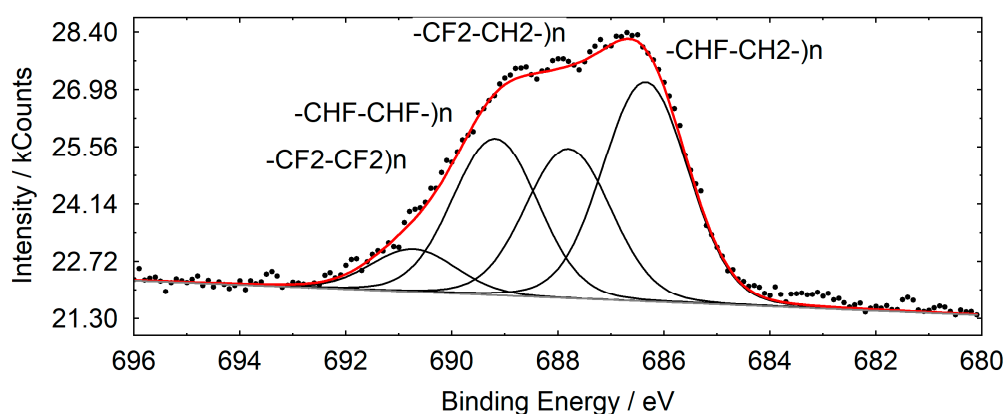


Figure S4: *F 1s* spectrum of CuNP I_formulated. PTFE is known for undergoing dehydrofluorination process: $-CF_2-$ and $-CFH-$ species or similar are likely present, as well as some terminal $-CF_3$ constituting a high number of deconvoluted species in the signal. It is reported that fluoropolymers show sensitivity to ionizing radiation leading to changes in the structure, bonding, reactivity of polymeric system. [Duraud, J.P., Le Moel, A., and Le Gressus, C. (1986) Aging of fluoropolymers irradiated by X-rays, low energy electrons and energetic heavy ion. *Radiat. Eff.*, 98 (November 2014), 151–157.]

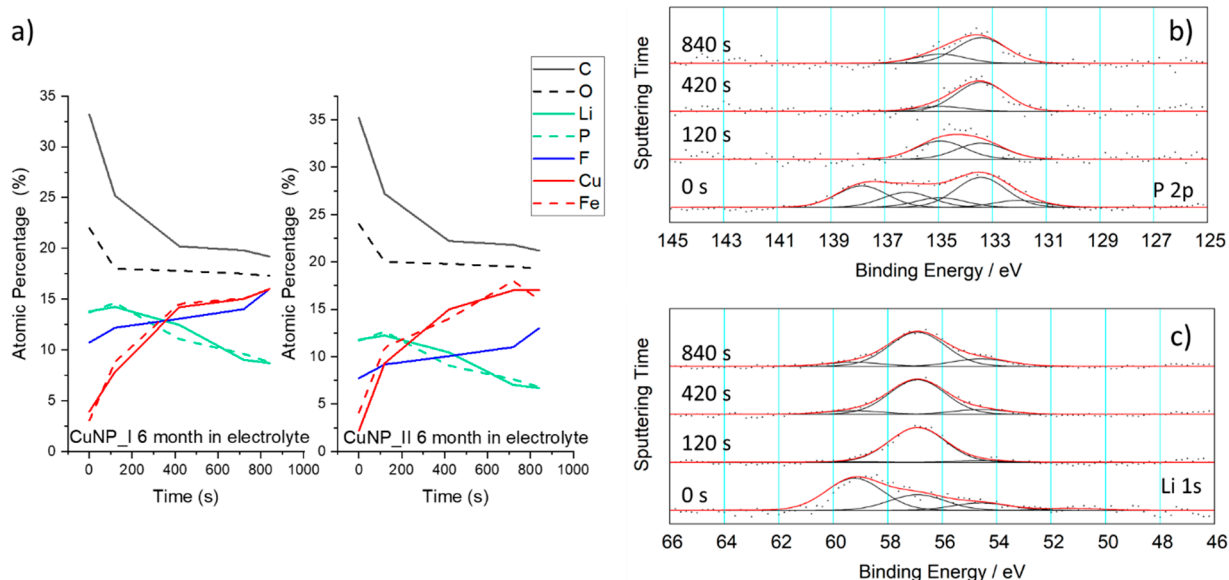
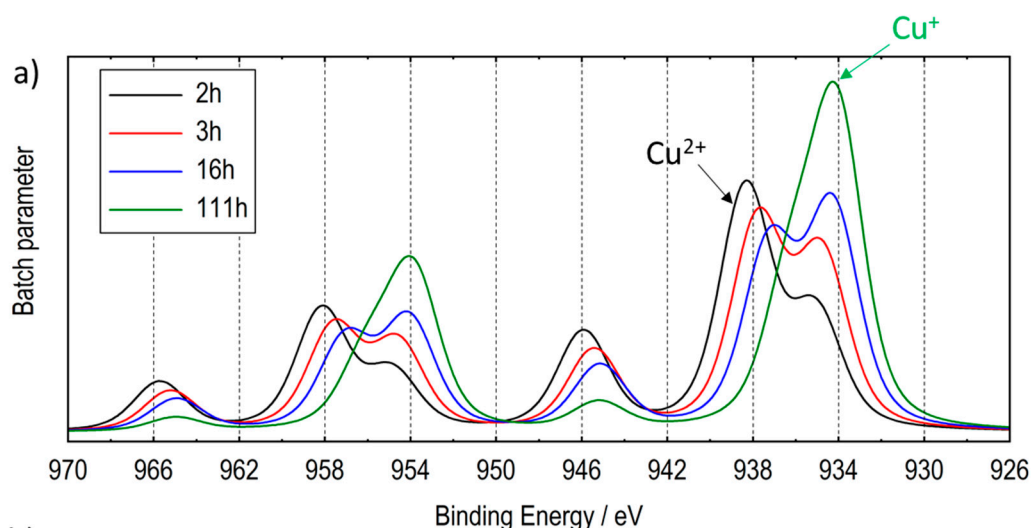


Figure S5: a) XPS depth profile of the evolution of atomic percentage with sputtering time on both samples. b) P 2p and c) Li 1s waterfall spectra of CuNP I six months in electrolyte: these figures display the curves obtained after fitting, in order to show the effect of sputtering. 100 s should correspond to about 1-2 nm (it is not possible to obtain an exact value). Therefore, in total 840 s (14 min) the sputtered depth should be around 12 ± 4 nm. It can clearly be seen that the $LiPF_6$ feature of the electrolyte (visible at the highest binding energies

in the spectra at $t=0$ s) is removed already after the first sputtering step. Thus, a clear distinction between the electrolyte and the interface layer is possible.



b)

Time (h)	Cu^+ (%)	Cu^{2+} (%)
2	31,76	68,24
3	45,34	54,66
16	54,77	45,66
111	92,08	7,92

c)

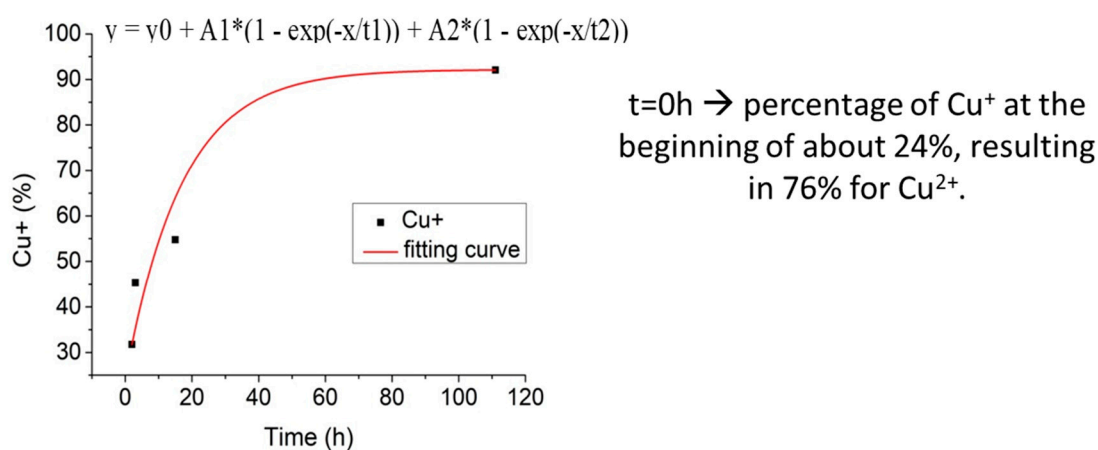


Figure S6: a) XPS evolution of Cu 2p detailed spectrum of sample II under UHV ambient. The figure displays the sum curve obtained by the fitting, in order to show the effect more clearly. b) time dependence of oxidation states on UHV exposure c) exponential fit of the data in the table. X-ray source was on only during the time necessary to record the spectrum. The idea is that the UHV ambient accelerates the already present reduction process; in fact, also extrapolating the value of Cu^+ for an exposure time equal to zero, a relevant amount of 1+ as oxidation state is found.

EXAFS analysis. The Extended X-ray Absorption Fine Structure (EXAFS) analysis was performed using the GNXAS package[1,2], which is based on the Multiple Scattering (MS) theory. Similar Fe and Cu local environments are retrieved in both compounds, highlighting the resemblance of the local structures around the photo absorbers.

Table S1: Selected structural parameters from the EXAFS fitting results on pristine electrodes.

Bond distances and Debye-Waller factors	Sample I – pristine electrode	Sample II – pristine electrode
Fe-C / Å	1.916	1.886
σ^2 Fe-C / Å ²	0.0021	0.003
C≡N / Å	1.154	1.17
σ^2 C≡N / Å ²	0.012	0.029
Cu-N / Å	1.973	1.159
σ^2 Cu-N / Å ²	0.0038	0.011

Table S2: Binding Energies of compounds. References:

- Andersson, A. M., et al. "Surface characterization of electrodes from high power lithium-ion batteries." *Journal of The Electrochemical Society* 149.10 (2002): A1358-A1369.
- Wagner C.D., Riggs W.M., Davis L.E., Moulder J.F., Muilenberg G.E. *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minn. 55344 (1979)
- M. Hekmatfar, A. Kazzazi, G.G. Eshetu, I. Hasa, S. Passerini, *Understanding the Electrode / Electrolyte Interface Layer on the Li- Rich Nickel Manganese Cobalt Layered Oxide Cathode by XPS*, (2019). <https://doi.org/10.1021/acsami.9b14389>.

Assignment	Measured binding energy/eV				
	C 1s	F 1s	Li 1s	O 1s	P 2p
LiF	-	685.1 [c]	56.1 [c]	-	-
LiPF ₆	-	688.2 [c]	56-58 [a]	-	137.8 [a]
Li _x PF _y	-	687.1 [c]	56-57 [a]	-	136.5 [a]
Li _x PO _y F _z	-	686.4 [c]	56-57 [a]	534.1 [c]	134.5-135 [a]
Teflon Area	290.0 – 293.0 [b]	687.5-690 [b]	-	-	-
Others	290.2 (C-O) [c]			529 (M-O) [c]	
				532 (C-O) [c]	

References.

1. Filipponi, A., Di Cicco, A., and Natoli, C.R. (1995) X-ray-absorption spectroscopy and n-body distribution functions in condensed matter. I. Theory. *Phys. Rev. B*, **52** (21), 15122–15134.
2. Filipponi, A., and Di Cicco, A. (1995) X-ray-absorption spectroscopy and n-body distribution functions in condensed matter. II. Data analysis and applications. *Phys. Rev. B*, **52** (21), 15135–15149.