

Electrochemical extraction of Lithium from end-of-life Li-ion batteries as a possible strategy for LiOH recovery



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Concept

In the last few years, there has been an exponential increase in the use of lithium-ion batteries (LIBs) due to the rise in electric mobility, electronic devices, and energy storage systems [1]. A production estimate of 4 million tons of LIBs by 2040, raises concerns about the supply chain for the critical resources required in manufacturing [2]. Current recycling processes lack selectivity in recovery control and involve significant consumption of reagents and energy. Moreover, selective recovery of Li is challenging. **This research aims to develop an electrochemical process for selective extraction of Li from the Electrode powder of End of Life LIBs (EoL-LIBs)**, mimicking the charging process of a Li-ion battery, with an aqueous electrolyte and a cathode material (counter electrode) that allowed the water reduction. The hydroxyls freed by water reduction and the Li⁺ cations deintercalated by the anode will form a LiOH solution

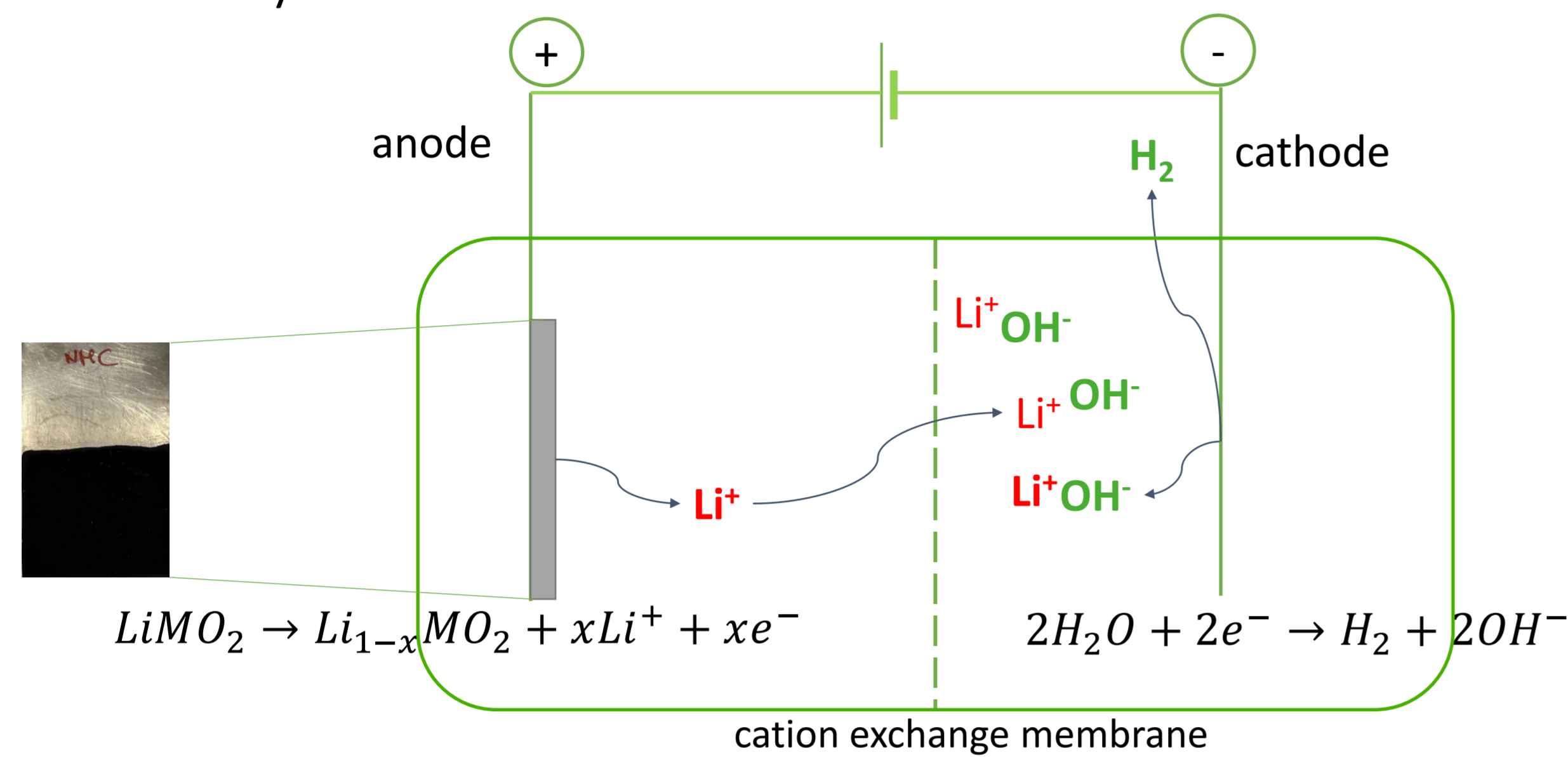
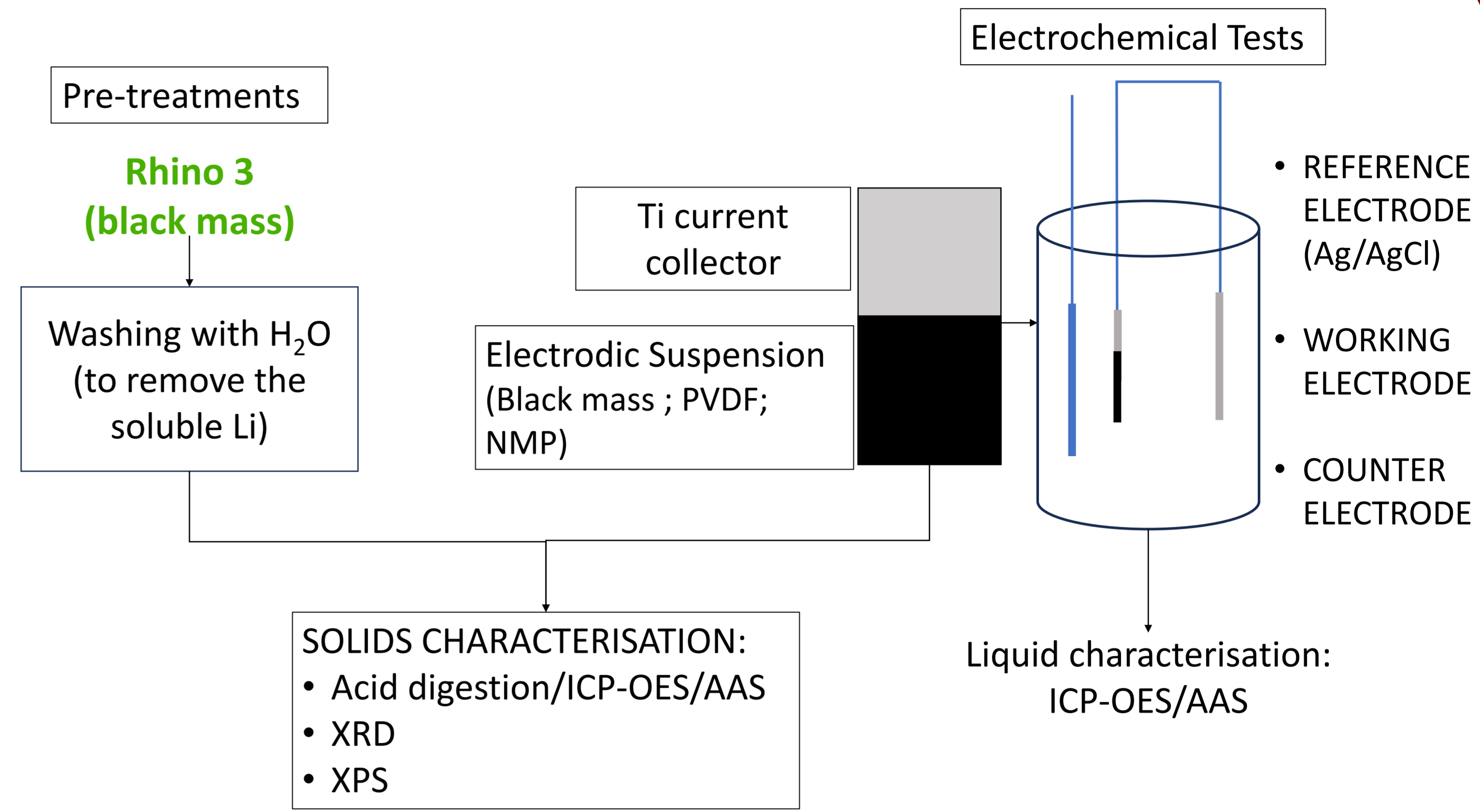


Figure 1. Electrochemical cell used for the Li recovery

Materials and method



$$\text{degree of lithiation} = \frac{\text{mol Li}}{(\text{mol Ni} + \text{mol Mn} + \text{mol Co})}$$

$$\% \text{ Li extraction} = \left(1 - \frac{\text{degree of lithiation}_{\text{final}}}{\text{degree of lithiation}_{\text{initial}}}\right) * 100$$

Results and discussions

- The delithiation process was carried out at two different potential values (1.5 V vs Ag/AgCl and 2 V vs Ag/AgCl) according to the voltammeteries in which we can see the complete oxidation voltage values for the metals of interest.
- Than to analyse the time contribution we decide to applied different charge excess (20 %, 100 % and 200%) from the charge calculated according to the black mass content.
- After the delithiation process on the two powders we obtain for the commercial powder a 99% Li recovery yield and for Rhino-3 (the powder comes from EoL-LiBs) an 84.2 % Li recovery yield. We also have registered a difference in the faradaic efficiency between the two powders.

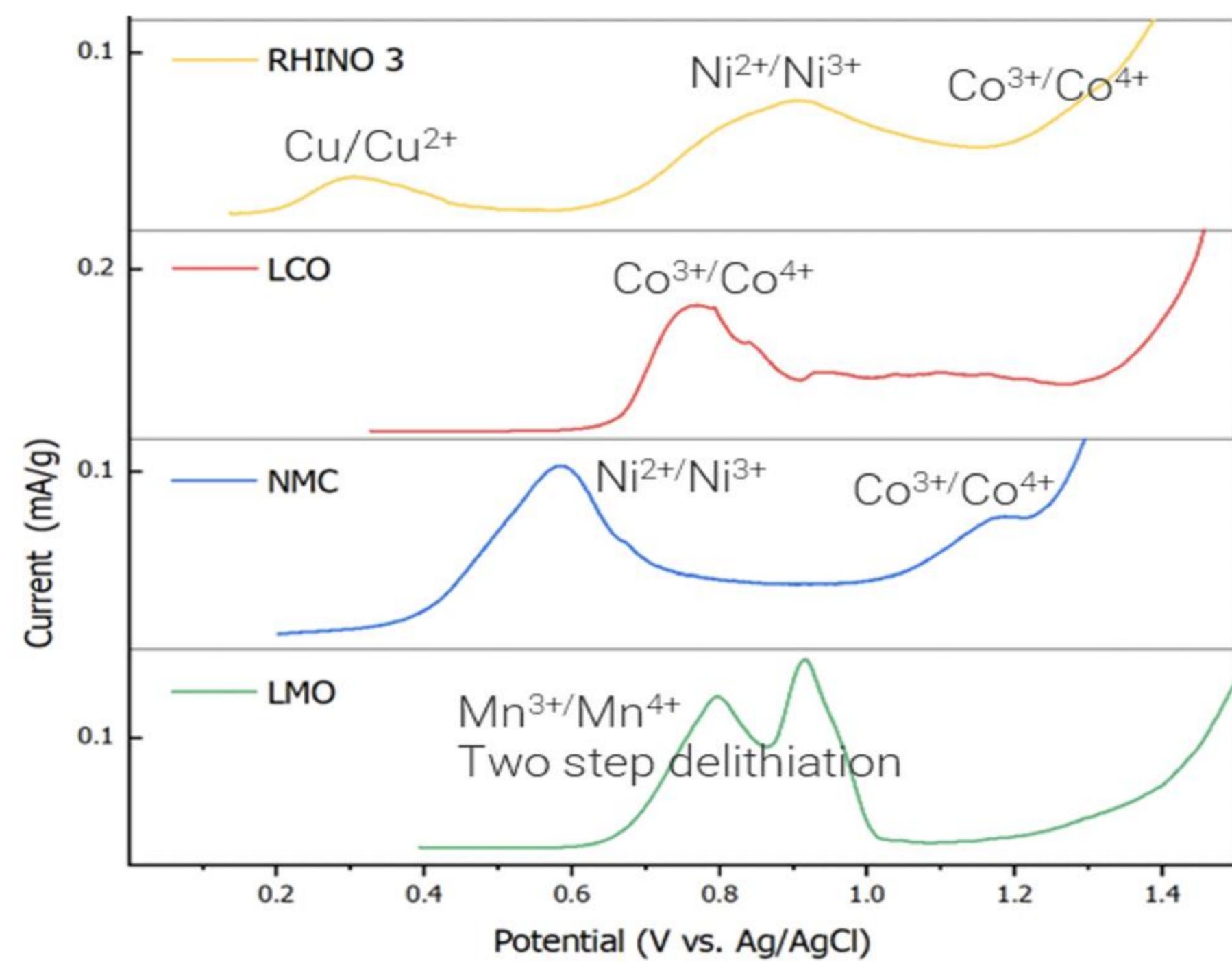


Figure 2. Voltammeteries for the different electrode powders. Rhino-3; Commercial LCO, Commercial NMC, Commercial LMO

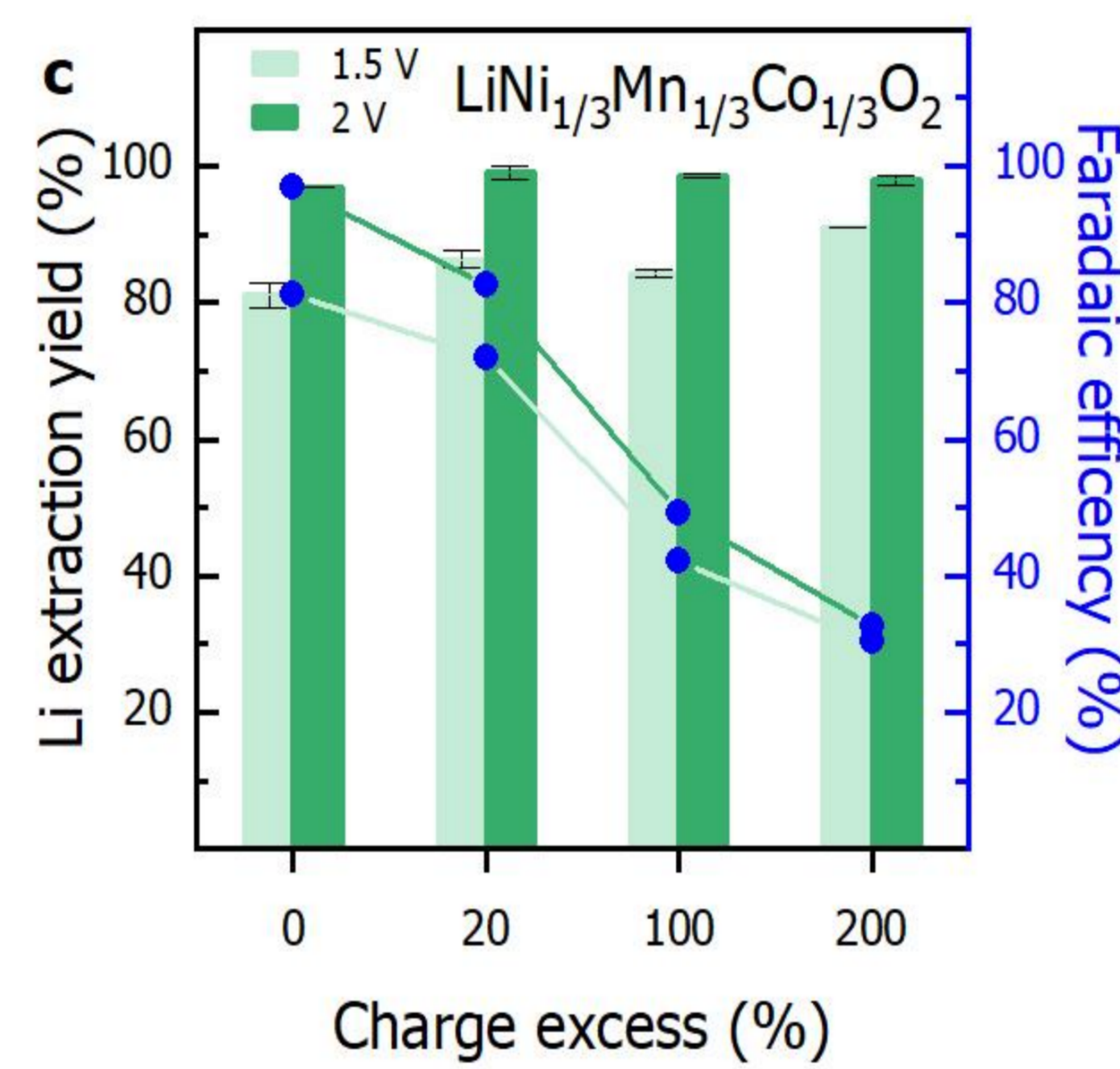


Figure 3. Li extraction yield for the commercial NMC 111 powder at different Potential values (1.5 V vs Ag/AgCl and 2 V vs Ag/AgCl), at different charge excess. Is also express the faradaic efficiency for the different trials.

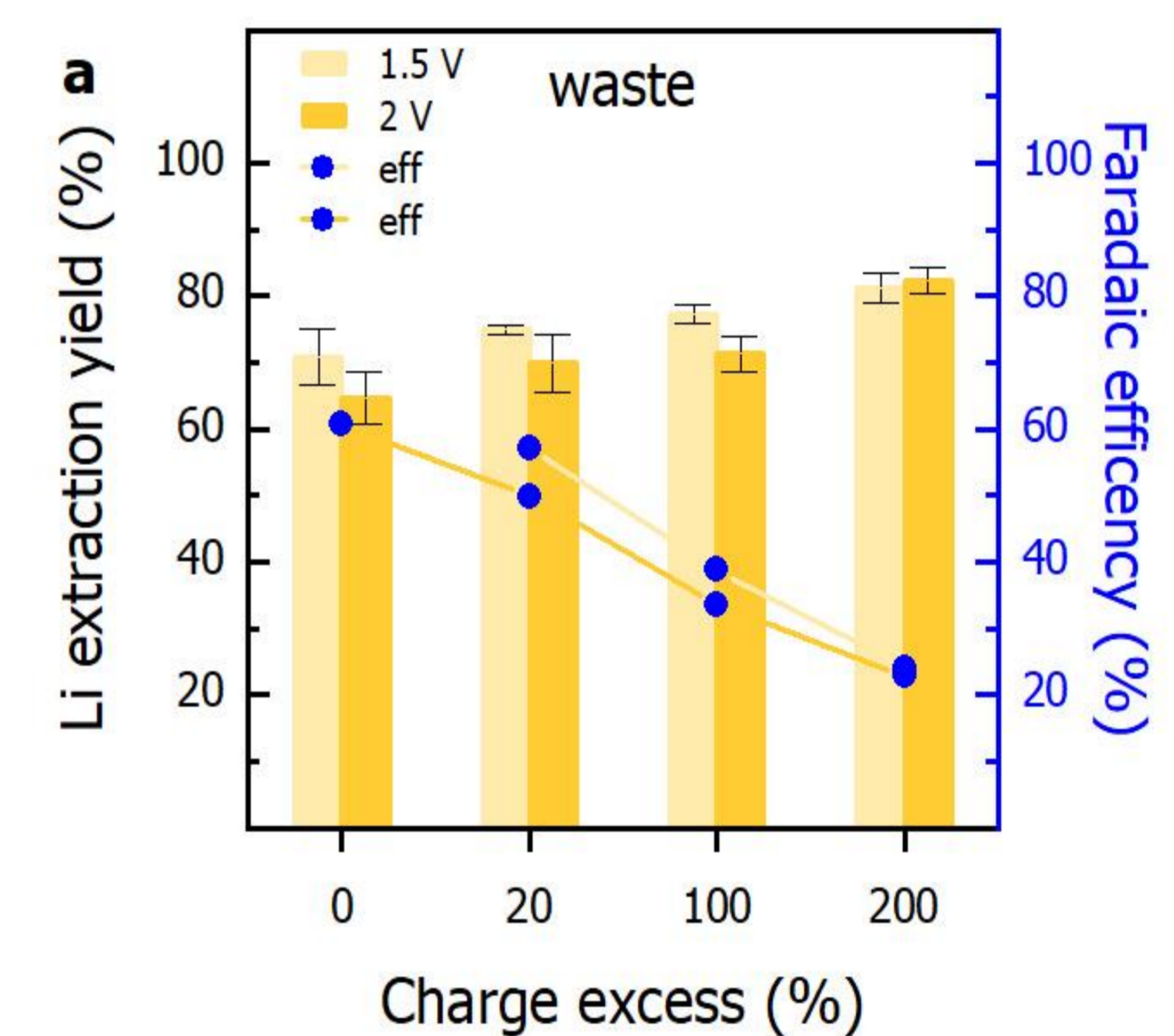


Figure 3. Li extraction yield for the the black mass comes from the EoL LIBs (Rhino-3) at different potential values (1.5 V vs Ag/AgCl and 2 V vs Ag/AgCl), at different charge excess. Is also express the faradaic efficiency for the different trials.

The aim is to understand the reason why we have low Li Extraction Yield and low Faradaic Efficiency in Rhino-3 to respect to the commercial NMC 111.

First, we decide to analyse the impurities (Al, Cu and Fe) → we found a Cu extraction yield up to 86%. But the necessary charge for the complete Cu oxidation of is only the 3% of total charge in the case of 200% charge excess respect theoretical charge for NMC oxidation.

We found, after the delithiation process, a pick at lower degree for Rhino-3. We made a voltammetry for an electrode composed only by Graphite and as you can see the graphite oxidation doesn't occur in the range of Potential, we use for the delithiation process.

With a voltammetry of an electrode composed only by the Carbon Black we found that the Carbon black oxidation occurs in the potential range we use for the delithiation process. To confirm it we made an XPS analysis in which is visible the increment of peaks related to the carbon oxidation after the delithiation process.

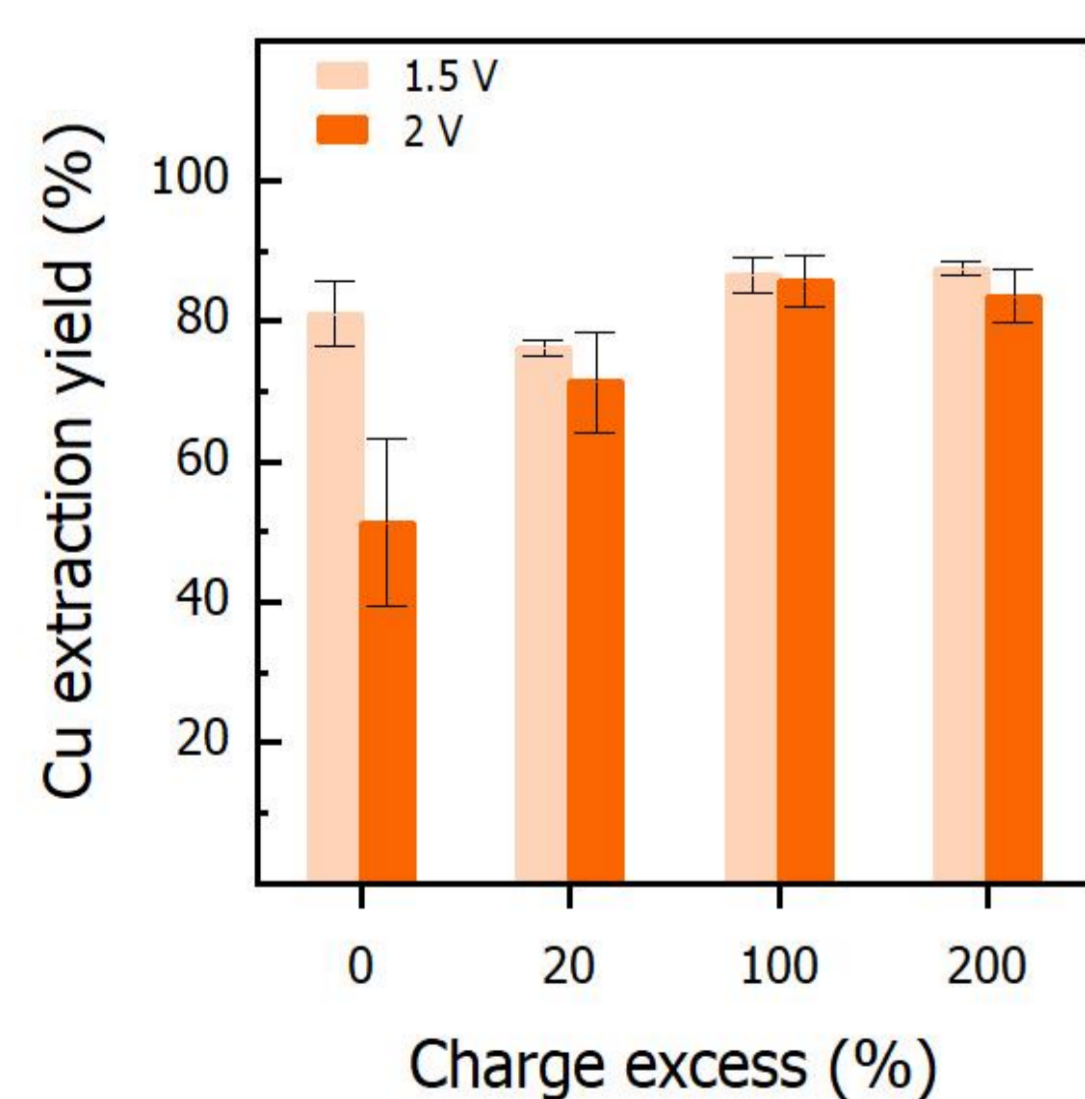


Figure 5. Cu extraction yield from the Rhino-3 powder at different Potential values (1.5 V vs Ag/AgCl and 2 V vs Ag/AgCl), at different charge excess, after the delithiation process.

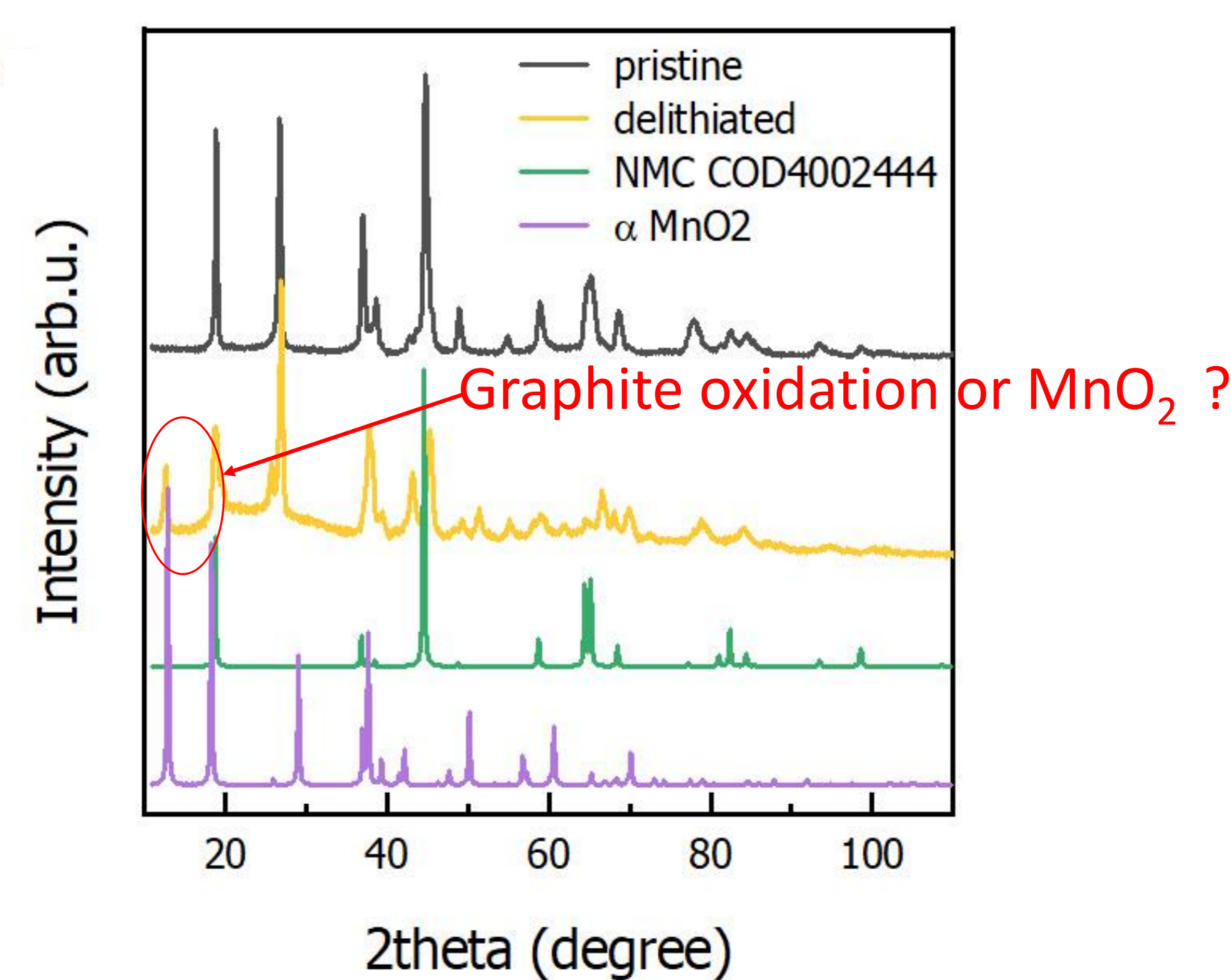


Figure 6. XRD characterization for Rhino-3 before and after the delithiation process. Commercial NMC111 and MnO2 XRD characterization

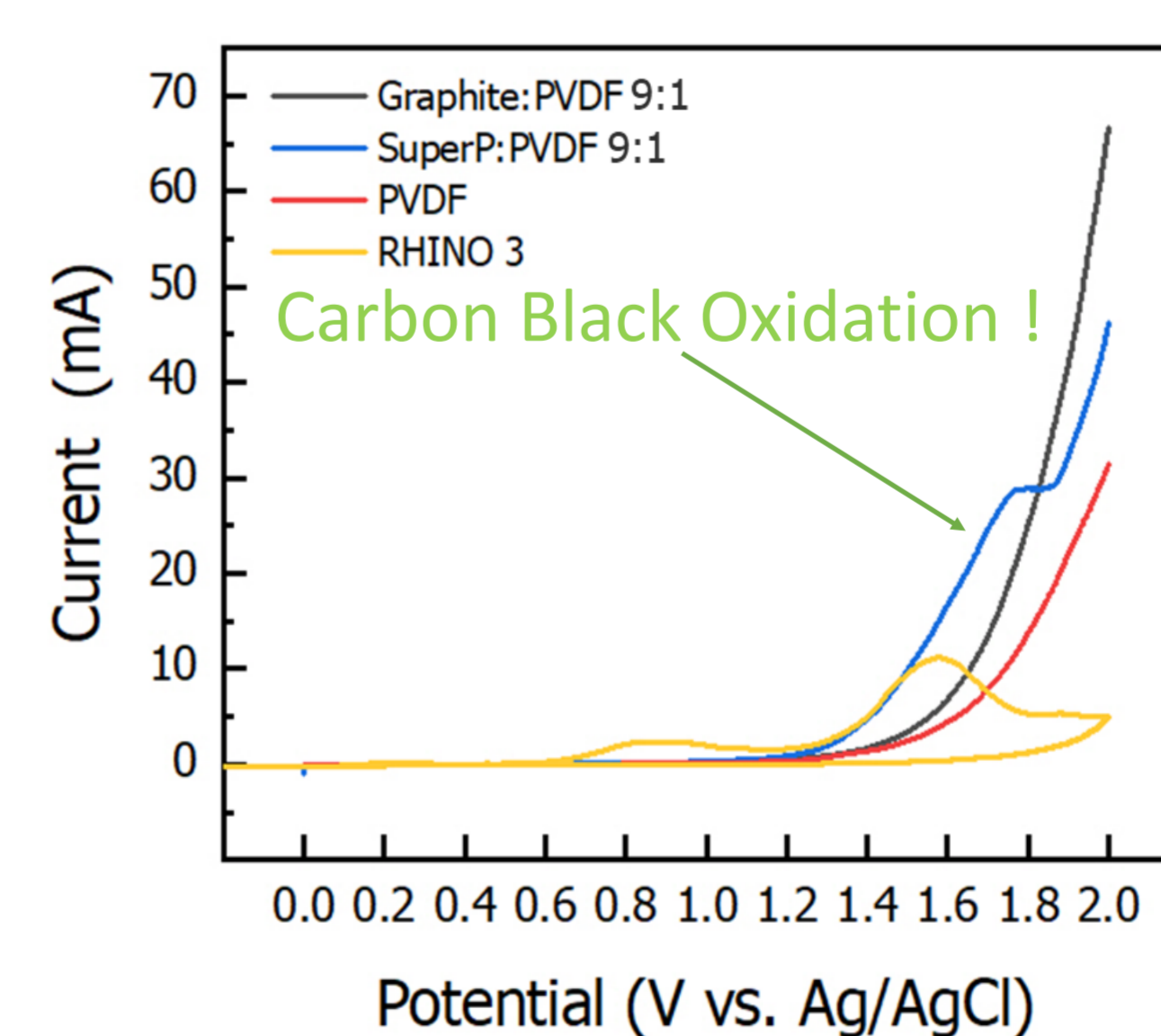


Figure 7. Voltammeteries of Electrode composed by Graphite:PVDF 9:1, Super P:PVDF 9:1, PVDF and Rhino3

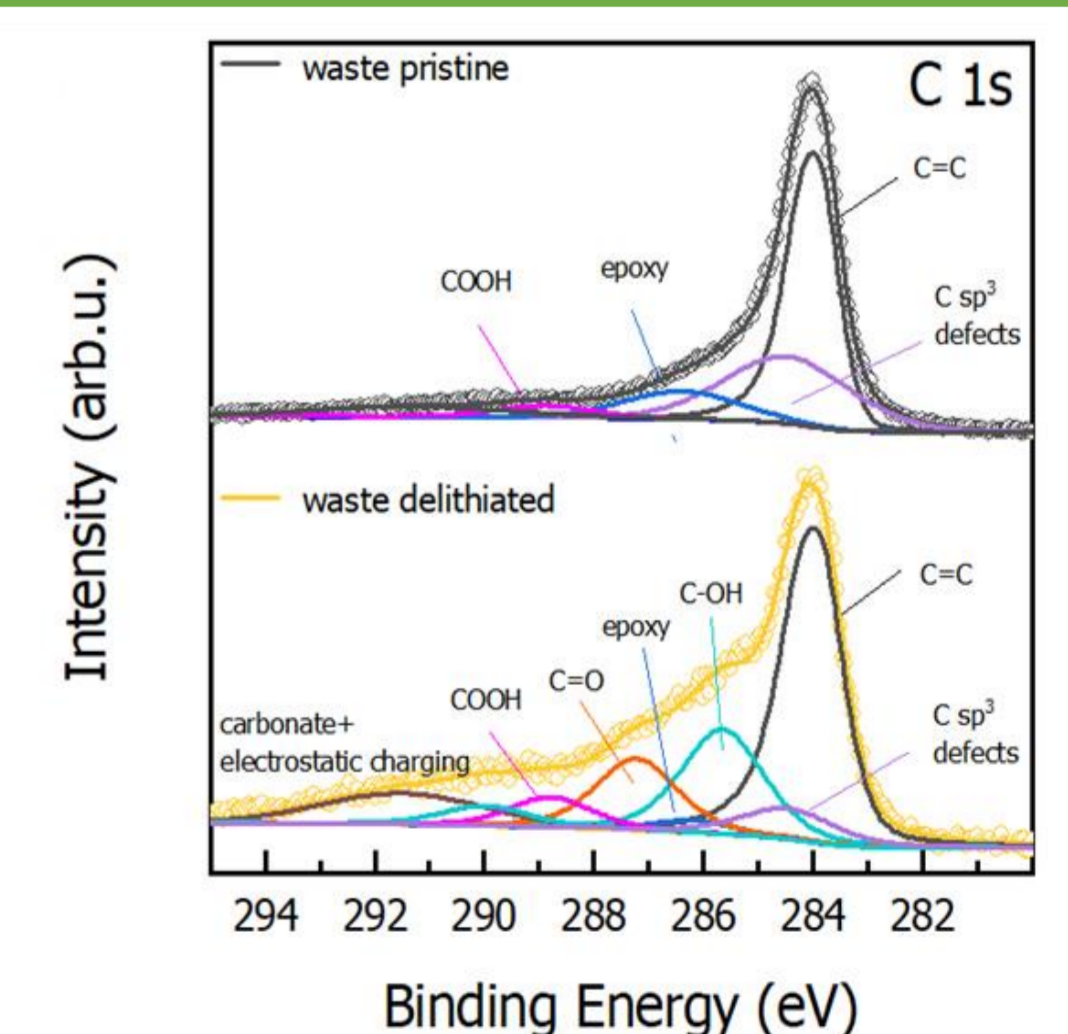


Figure 8. XPS analysis for Rhino-3 before and after the delithiation process.

Conclusions

Electrochemical delithiation on the commercial powder led to an Li extraction of 99%. Electrochemical delithiation on the waste powder led to an Li extraction of 82%. The lower Li extraction on end-of-life electrode powders compared to commercial ones is due to the presence of SuperP, which simultaneously oxidises under delithiation conditions. The copper and graphite oxidation do not contribute to the loss of Li extraction yield and faradic efficiency between the commercial and waste powders.

References:

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- [2] X. Duan, W. Zhu, Z. Ruan, M. Xie, J. Chen, and X. Ren, "Recycling of Lithium Batteries-A Review," Energies, vol. 15, no. 5. MDPI, Mar. 01, 2022. doi: 10.3390/en15051611.



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