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Upcycling of Waste Lithium-Cobalt-Oxide from Spent Batteries into Electrocatalysts for Hydrogen Evolution Reaction and Oxygen Reduction Reaction: A Strategy to Turn the Trash into Treasure --Manuscript Draft--

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Abstract:	Getting inspiration from the 'waste to resource' strategic theme of circular economy, herein, we present the upcycling of the critical raw material i.e. Co-containing waste cathode from spent lithium-ion batteries (LIBs) into platinum group metal-free (PGM-free) electrocatalysts for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Lithium cobalt oxide (LCO) was recovered from spent LIBs (Waste LCO) and subsequently treated with choline chloride: citric acid 1:1 deep eutectic solvent (DES) to obtain the full degradation of the LCO and, post thermal treatments, cobalt oxide in a carbonaceous matrix (ChCl.Citric). HER and ORR activities of derived materials were investigated in alkaline media using the rotating disk electrode (RDE) and rotating ring disk electrode (RRDE), respectively. To elucidate the role of cobalt present in the derived electrocatalysts, inks were prepared by supporting the electrocatalysts with different proportions of Ketjenblack (10:90 and 50:50 ratios). Waste LCO closely followed the electrochemical response of commercial LCO and demonstrated the least overpotential (277 mV at -10 mA cm ⁻²) for HER with an electrode configuration of 50:50. Whereas, ChCl.Citric 50:50 outperformed the other counterparts for ORR and exhibited a remarkable onset potential of 0.85 V(vs RHE) with the least peroxide production.
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Milan, September 19th, 2022

OBJECTIVE: Submission of an original manuscript to Journal of Power Sources

Dear Editors in Chief:

Dear Editors of Journal of Power Sources:

I am excited to submit to Journal of Power Sources a very important manuscript with the title **“Upcycling of Waste Lithium-Cobalt-Oxide from Spent Batteries into Electrocatalysts for Hydrogen Evolution Reaction and Oxygen Reduction Reaction: A Strategy to Turn the Trash into Treasure”** that present a comprehensive study on the valorization of waste cobalt derived from lithium ion batteries into electrocatalysts for hydrogen evolution reaction and oxygen reduction reaction operating in alkaline media. This work was conducted in a joint collaboration between the University of Milano-Bicocca (Milan, Italy) and the CNR-ICCOM (Florence, Italy). This manuscript is submitted to the JPS Special Issue on Fuel Cells and Electrolyzers.

Energy Revolution relies on both batteries and hydrogen technology. Unfortunately, both technologies rely on critical raw materials such as Co (batteries) and Pt and Ir (Fuel cells and electrolyzers). Their substitution is crucial for making these green technologies largely deployed commercially and available to everybody. In this context, large scientific effort is devoted to diminishing the content or completely substitute these critical materials. Large effort is also put into recycling and recovering critical raw materials especially in batteries that nowadays are more mature technologies.

In this work, we have recovered the cathode of a used lithium ion batteries (LIBs) containing cobalt and we have tested it as a platinum group metal-free electrocatalyst for both oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Moreover, we have collected the exhausted LIBs cathode that was subject to upgrading process and we have also test it for ORR and HER. Surface chemistry and morphology were analyzed and discussed. The PGM-free electrocatalysts were tested electrochemically through rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) technique for HER and ORR respectively. Due to the promising results, several new routes can be pursued within the core of the circular economy, in which transition metals used in lithium ion batteries cathodes can be successfully transformed into valuable PGM-free electrocatalysts to be widely used for other electrochemical reactions and applications.

We are confident that this manuscript will capture the attention of a great part of the scientists worldwide and resonate widely in the community involved into electrocatalysis, fuel cells and also within national and international institution.

We think that this study will fit perfectly on Journal of Power Sources since the study presented in this work relates to the Aims and Scope of the Journal. This study was not submitted before and none of the parts have been presented elsewhere.

We believe that our combined track record in electrochemistry, electrocatalysis, material science and electrochemical energy conversion and storage systems has yielded to this comprehensive novel work that should resonate with the interests of **Journal of Power Sources** readership.

Yours sincerely,

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Upcycling of Waste Lithium-Cobalt-Oxide from Spent Batteries into Electrocatalysts for Hydrogen Evolution Reaction and Oxygen Reduction Reaction: A Strategy to Turn the Trash into Treasure

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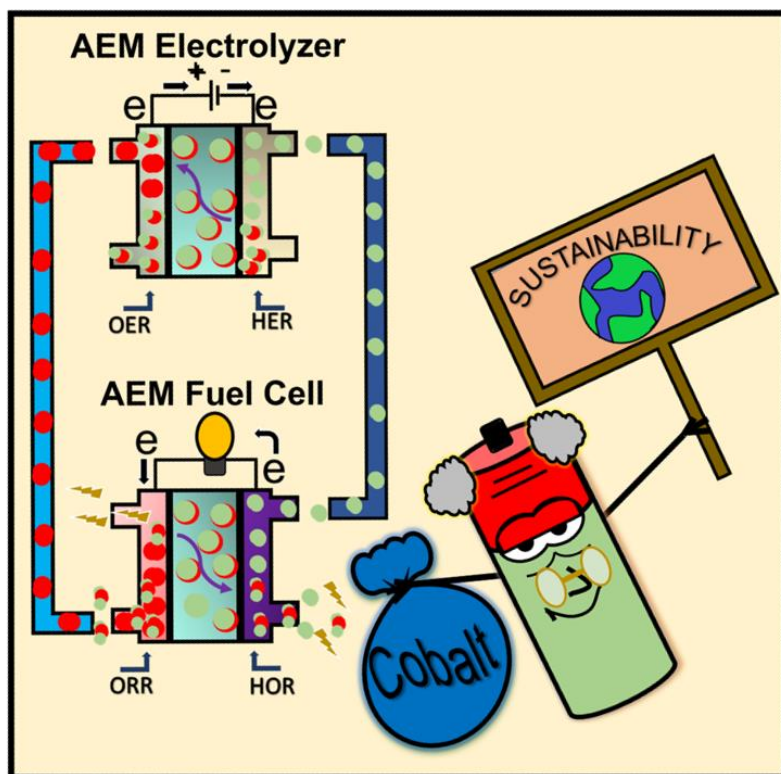
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Abstract

Getting inspiration from the ‘waste to resource’ strategic theme of circular economy, herein, we present the upcycling of the critical raw material i.e. Co-containing waste cathode from spent lithium-ion batteries (LIBs) into platinum group metal-free (PGM-free) electrocatalysts for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Lithium cobalt oxide (LCO) was recovered from spent LIBs (Waste LCO) and subsequently treated with choline chloride: citric acid 1:1 deep eutectic solvent (DES) to obtain the full degradation of the LCO and, post thermal treatments, cobalt oxide in a carbonaceous matrix (ChCl.Citric). HER and ORR activities of derived materials were investigated in alkaline media using the rotating disk electrode (RDE) and rotating ring disk electrode (RRDE), respectively. To elucidate the role of cobalt present in the derived electrocatalysts, inks were prepared by supporting the electrocatalysts with different proportions of Ketjenblack (10:90 and 50:50 ratios). Waste LCO closely followed the electrochemical response of commercial LCO and demonstrated the least overpotential (277 mV at -10 mA cm^{-2}) for HER with an electrode configuration of 50:50. Whereas, ChCl.Citric 50:50 outperformed the other counterparts for ORR and exhibited a remarkable onset potential of 0.85 V(vs RHE) with the least peroxide production.

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Graphical Abstract



Keywords: oxygen reduction reaction, hydrogen evolution reaction, lithium-ion batteries, waste to resource, circular economy

1. Introduction

In the pursuit of a sustainable society, the motive of *Green Energy* is glossing under the spotlight of current research. Owing to various advantages over contemporary energy storage systems, cobalt-containing lithium-ion batteries (LIBs) are the dominating energy storage technology enabling the widespread distribution of portable electronic gadgets and of electric vehicles in the transportation sector [1]. Where the mass-scale production of LIBs outbalances the supply and demands of critical and strategic raw materials i.e. cobalt and lithium, the gigantic generation of spent batteries is provoking irrepressible complications in waste management, recycling, and reuse [2–4]. Cobalt, being largely exploited for the cathode fabrication of LIBs, has been recognized as a critical raw material because its occurrence is mainly restricted to a few

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4 geopolitically unstable regions [5]. Despite the aforementioned consideration, it is a grim reality
5 that 30% of the worldwide production of cobalt was demanded just by the batteries industry and
6 this figure is expected to escalate up to 53% by the year 2025 [6,7]. The scenario is becoming more
7 challenging due to a 16.5% annual increment in the global consumption of LIB [8]. As a result,
8 around 500 thousand tons of spent LIBs equivalent to 25 billion units were estimated to be amassed
9 in the year 2020 [9,10]. Regardless of the enormous production of spent LIBs, a negligible focus
10 on their viable recycling is given [11] and eventually spent LIBs have to arrive at unjustified
11 disposal pathways i.e. landfilling, which could engender severe ecological hazards due to the
12 presence of highly toxic metals like cobalt [12]. No doubt, several acknowledgeable endeavors for
13 cobalt recovery from spent LIBs have been invested in the recent past [9,13–16]. However, the
14 reusability of recycled cobalt and lithium cobalt oxide (LCO) in LIBs presents extra technology
15 apprehensions since it is not straightforward to achieve the integrity of recovered material truly
16 comparable to the commercial grade [17,18]. Therefore, harvesting the additional rewarding
17 applications of recycled cobalt and LCO in a circular approach becomes extremely relevant.
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30 In parallel, the hydrogen economy (HE) with a portfolio of green and sustainable hydrogen as
31 an energy vector is an emerging candidate to address the predicted energy crises without
32 contributing to the global carbon footprints. HE mainly relies on electrolyzers and fuel cells where
33 the lethargic cathodic reactions are the key bottlenecks. Sluggish kinetics and high overpotentials
34 of hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) at the cathode of
35 electrolyzers and fuel cells, respectively, are typically dealt with overpriced and scarce platinum
36 group metals (PGMs). First row transition metals (TM) such as Mn, Fe, Co, Ni and Cu in the form
37 of a single atom, atomically dispersed and coordinated with nitrogen (M-N-C form), carbides,
38 nitrides and oxides can have promising activity towards HER and ORR, especially when operating
39 in neutral and alkaline electrolyte [19–24].
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Despite being considered as a critical and strategic material, cobalt is considered one of the most potential replacements for PGMs for both HER and ORR [25–29]. Therefore, the application of LIBs recycled cobalt for HER and ORR can open an innovative window within the core of the circular economy closing the circle by actually reusing waste into a valuable electrochemical production and conversion system. Recently, considerable scientific interest in the waste-derived HER and ORR electrocatalysts has been witnessed where waste plastics and biomass have been deployed to fabricate advanced electrocatalysts [30–38]. A similar approach can be introduced for

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4 spent batteries considering them the cheaper source of cobalt contributing to giving waste a second
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6 life.

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8 The recycling cost of LIBs cathodic materials can be further rationalized through the far-
9 reaching and simplistic utilization of present TMs in electrocatalytic applications [39,40]. Not long
10 ago, Wei et al. took an initiative to directly reuse nickel-manganese-cobalt oxides from spent LIBs
11 for the fabrication of a bi-functional oxygen electrocatalyst which exhibited optimistic results after
12 being applied in air batteries [41]. By the same token, Pegoretti and coworkers formulated a study
13 to recover cobalt as $\text{Co}(\text{OH})_2$ which was afterward utilized to produce high-temperature LiCoO_2
14 and then they evaluated its suitability for oxygen evolution reaction (OER) considering the
15 presence of favorable $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple [42]. It is noteworthy that such a kind of structure
16 could also be favorable for ORR if engineered properly [43,44].
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20 In very recent years, new promising methods for the degradation and recycling of LiCoO_2 from
21 spent LIBs have appeared in the literature[45–50]. Among these methods the solvometallurgical
22 model exploiting Deep Eutectic Solvents, DESs, are stimulating high interest due to the high
23 solubility of metals in these systems, high yields of recovery, low amounts of generating waste
24 waters, and overall high sustainability [51–53]. The choline chloride: citric acid 1:1 DES has been
25 recently proposed as an effective leaching agent for the full degradation of LiCoO_2 (>99%),
26 allowing for the recovery of > 80% of cobalt [54]. Differently from this previous report, in the
27 present study, we propose a new route for the final recovery of Co that has been performed to
28 obtain cobalt as oxides, maintaining a carbonaceous fraction that can be beneficial for the final
29 functional application.
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33 In this study, commercial LCO powder purchased from Sigma Aldrich (acronym Com LCO),
34 LCO recovered “as it is” from a spent Li-Ion battery (Waste LCO) and LCO recovered after the
35 recycling process based on the leaching of the Waste LCO using the choline chloride: citric acid
36 1:1 DES followed by thermal treatment at 350°C to degrade the DES and obtain Co as oxide
37 supported on carbonaceous matrix, named as ChCl.Citric were all mixed on commercial carbon
38 black (Ketjen Black 600), characterized chemically and morphologically and tested
39 electrochemically as HER and ORR electrocatalysts in alkaline media using the rotating disk
40 electrode (RDE) technique.
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43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 **2. Materials and Methods** 60 61 62 63 64 65

2.1. Recovery of LCO from Spent Batteries

The sample labeled as Waste LCO was recovered from a spent battery. The cylindrical battery has been dismantled manually after discharge in salt water (NaCl 5 M for 24 h); the electrodes have been peeled off and the powders removed manually after sonication in acidic solution. The cathode powders have been characterized through XRD, SEM, and thermal analysis confirming that the cathode is 93 % LiCoO₂ (LCO in the following) while ~7 % is due to the carbon and binder content. The obtained active materials have been characterized and tested without any further purification. The sample labeled as Com LCO was commercially available LiCoO₂ purchased from Sigma Aldrich. The sample labeled as ChCl.Citric was Waste LCO that underwent a degradation process exploiting the choline chloride: citric acid DES. This choline chloride: citric acid DES has been prepared as previously reported [54] and subsequently used for the degradation of the Waste LCO under similar experimental conditions reported in the original paper leading to the complete degradation of the LCO [54]. The leached solution has been treated differently from the original paper and a new route for the Co recovery is here presented. The leached system has been heated at 200°C for 12 hours to allow for water evaporation and then thermally treated at 350°C for 6 hours to degrade the DES component. The black powdered residues have been ground and washed several times with water to obtain Co in form of crystalline/amorphous oxides supported on a carbon matrix.

2.2. Materials Characterizations

Scanning Electron microscopy images were acquired with a TESCAN GAIA3 2016 dual beam equipped with a Triglav column and a field emission electron source. Images were taken at an acceleration voltage of 30 kV with the analysis mode (magnetic field-free imaging mode) using an in-chamber secondary electron detector. EDX analyses were performed with a 70 mm² SDD EDAX Octane Elite detector equipped with a Si₃N₄ detector. Spectra were collected at 30 kV at a working distance of 5 mm and a take-off angle of 25°. However, due to the roughness of the sample and the occurrence of large agglomerates with the tilted surface, the quantification was not pursued.

Elemental analysis was carried out using Energy-dispersive X-ray fluorescence (XRF) comprising molybdenum anode (Bruker Artax 200 spectrometer). X-ray diffraction (XRD, Rigaku Miniflex 600) equipped with a copper source was used to perform crystallographic investigations

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4 in the 2θ range of $10-90^\circ$. To study the thermal behavior of the samples, thermogravimetric
5 analysis (TGA) assembled with differential scanning calorimetry (DSC1, STARe system, Mettler
6 Toledo TOLRDO) was employed. Thermal analysis was performed by heating the sample from
7 room temperature to 700°C in the air at a rate of $10^\circ\text{C min}^{-1}$. XPS experiments were carried out
8 in a UHV chamber with a base pressure lower than 10^{-10} mbar. The chamber was equipped with
9 non-monochromatized Al ($h\nu=1486.6$ eV) radiation and with a hemispherical electron/ion energy
10 analyzer (VSW mounting a 16-channel detector). The operating power of the X-ray source was
11 120 W (12 kV and 10 mA). Photoelectrons were collected normally to the sample surface and the
12 analyzer maintained as well the angle between the analyzer axis and the X-ray source fixed at
13 54.5° . All the samples were measured in fixed analyzer transmission mode with a pass energy of
14 44 eV. The binding energy (BE) was calibrated by setting the C1s adventitious component to 284.8
15 eV [55].
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27 28 **2.3. Electrochemical Characterizations**

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30 Electrochemical analyses were carried out using Pine WaveVortex RDE assembled with a
31 Pine bipotentiostat whereas SP-100 Biologic® potentiostat was used to obtain 85% iR-
32 compensations. The electrochemical cell, in a three-electrode arrangement, was comprised of: 1)
33 Pt wire as a counter electrode, 2) standard calomel electrode (SCE) as a reference electrode, 3) the
34 rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) as the working electrode
35 for HER and ORR, respectively. Eventually, all the potential values were converted to RHE by
36 adding the factor of $E_{\text{SCE}} + 0.0591 \times \text{pH}$ to the measured potential where E_{SCE} was 0.241 V.
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43 To prepare the inks for testing, the electrocatalysts were thoroughly mixed with conductive
44 carbon black support (Ketjenblack EC-600JD, KJ Black) in two different ratios of 10:90 and 50:50
45 using a mortar grinder at least for 40 min. The purpose of using two different ratios was to explicate
46 the catalytic role of the electrocatalyst. Hence the nomenclature of electrocatalytic samples was
47 modified with a specification of '10-90' and '50-50' to specify the ratio between the actual
48 electrocatalysts and KJ black, respectively. Eventually, the 3 mg of the electrocatalyst-containing
49 blend was dispersed in the mixture of 500 μl ethanol and 50 μl Nafion® D-520 ionomer solution.
50 The suspension was then probe sonicated for 15 mins followed by bath sonication for further 45
51 mins at room temperature.
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2.3.1. HER analysis

To examine the HER performance, the working electrode was first configured by precisely depositing the above-mentioned ink on the disk of RDE (E5 series with a disk area of 0.1963 cm²) using a precision pipette. After drop-casting 0.6 mg cm⁻² loading of the electrocatalyst on the glassy carbon disk of RDE, the achieved working electrode was dried at room temperature. The HER performance was studied in nitrogen-saturated 1 M KOH solution while keeping the rotation speed of RDE at 1600 rpm. Nitrogen gas was continuously purged into the electrolyte during the whole measurement. Linear sweep voltammograms (LSVs) were acquired at 5 mVs⁻¹ after conditioning the electrocatalysts by applying multiple cyclic voltammograms (CV) at 50 mVs⁻¹ to obtain stable current values whereas the potential window was maintained between -1.05 and -2.05 V vs SCE.

2.3.2. ORR analysis

RRDE (E6R2 series) with a disk area of 0.2376 cm² was employed to configure the working electrode for ORR tests with two different mass-loadings of each electrocatalyst i.e. 0.2 mg cm⁻² and 0.6 mg cm⁻². The RRDE collection efficiency (N) was 38% while the area of Pt ring was 0.2356 cm². ORR measurements were taken in 0.1 M KOH solution by keeping the rotation speed of RRDE at 1600 rpm. The electrolytic solution was vigorously flushed with oxygen for at least 30 mins before the commencement of experimentation and then uninterruptedly bubbled throughout the measurements to guarantee an ample level of oxygen saturation. ORR potential window was investigated between 0.15 V to -1.05 V vs SCE and the ring potential was fixed at 0.15 V vs SCE. Polarization curves at 5 mVs⁻¹ were obtained after achieving a steady trend in the current values by running multiple CV cycles. Peroxide yield (%) and transformation of electrons (n) during ORR were estimated by monitoring the disk current density (I_{disk}) and ring current density (I_{ring}) according to eq.1 and eq.2, respectively.

$$\text{Peroxide (\%)} = \frac{200 \times \frac{I_{ring}}{N}}{I_{disk} + \frac{I_{ring}}{N}} \quad (\text{eq.1})$$

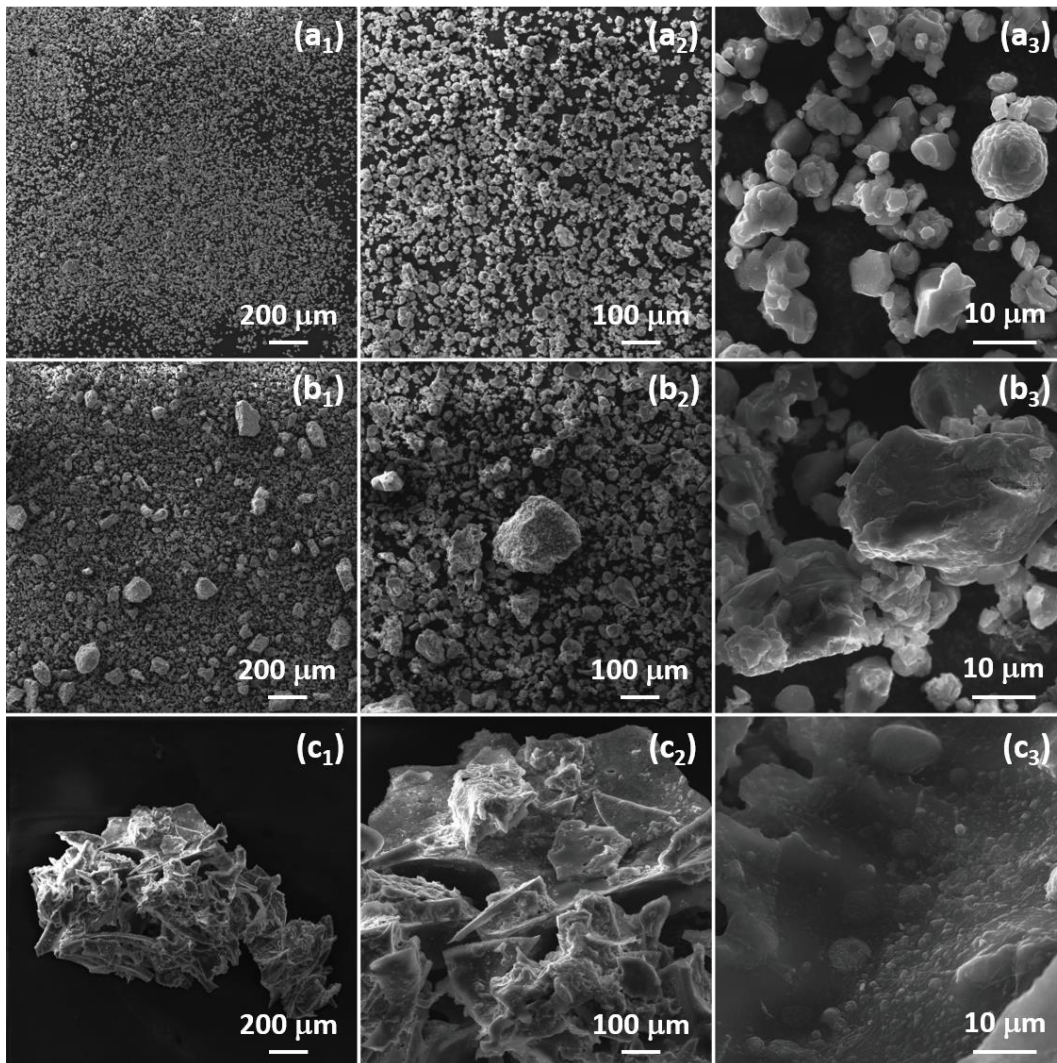
$$n = \frac{4 I_{disk}}{I_{disk} + \frac{I_{ring}}{N}} \quad (\text{eq.2})$$

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4 **3. Results and Discussion**
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7 **3.1. Surface chemistry, morphology and composition characterization**
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10 **3.1.2. Scanning electron microscopy images**
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12 **Figure 1** shows the low magnification images of the Com LCO (a), Waste LCO (b) and the
13 ChCl.Citric (c). The Com LCO shows a homogeneous distribution of the particles (**Fig.1 a₁-a₃**)
14 roughly in the range 5-10 μm . A variety of shapes exist from polyhedrons to rough spheres (**Fig.**
15 **1 a₃**). For the Waste LCO sample, particles in the 10 μm range were found plus larger particles
16 that may result from agglomeration with a size up to a few hundred μm (**Fig. 1 b₁-b₃**). The ChCl.
17 Citric sample (**Fig. 1 c₁-c₃**) consisted mainly of large agglomerates with sizes exceeding 1 mm.
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4 **Figure 1.** Secondary electron images of the samples: Com LCO (a₁-a₃), Waste LCO (b₁-b₃) and
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6 ChCl.Citric (c₁-c₃)
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10 The geometry of the samples did not allow a quantification of the energy dispersive X-ray
11 spectra due to the roughness and geometry of the samples[56,57]. However, EDX spectra show
12 that the Com LCO sample only consists of Co, O and a little carbon. The waste LCO show again
13 the occurrence of Co, O and C with the local occurrence of Ni, Mn, Si, P, S, Al, Na. In the case of
14 the ChCl.Citric sample Co, O, Cl, N and C were found as major constituents with a limited amount
15 of Na, F and Si and Ca traces.
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22 **3.1.3 XRF and XPS analysis**

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25 With the aim of qualitative elemental analysis, XRF was utilized and achieved spectra,
26 presented in [Figure 2 a-c](#), categorically showed the sharp peaks of Co in all three samples whereas
27 the traces of Ni and Mn were additionally observed in the case of Waste LCO which are typical
28 components of cathode material [58–60]. While the XRF of ChCl.Citric identified the presence of
29 Co along with minor peaks of Cl. The presence of Cl can be linked with the choline chloride
30 treatment involved in the processing of this sample. Importantly, it can be speculated that both
31 Waste LCO and ChCl.Citric will contain fluorine as fluorinated binders are commonly used in
32 LIBs [61–64]. However, fluorine cannot be detected by XRF due to system limitations.
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39 To further reveal the crystallographic details of the samples and characterize the phase
40 composition of the considered materials, XRD was employed in the 2 θ range between 10° and 90°.
41 As can be clearly seen in [Figure 2 d](#), the diffraction patterns of Com LCO and Waste LCO came
42 out to be similar as the experimental patterns are fully consistent with standard LiCoO₂ (JCPDS
43 00-050-0653)[65]. However, the XRD data for the ChCl.Citric indicates the presence of an
44 amorphous phase with a few broad diffraction peaks that can be compatible with the presence of
45 Co₃O₄ (JCPDS 01-080-1542) [66,67]. Indeed, the thermal treatment of the leached solution
46 obtained after LCO degradation with DES leads to the formation of a carbonaceous matrix with
47 an amorphous structure and promotes the formation of cobalt oxides; at the same time the low
48 temperature involved does not allow for the full crystallization of the newly formed species thus
49 the presence of other cobalt-based phases can be inferred. To summarize, while the Com LCO and
50 Waste LCO are very similar as they are constituted by highly crystalline LiCoO₂ as the dominant
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phase (> 90%w), the ChCl.Citric sample is significantly different as it presents a high fraction of amorphous carbon and cobalt in different species, is not fully crystallized, and cobalt is present in different oxidation states. Such hypotheses are supported by the thermal analysis results obtained for all the samples and reported in [Figure S1](#). Indeed, the thermal profile acquired for the Com LCO indicates that no weight losses are observed in the 25-700 °C temperature range, as expected. In the same range, the Waste LCO shows a loss of 7.63 % that has been associated with the thermal degradation of the organic binder and of the carbonaceous material present in the electrode formulation. The ChCl.Citric on the contrary undergoes a severe thermal degradation with two steps in the 50-150 °C and 350-650 °C temperature ranges. The first one is associated with a smaller weight loss (~20%) and imputable to the decomposition of the organic moieties of the DES while the second one is associated to the decomposition of the carbonaceous materials formed during the first step and associated with 50 % weight variation. Considering that the ChCl.Citric samples has been treated at 350 °C, it can be inferred that the carbon content of this product is ~60% and 40% is constituted by cobalt oxide(s), in good agreement with the XRD pattern observed for this compound.

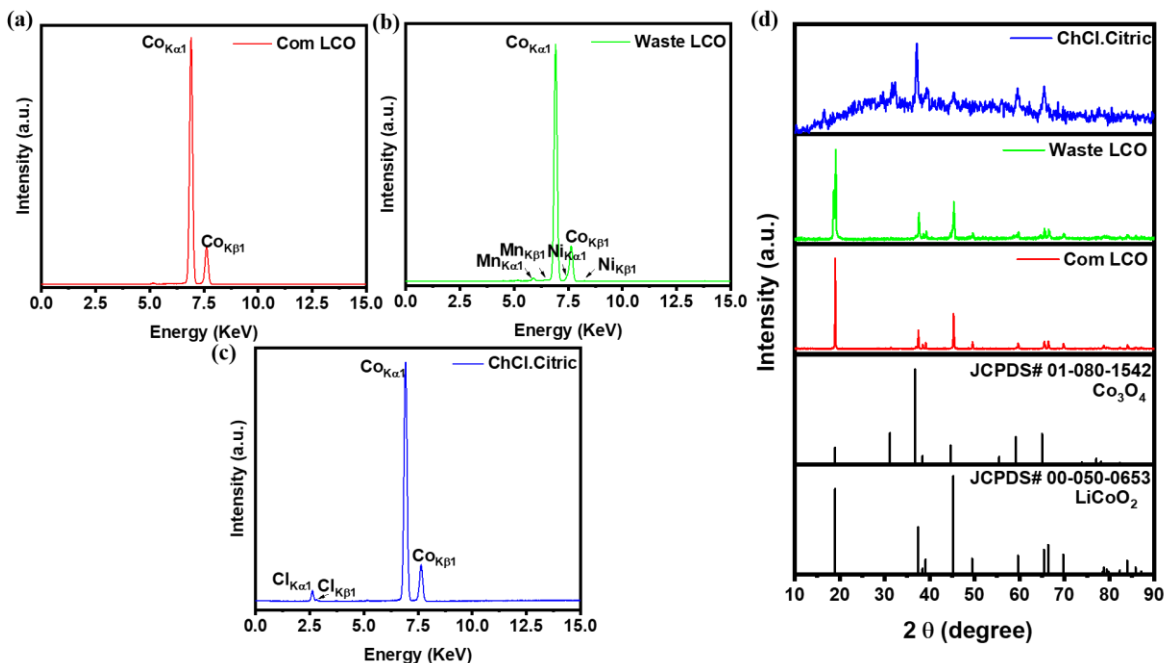


Figure 2. XRF spectra of Com LCO (a), Waste LCO (b) and ChCl.Citric (c). XRD results of the same samples are presented in panel (d).

Afterwards, XPS was employed to evaluate the chemical state of Co and to verify the environment of the metal. The acquired data were compared with literature reference data to distinguish between different chemical states and environments [68–70]. The analyzed samples are reported in Figure 3 a-c and are compared with the reference spectra of Co(OH)₂, CoF₂, Co₃O₄ and CoO, respectively. As is possible to see from Figure 3 a the sample Com LCO is characterized by the same line shape of the reference spectra reported in ref. [68] with the peak of the Co 2p_{3/2} centered at 779.8 eV; in the other two samples, ChCl.Citric and Waste LCO the line shape results more complex with the peak of the Co 2p_{3/2} centered at 780.5 eV and 783.4 eV, respectively. Those two samples are mostly composed of more than one chemical component; for this reason, the reference spectra [68–70] have been used as bases to obtain a reconstructed spectrum employing multiple-linear regression like reported in Figure 3 a-b to roughly estimate the composition of the sample. As a point of fact, we have to argue that this method gives us an interpretation of the composition of the system with an averaging error of the 15-20% (obtained from the R² of the multiple-regression).

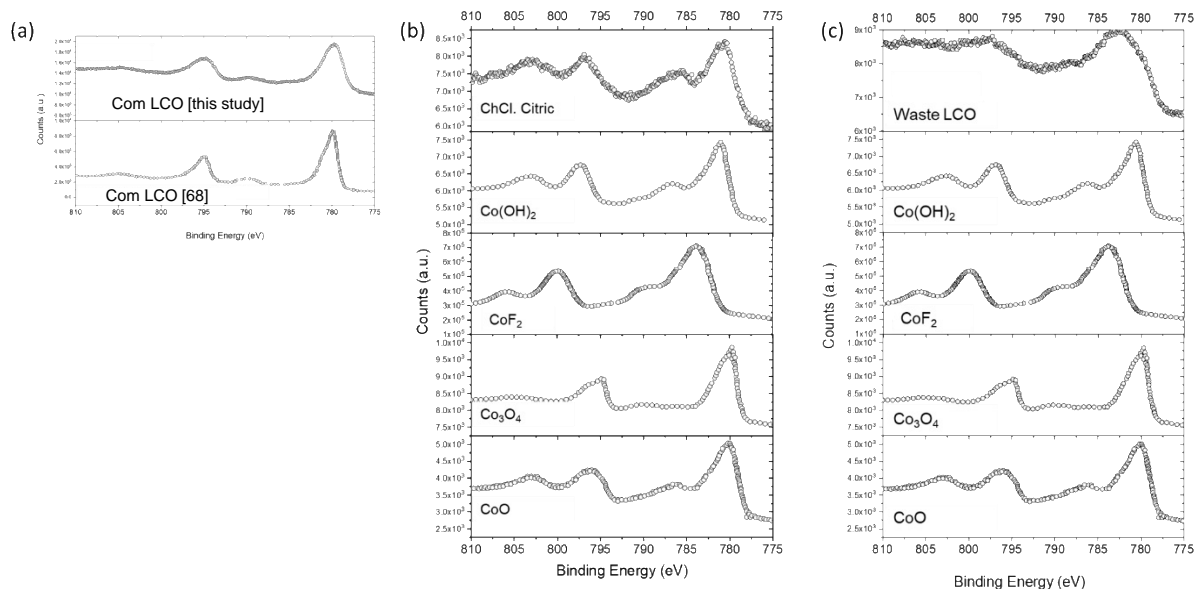


Figure 3. Experimental spectra of Com LCO (a), ChCl.Citric (b) and Waste LCO (c) samples compared with the reference spectra.

As it is possible to see from Figure 4 a-b, all the reference components are present in the reconstructed spectra, hypothesizing to have a mixture of oxidation numbers of the cobalt. For the ChCl.Citric sample, the spectrum is characterized by CoO, Co₃O₄ and Co(OH)₂ in a ratio of ca. 6/1/2, respectively, plus a small amount of CoF₂ (less than 5%). Indeed, for the Waste LCO sample the composition of the reconstructed sample, results characterized by a mixture of CoF₂, CoO and Co(OH)₂ of ca. 50, 10 and 40 % respectively.

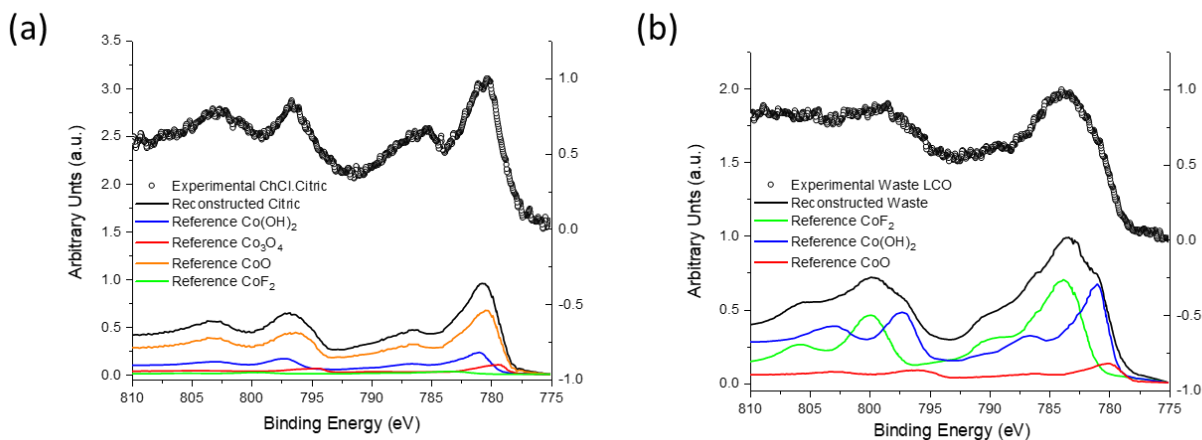
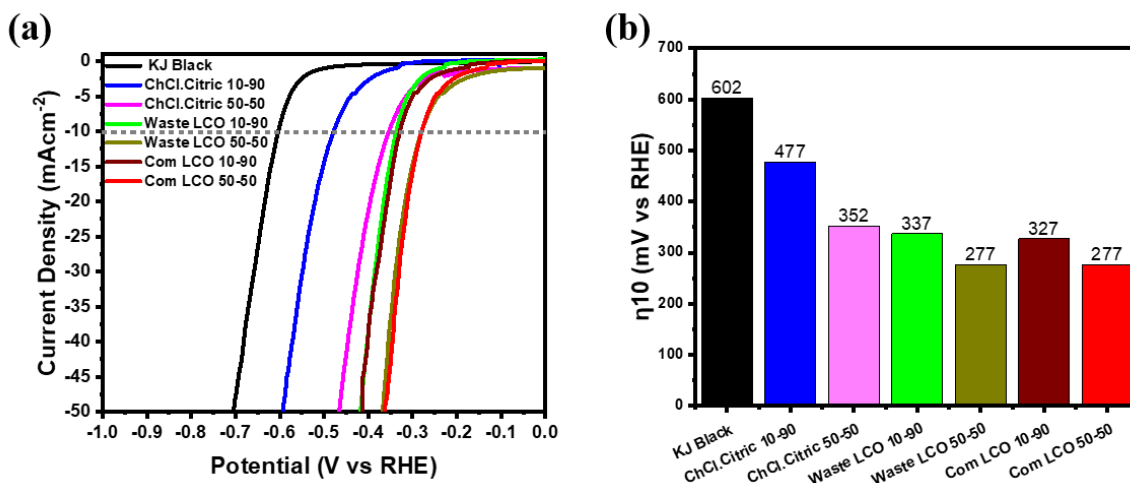


Figure 4. Experimental spectra of ChCl.Citric (a) and Waste LCO (b) samples compared with the reconstructed spectra obtained by multiple regression.

3.2. Electrochemical results

3.2.1. HER Electrocatalysis results



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4 **Figure 5.** HER LSVs acquired at 5 mVs⁻¹ in N₂ saturated 1M KOH (a) and measured HER
5 overpotential at 10 mAcm⁻² (b). HER was performed with RDE while keeping the rotation speed
6 at 1600 rpm and the acquired data are presented with 85% IR compensation. The electrode was
7 configured with a mass loading of 0.6 mg cm⁻² on RDE. The Co-based electrocatalysts were either
8 supported by over 50 wt.% of carbon (50:50) or 90 wt.% of carbon (10:90).
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15 After characterizing the LCO-based electrocatalysts, HER and ORR performance in
16 alkaline media were investigated to identify their electrocatalytic activity and to exploit their
17 possible suitability in anion-exchange membrane water electrolyzers (AEM-WEs) or alkaline
18 water electrolyzers (A-WE) and anion-exchange membrane fuel cells (AEMFCs), respectively.
19 AEM-WEs, A-WEs and AEMFCs provide an outstanding opportunity to economize the concept
20 of HE without relying on expensive PGMs and acid-tolerant stack assembly [71,72]. However,
21 cathodic reactions involving HER and ORR in AEM-WEs and AEMFCs, respectively, are the key
22 bottlenecks of the given fields. In literature, the activity of HER electrocatalyst activity is evaluated
23 considering the overpotentials recorded at a current density of 10 mA cm⁻² [73,74]. From HER
24 polarization curves presented in **Figure 5 a**, it is quite evident that the pristine carbon support (KJ
25 Black), used as control, is electrochemically languished and imparts a very high overpotential of
26 602 mV (**Figure 5 b**). However, KJ Black was used as carbon support for the three LCO
27 electrocatalysts to reduce the actual content of Co in the operating electrocatalysts while keeping
28 high the electrocatalytic activity leading to a higher valorization of the waste. Moreover, it was
29 quite complicated to prepare an ink to deposit on the glassy carbon being difficult to homogenize
30 the LCO within the solvent and the binder. Therefore LCO-based electrocatalysts were mixed with
31 KJ black following two proportions of LCO to KJ black of 10-90 and 50-50. In both cases of HER
32 and ORR electrocatalysis, increasing the relative amount of cobalt uplifted the reaction kinetics.
33 Waste LCO derived from spent LIBs (Waste LCO) with KJ black ratio of 50-50, tested in terms
34 of HER activity, presented the lowest onset potential together with a minimum overpotential (η_{10})
35 of 277 mV at -10 mA cm⁻². Notably, the HER performance of Waste LCO without any subsequent
36 treatment was identical to the one of commercial LCO. Interestingly, for HER, LCO subject to
37 acid washing with citric acid (ChCl.Citric) was the less performing among the samples containing
38 Co. Particularly, overpotential (η_{10}) of 352 mV at -10 mA cm⁻² when was in 50:50 ratio with KJ
39 Black and 472 mV at -10 mA cm⁻² when was in 10:90 ratio with KJ Black (**Figure 5**). The leading
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4 HER performance of the Waste LCO sample can be attributed to the presence of multiple Co-
5 based species as confirmed by XPS and their synergic effect can be a possible reason for the least
6 overpotential [27]. Jin and coworkers observed the collaborative effect of metallic cobalt and
7 cobalt oxide in CoO_x@CN electrocatalysts towards HER in alkaline media [75] where cobalt oxide
8 can be hydroxylated to dissociate water [75,76]. Similarly, Zhang et al. have also witnessed
9 outstanding HER performance of Co/CoO_x encapsulated carbon-based electrocatalysts [77]. In
10 addition to cobalt oxide, the efficacious role of Co(OH)₂ in performing HER electrocatalysis is
11 also known [78] and interestingly this specie was also present in Waste LCO in significant
12 proportion. XPS further indicated the presence of a majority of Co-based moieties in the form of
13 CoF₂ in Waste LCO where fluorine might have by default come from the binders/additives.
14 Interestingly, fluorine incorporation in cobalt oxide-based electrocatalysts has already been
15 explored for the enhancement of HER performance [79].
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28 **3.2.2. ORR Electrocatalysis**

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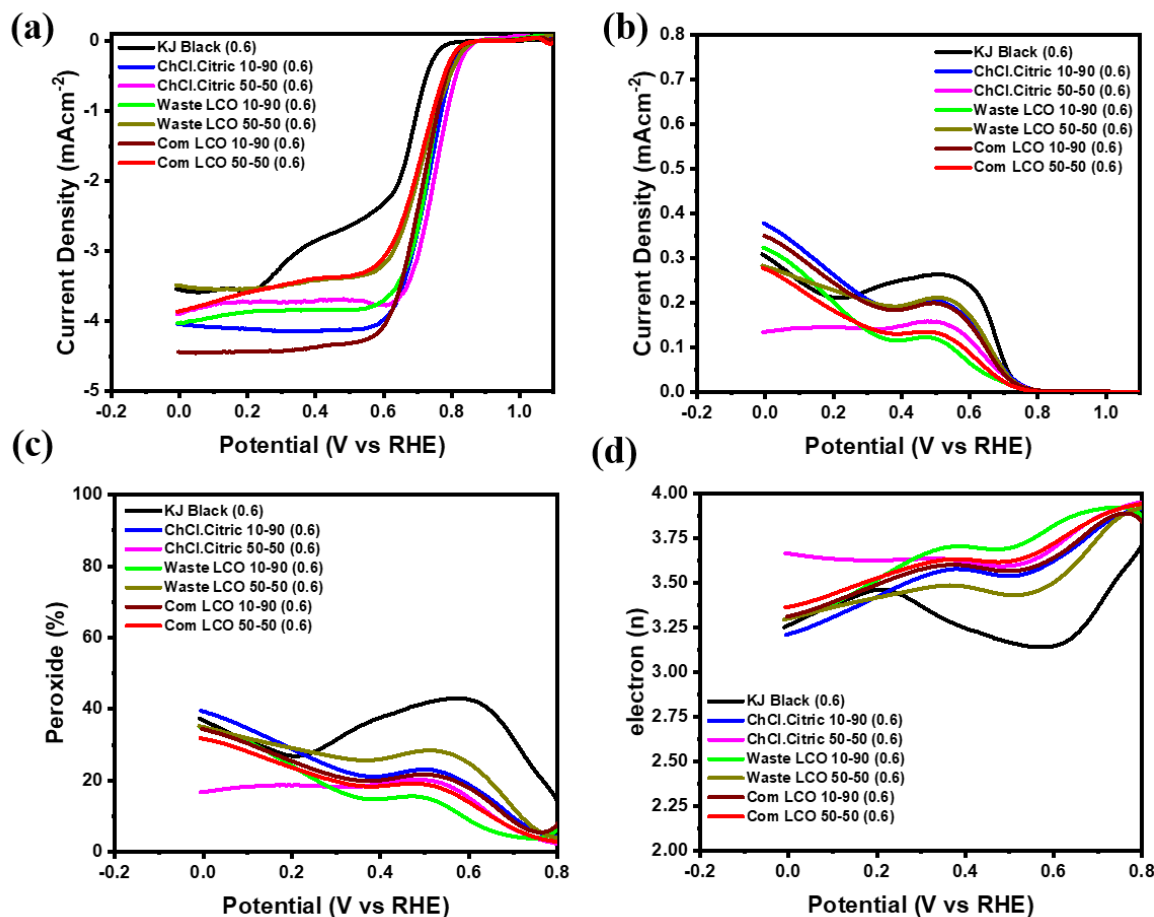


Figure 6. ORR LSVs (at the scan rate of 5 mVs⁻¹) in O₂ saturated 0.1M KOH (a), ring current densities (b), trends of peroxide production (c) and electron transfer during ORR (f). RRDE was used to fabricate the working electrode for ORR while keeping the mass loading of 0.6 mg cm⁻² on RRDE. The rotation speed of RRDE was maintained at 1600 rpm. Where the Co-based electrocatalysts were either supported by over 50 wt.% of carbon (50:50) or 90 wt.% of carbon (10:90).

To probe the activity of derived samples for the FCs application as ORR electrocatalysts, RRDE measurements in oxygen-rich 0.1 M KOH were executed. It is known in the community that an increase in the mass loading on the RRDE can modify the electronic pathway of oxygen electro-reduction by entrapment and subsequent reduction of undesirably produced peroxide within the thicker deposited layer [80–83]. Therefore, two different loadings of 0.2 and 0.6 mg cm⁻² were employed in the study. ORR results with 0.2 mg cm⁻² mass loading on RRDE are separately

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4 illustrated in supplementary [Figure S2 a-d](#). Remarkably, all the samples came out to be
5 electrochemically active for ORR electrocatalysts where the least activity was demonstrated by
6 pristine KJ black, indicating the boosting of ORR kinetics primarily due to Co. Contrary to HER,
7 the ChCl.Citric performed the best for ORR among the derived electrocatalysts as shown in [Figure](#)
8 [6 a](#). Whereas ChCl.Citric 50-50 with mass loading of 0.6 mA cm^{-2} demonstrated a promising onset
9 potential (E_{onset}) of 0.85 V (vs RHE) together with a half-wave potential ($E_{1/2}$) of 0.76 V (vs RHE)
10 where Waste LCO 50-50 drove the ORR with E_{onset} of 0.83 V (vs RHE) and $E_{1/2}$ of 0.7 V (vs RHE).
11 Ring current densities (I_r) of all the samples went on increasing with a subsequent increment in the
12 overpotential which as a result influenced the following path of ORR. However, this phenomenon
13 got restricted to ChCl.Citric 50-50 particularly when its loading on RRDE was three-fold increased
14 ([Figure 6 b](#)). With 0.6 mg cm^{-2} loading, ChCl.Citric 50-50 yielded peroxide maximum up to 20%
15 with electron transfer number above 3.5. Moreover, Waste LCO and commercial (Com) LCO
16 again performed similarly, however, relatively higher peroxide production categorizes them as
17 peroxide-producing electrocatalysts. It can be noticed that the peroxide produced increased at a
18 higher overpotential indicating that the electrocatalysts were peroxide producers. Comparing the
19 electrochemical performance at two different loadings (0.2 and 0.6 mg cm^{-2}), an uplift in the
20 kinetics descriptors (i.e. $E_{1/2}$) can be noticed while a lower percentage of intermediate indicates
21 that the peroxide is reduced within the thicker electrocatalytic layer. It is quite interesting that
22 ChCl.Citric outperformed Waste LCO which previously showed peak HER performance and the
23 reason for this discrepancy could be linked with structural attributes and surface chemistry. In
24 ChCl.Citric, where the XRD measurements confirmed the occurrence of Co_3O_4 in the matrix of
25 amorphous/disordered carbon, XPS additionally indicates the co-presence of CoO and $\text{Co}(\text{OH})_2$.
26 Such an assorted structure might be helpful in boosting the overall ORR activity. Porous disordered
27 carbon could be beneficial in maintaining the high conductivity and mass-transportation to active
28 sites while the carbon defects are already known for the binding of oxygen [84–87]. Moreover,
29 both Co_3O_4 and CoO are known as PGM-free electrocatalysts with high activity, stability and
30 robustness in alkaline conditions [28,88–91]. Inner oxygen vacancies and proportion of
31 $\text{Co}^{3+}/\text{Co}^{2+}$ are also relatable to the enhancement of ORR [28,92].
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Perspective

The Green Revolution will occur involving both batteries and hydrogen production and conversion technologies. These technologies rely on critical raw materials such as Co (batteries) and Pt and PGM (fuel cells and electrolyzers). The massive deployment of green electrochemical technologies is therefore hindered and slowed down and could be jeopardized by the lack of these critical elements. Battery systems are more technologically advanced and much more diffused compared to fuel cells and electrolyzers. However, also hydrogen-related technologies are in the near process to be massively deployed and actually, the materials used in LIB could help boosting this process.

The problem related to massive utilization of critical raw materials in the case of lithium-ion batteries is partially alleviated by the tentative of reducing the Co used by adding other TMs or completely substituting Co with Ni coupled with Fe or Mn with promising initial results [93–96]. Another route that is importantly considered is the recycling of Li batteries and related recovery of the materials of interest with the main attention focused on Co. As reported in the introduction, many routes have been considered sharing mainly negative features such as high cost, utilization of many chemicals not necessarily environmentally friendly, production of hazardous subproducts. Moreover, the recovery of Co can reach high figures (85%) but the complete recovery remains difficult.

In parallel, hydrogen production technologies and hydrogen conversion technologies rely on PGM that can be substituted with PGM-free materials containing the first raw earth-abundant transition metals (Ni, Fe, Co, Mn). These materials are very efficient and durable when operating in alkaline conditions. The TM elements needed in fuel cells and electrolyzers are exactly the TMs that are currently used in LIB and are the TMs that are at this time studied to substitute the nowadays widely used Co.

This work demonstrates the possibility of utilizing directly the waste cathode of used LIB as valuable electrocatalysts for cathode reactions occurring in electrolyzers and fuel cells operating in alkaline environments. The results presented concerning HER are quite promising and exciting at the same time. The results related to ORR show good electrocatalytic activity.

This work is the precursor of a novel line of research within the core of the circular economy. In fact, waste cathodes of exhaust Li-Ion batteries could be upgraded and used (also “as it is”) as electrocatalysts for reactions occurring in electrolyzers and fuel cells helping the large

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4 deployment of this technology at a contained cost. The change of chemistry used in the Li-Ion
5 batteries pursued to decrease the Co usage will also lead to the insertion of other elements such as
6 Ni, Fe and Mn that could be of even greater interest for ORR and HER leading to higher
7 electrocatalytic activity. These TMs contained in LIB and the new alternative formulations that
8 will be soon adopted, open new routes for recovering the TMs and using these wastes as valuable
9 electrocatalysts for electrochemical devices for the production of hydrogen or its conversion to
10 electricity. Moreover, these TMs could be also exploited in other emerging electrochemical
11 systems such as for the carbon dioxide reduction reaction, nitrogen fixation, or nitrate reduction
12 reaction. Future works will comprehend these directions as well as transforming and upgrading
13 the waste LIB cathode to other chemical structures and coordinations that might be more active
14 for the reactions of interest using fewer impacting techniques and chemicals compared to the one
15 nowadays used for recovering Co for reusing it in LIB
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28 **Conclusions**

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30 In a nutshell, the study underlines the prospects of valorizing the waste cathode of spent
31 LIBs into PGM-free electrocatalysts for HER and ORR in alkaline media. Waste LCO was
32 recovered directly from the cathodic waste of the spent batteries and subsequently subjected to a
33 leaching treatment in choline chloride: citric acid 1:1 DES and then heated at 350°C to degrade
34 the DES, giving cobalt oxide containing carbon matrix (ChCl.Citirc). As the proportion of Co-
35 based derived electrocatalysts increased in the electrochemical inks containing KJblack as carbon
36 support, the overall activities were enhanced drastically, indicating the sole contribution of cobalt
37 in uplifting the reaction kinetics. Waste LCO directly acquired from the waste cathode without
38 any further treatment showed electrocatalytic activities comparable to that of commercial LCO
39 and demonstrated suitability for HER while ChCl.Citric came out to be the most active for ORR.
40 The least HER overpotential of 277 mV at -10 mA cm⁻² in the case of Waste LCO 50-50 could be
41 attributed to the synergic effect of different Co-based species as confirmed through XPS. On the
42 other hand, cobalt-based oxides including Co₃O₄ in the matrix of amorphous/disordered carbon
43 could be linked with the excellent ORR activity of ChCl.Citirc. With mass loading of 0.6 mg cm⁻²
44 on RRDE, ChCl.Citric 50-50 demonstrated an outstanding E_{onset} of 0.85 V with a nearly tetra-
45 electronic pathway of ORR while keeping peroxide production maximum at 20%. No doubt, the
46 electrocatalytic activities of the derived electrocatalysts are inferior compared to scarce and
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4 economically unviable PGM-based electrocatalysts but prospective endeavors could improve the
5 electro-kinetics of the waste-derived electrocatalysts. Such approaches can give rise to new
6 opportunities for green and cost-effective energy within the framework of the circular economy.
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

On behalf of the corresponding author and the other authors

Yours sincerely,



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