Sustainable SoluTions FOR recycling of end-of-life Hydrogen technologies

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Technical report on open-loop analysis of different scenarios

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Summary

1 Executive summary

State-of-the-art SOCs are commonly constituted by a composite NiO-YSZ (Yttria-stabilized Zirconia) fuel electrode, a thin YSZ electrolyte and an LSC (Lanthanum Strontium Cobaltite) oxygen electrode. Co is considered a Critical Raw Material, while Ni is a Strategic Raw Material; YSZ is not identified in any specific list but its use might significantly increase with the market growth of SOFCs. BEST4Hy project succeeded in demonstrating the efficacy of recovering critical raw materials (CRMs) and rare-earth elements (REEs) derived from end-of-life (EoL) solid oxide cells (SOCs) and re-using them for the manufacturing of new cells containing at least 30 wt% of recovered materials. However, opportunities for use of Ni and Co in particular exist also in parallel supply chains such as batteries manufacturing and catalysts applications.

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2 Analysis of different open-loop scenarios for critical materials recovered from EoL SOCs

2.1 Introduction

In the frame of fuel-cell and hydrogen (FCH) technologies, the BEST4Hy project succeeded in demonstrating the efficacy of recovering critical raw materials (CRMs) and rare-earth elements (REEs) derived from end-of-life (EoL) solid oxide cells (SOCs) and re-using them for the manufacturing of new cells containing at least 30 wt% of recovered materials.

The possibility of reintroducing the materials inside the *closed-loop* production cycle of SOCs is in fact an essential aspect for the full exploitation and boost of this hydrogen technology, enabling to partially substitute the original virgin powders during the production phase. However, the perspective of using the whole range of recovered materials for different purposes and applications should be equally considered and analyzed. Indeed, an *open-loop* recycling strategy will allow to effectively reduce waste and keep the materials value in the economy, even when recovered materials do not meet the target in term of composition and/or physical characteristics (particle size, surface area) needed for *closed loop* scenario.

The materials constituting SOCs are key in the entire frame of low-carbon technologies. The shift towards a low-carbon society comes in fact with significant growth in renewable energy technologies, electric infrastructures, and batteries for electric vehicles (EVs) to enable sustainable energy production and sustainable transports. The use of metals and rare-earth elements is crucial to ensure high performances in both areas and achieve the transition. According to a report released by the International Energy Agency *[0]*, the total demand for minerals is set to quadruple within 2040 in a Sustainable Development Scenario (SDS) in line with the Paris agreement. Figure 1 shows the **prospected growth in demand for lithium, cobalt, nickel, copper, and rare-earth elements (REEs)**.

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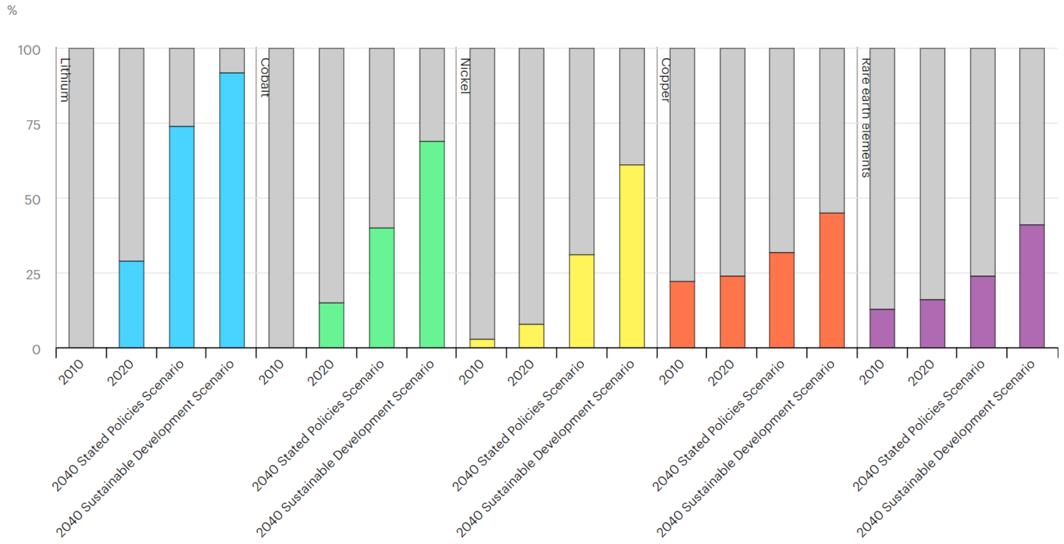

Figure 1 Share of clean energy technologies in total demand for selected minerals by scenario, 2010-2040. *(Credit: IEA, World Energy Outlook, Paris https://www.iea.org/data-and-statistics/charts/share-of-clean-energy-technologies-in-total-demand-for-selected-minerals-by-scenario-2010-2040, p.7)*

State-of-the-art SOCs are commonly constituted by a composite NiO-YSZ (Yttria-stabilized Zirconia) fuel electrode, a thin YSZ electrolyte and an LSC (Lanthanum Strontium Cobaltite) oxygen electrode. Among these materials, La is a REE, and Co has been classified as a critical material since 2020 in the Fourth List of CRMs, by the European Commission due to its high supply-related risk, while Ni is considered a Strategic Raw Material. Yttria-stabilised Zirconia is not listed but it is becoming an important material. In the following sections, the different matreials will be analysed for their supply chain criticalities.

2.2 Cobalt

The extraction of cobalt primarily occurs in the Democratic Republic of the Congo (DRC) and it is subsequently transported to China, where approximately 60% of the global cobalt processing takes place *[0]*. These two Countries and their interconnection therefore plays a pivotal role in the cobalt value chain, resulting in a high risk of supply-chain disruptions [1]. Any inability of the Democratic Republic of the Congo to supply cobalt to China for processing would in fact disrupt the entire value chain; this highlights the risks associated with relying on a single nation for mineral extraction including shortage risks resulting from potential geopolitical conflicts, natural disasters or global pandemics.
In the last decade, over 60% of the refined and produced cobalt remained stored in End-of-Life (EoL) products [2], which end up in landfills, posing high

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environmental and health risks. Recycling is therefore fundamental, as it would contribute to securing future supply, lowering the social and environmental impacts of cobalt production, and reducing the need for primary production.

2.3 Nickel

Compared to cobalt, nickel is currently deemed non-critical according to the EU Commission as it does not meet the CRM threshold. However, in the most recent list of CRMs – the *Fifth List of CRMs,* European Commission, 2023 based on the *Study on the Critical Raw Materials for the EU 2023*, it was indicated as Strategic Raw Materials. **Nickel has a resilient supply chain but, considering its high economic importance, especially in light of its pivotal role in batteries and low-carbon technologies, its supply is currently under monitoring**. In fact, two primary types of nickel products exist: class-1 high-purity nickel (> 99.8%) and class-2 low-purity nickel (< 99.8%). Although its demand is overall likely to be met, class-1 nickel products face potential shortages. The increasing demand for class-1 nickel from battery production, coupled with the majority of new production originating from laterite sources that primarily produce class-2 nickel, raises in fact concerns about potential shortages of class-1 nickel despite overall production sufficiency (*IEA, 2021*). Considering a projected growth ranging from 6 (STEPS scenario) to 19 times (SDS scenario) current demand by 2040, higher recycling rates are necessary. While nickel in ordinary metal products can be substituted by alternative minerals like titanium or chromium, critical applications such as most lithium-ion battery (LIB) chemistries cannot substitute nickel *[European Commission, 2017]*, making its recycling even more urgent. On top of supply reasons, **Ni (like Co) is highly harmful for the health and environment**, and its recycling would reduce the impact of mining and prevent the disposal of scrap materials.

2.4 Yttria-stabilised Zirconia (YSZ)

Despite not possessing any specific criticality, **YSZ is also considered impactful, as its market is poised for substantial growth in the coming years**. The demand for YSZ is mainly driven by the increasing adoption of **fuel cells, dental restoration and thermal coatings in aerospace**. For these applications, YSZ possesses an exceptional ionic conductivity, a good biocompatibility combined with superior mechanical properties, and a high thermal stability, respectively [3]. However, it poses high production costs due to the precise control and stabilization required during the production process, especially for medical and aerospace applications, with the risk of inhibiting a widespread adoption on the market. Considering the high amount of YSZ involved in the manufacturing of SOCs, it is of primary importance to define a recycling pathway for this material. YSZ is in fact the main ceramic component of SOCs, constituting about 45 wt% of an entire cell

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(90 wt% considering the NiO-YSZ composite). Noteworthy, YSZ contains Y (3 or 8 mol%), which is a Heavy REE (HREE).

2.5 Open loop scenarios

According to the E4tech report [4], focused on the study of the value chain and manufacturing competitiveness for Hydrogen and Fuel Cells Technologies, a 6-fold increase in the amount of materials for FCH applications has been estimated. These are significant additions to the existing requirements of the industry, also considering that a few of the above materials are required in other growing markets, from electronics to batteries for electric vehicles. The mining of these minerals, especially Ni and Co, results in substantial adverse environmental impacts on the nearby ecosystem, causing both direct and indirect pollution, with detrimental effects on ecosystems, biodiversity, water sources, and the local population. In this scenario, recycling is fundamental to limit the overall use of virgin materials. **Different possible open-loop scenarios are therefore presented below for Ni, YSZ, Co and La recovered from end-of-life SOCs**.

According to the above-mentioned expected demand for minerals, one impactful area of application in view of *open-loop* recycling from SOCs would be the battery field, with special focus for Ni and Co. The demand for Lithium-ion batteries, particularly for **electric vehicles** but also for **smart grid applications** and **wearable** and **electronic devices**, is in fact projected to **increase by over 300%** throughout the next decade [5] due to their high energy density, long cycle life, and relatively good power capability [6]. Between 2015 and 2050, the global EV stock needs to jump from 1.2 million to 965 million passenger cars and battery storage capacity needs to climb from 0.5 to 12,380 GWh [7] to enable the energy transition. The increase in mineral demand specifically related to the battery field is reported in **Figure 2**.

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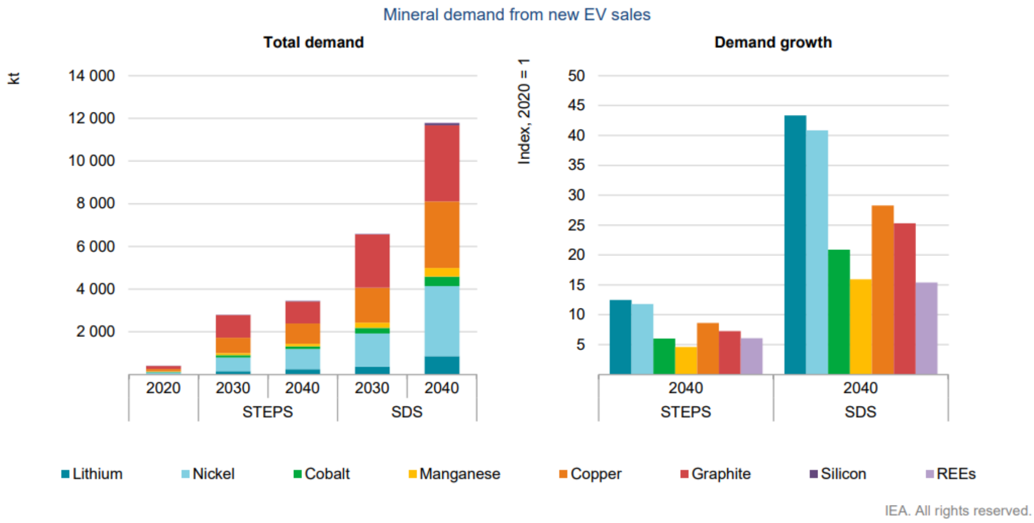

Figure 2 Mineral demand for EVs in the SDS grows by nearly 30 times between 2020 and 2040, with demand for lithium and nickel growing by around 40 times. *(Credit: IEA, World Energy Outlook Special report, The Role of Critical Minerals in Clean Energy Transitions, https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions, p. 98)*

The electrochemical performance of lithium-ion batteries (LIBs), encompassing factors such as volumetric/gravimetric energy density, cycle performance, output potential, and safety, is significantly influenced by electrode materials, including cathodes and anodes. Notably, it has been observed that cathode materials play a pivotal role in limiting the energy density and power density of LIBs. Over the past two decades, traditional cathode materials like $LiCoO_2$ [8] with a hexagonal layered structure have undergone extensive study.
In recent times, the focus has shifted to the next generation of layered oxide cathodes, particularly Ni-rich oxides $Li[Ni_xMn_yCo_z]O_2$ (NMC), whose structure is shown in **Figure 3**. The remarkable electrochemical performances of this class of materials, considering reversible capacity, specific energy and working potential [9] have propelled them into the forefront of research interest [10], also in light of their cost-effectiveness.

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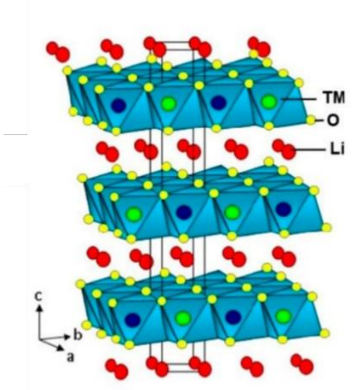

Figure 3 Layered structure of NMC cathodes. *(Credit: Figure 2a from Energies 2020, 13, 6363; https://doi.org/10.3390/en13236363)*

In NMC layered structures, the ratios of nickel, manganese, and cobalt can be altered to achieve different effects [11]. The fundamental characteristics of the NMC electrodes were evaluated in a wide range of Ni concentrations (1/3 ≤ *x* ≤ 0.85) for Li-ion batteries in an important study carried out in 2013 by H. Noh et al. [12]. From this investigation, an increased Ni content resulted in an increased capacity, despite leading to a decreased capacity retention and safety characteristics, as displayed in the following graph (**Figure 4**):

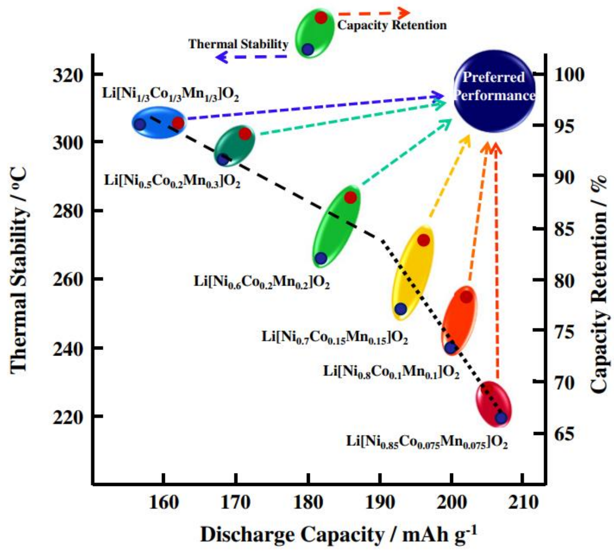

Figure 4 Effect of varying Ni concentration (1/3 ≤ *x* ≤ 0.85) on the thermal stability and capacity retention of $Li[Ni_xMn_yCo_z]O_2$ (NMC) cathodes. *(Credit: Graphical abstract from Journal of Power Sources 2013, 233, 121-130; https://doi.org/10.1016/j.jpowsour.2013.01.063)*

Considering the increasing concerns regarding the supply of the cobalt raw material and its related costs, the development of cobalt-free layered oxides has gained increasing interest. Co-free lithium-rich layered oxides (LRLOs) material

with a high lithium content and limited nickel content, i.e., $Li_{1.25}Mn_{0.625}Ni0_{.125}O_2$ have been developed and demonstrated to reversibly exchange an outstanding specific capacity at room temperature (230 mAh g^{-1} at C/10) for almost 200 cycles, and to sustain high current rates (118 mAh g^{-1} at 2C) [13].
Moreover, a new class of "Co-free" cathode materials in a spinel structure (**Figure 5**) has also recently emerged for LIBs. Among them, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising candidate thanks to its operating voltage of ~4.7 V (vs Li+/Li) and theoretical specific capacity of around 147 mAh g^{-1}. [6].

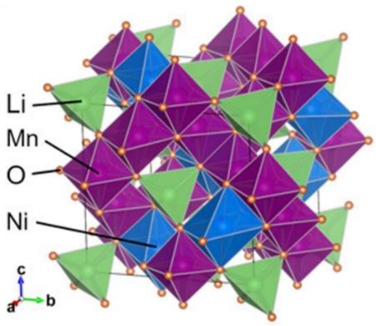

Fig. 5 Ordered spinel structure of Co-free LNMO cathodes.
(Credit: Figure 1b from Chem. Mater. 2022, 34, 14, 6529-6540; https://doi.org/10.1021/acs.chemmater.2c01360)

Overall, as it emerged from this review, LIB chemistries are increasingly shifting toward lower cobalt concentration due to the high-related supply risks and costs, resulting in a corresponding increase in nickel and lithium concentrations to ensure optimal electrochemical performances. The interdependence between LIBs and nickel demand is therefore likely to persist in the incoming decades.
Given the substantial nickel content in SOCs fuel electrodes (approximately 45 wt% of an entire single cell), repurposing SOCs **recovered nickel for battery cathode applications represents a noteworthy illustration of open-loop recycling**. However, the feasibility of this approach hinges on ensuring that the recovered nickel precursors align with the physical-chemical characteristics demanded by battery applications. On the other hand, repurposing recovered cobalt could find suitability in battery applications that employ cathodes with low-cobalt concentrations, aligning with the inherently low cobalt content in SOCs. Co-containing LSC oxygen electrodes, with a thickness ranging from 5 to 10 µm, stands in fact in stark contrast to the 400µm-thick NiO-YSZ fuel electrodes.
In a positive perspective, the effective possibility of repurposing SOCs critical materials for batteries would enable an interchangeable use of minerals among different low-carbon technologies within the energy field.
Beside the potential re-use of Co to manufacture electrode components, an alternative *open-loop* scenario focuses on materials for **catalytic applications**, since **Co**-based **catalysts** are known to be **more catalytic active** than iron, nickel

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or alkali metals for a wide range of applications but more expensive and critical for supply due to the reasons reported above. In particular, supported Ni-Co bimetallic catalysts with various Ni/Co mass ratios have been proved to have superior catalytic activity and stability for steam methane reforming, which is an ideal and important reaction to produce environmentally-friendly hydrogen from CH_4 [14], CO_2 methanation [15] and Fatty Acid Hydrogenations [16].

The recovery pathways developed in the frame of the BEST4Hy project enable the recovery of Ni and Co precursors from the electrode components in the form of nitrate solutions. The latter can be easily used for preparing supported Ni and Co nanoparticles by solution impregnation on ceramic (Al_2O_3) or carbon supports. More recently the applications along with the rational design of Ni-based nanostructure catalysts for hydrogen evolution reactions have been critically reviewed [17], evidencing the most recent progress in the field and the open challenges in the practical applications.

Regarding the use of recovered YSZ in an *open-loop* perspective, one of the most attractive emerging research topics is the development of ceramic formulations for 3D printing applications in several applications fields, including the energy sector. In this frame, Albert Tarancòn and Vincenzo Esposito have edited an insightful and cutting-edge exploration of the applications of 3D printing to the fabrication of complex devices in the energy sector [18]. Among the wide range of reviewed applications, inkjet deposition has been successfully employed to obtain microlayers of YSZ onto anode-supported NiO-YSZ and to print YSZ micro-pillars and square lattices on NiO-YSZ anode substrates to improve the cell performance by structuration of the electrolyte/electrode interface. These are not exhaustive examples of possible re-use of recovered YSZ to develop formulations suitable for 3D printing technologies of advanced complex-shaped solid oxide fuel cells.

3 Conclusions

Ni, YSZ, Co and La recovered from end-of-life SOCs have the opportunity to be used in open-loop recycling applications, with special focus for Ni and Co mostly within the batteries sector. More specifically, low cobalt concentration or “Co-free” cathode materials LIB are particularly aligned with the low concentration of Cobalt in SO fuel cells. Such type of materials conversely use higher concentrations of Nickel. Other applications for Ni and Co from SOFCs could include catalysts used for example in steam reforming of methane for production of hydrogen.

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