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Original pathway to selectively precipitate cobalt from an old battery solution thanks to imidazole linker

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Keywords

Recycling, cobalt, batteries, Zeolitic Imidazolate Frameworks (ZIFs), Metal-Organic Frameworks (MOFs)

Abstract

Owing to its specific properties, cobalt is a critical material for catalysis, stainless steel, and of course for Li-Ion batteries. Due to the intensive development of Li-ion batteries for transport applications (All-Electric and Plug-in Hybrid Electric Vehicles), the need for cobalt will dramatically increase. Unfortunately, resource is scarce and more than half of the cobalt production is presently concentrated in only one country (Democratic Republic of the Congo). Recycling and reusing cobalt from used batteries in a closed-loop process in order to limit cobalt imports becomes mandatory. In this paper, we propose a disruptive and very efficient route to selectively precipitate cobalt from a spent batteries solution, which consists in using imidazole linkers. The resulting hybrid material can be directly used as a precursor to produce a new cobalt-cathode based material.

1. Introduction

Cobalt is currently used in industrial sectors such as aerospace (superalloys), defense (permanent magnets, specialty steels), energy (catalyst, land-based turbines) and other fields (e.g cemented carbides). 60% of the world's cobalt relatively poor crustal abundance resource is located in only one country (Democratic Republic of Congo). Cobalt is usually produced as a side product of copper and nickel mining, and is classified as a critical material since 2011 by the European Commission.[1] Cobalt is also used as a key material in the manufacturing of lithium-

ion batteries, and the expected rapid take-off of the electromobility market will lead to a huge increase of cobalt needs. Studies forecast that the number of electric vehicles will be multiplied by 15 - 33 before 2030.[2] Recycling high value battery materials at their end of life becomes thus mandatory.[3] In lithium-ion batteries, cobalt is used in large quantities to manufacture cathode materials such as LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ or $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (with $x+y+z=1$) oxides. Current recycling routes are based on hydrometallurgical or pyrometallurgical processes.[4–6] They allow to separate various elements of a battery (Li, Al, Mn, Ni, Fe, Mn, Cu, Co), but their multistep nature makes these solutions expensive. Many researchers are currently working on discovering alternative pathways, especially to selectively remove cobalt from a mixed metals solution.[7-10] The possibility to synthesize metal-mixed Metal-Organic Frameworks (MOFs) was shown by Wang et al..[11] In this publication, authors synthesize the well-known MOF-74 compound with a mix of divalent metals (Ni, Co, Mn...). This pathway was exploited in 2016, by Perez et al. who studied how carboxylic acid (1,4-benzenedicarboxylic acid and 1,3,5-benzenetricarboxylic acid) and phosphonate organic linkers (1,4-benzenediphosphonic acid and 1,3,5-benzenetriphosphonic acid) could produce MOFs from a simulated battery waste solution.[12,13] In 2020, the same group managed to synthesize aluminium or copper-based MOFs from Li-ion battery waste solutions.[14–16]

In the literature, Zeolitic Imidazolate Frameworks (ZIFs) structures are mainly reported using zinc or cobalt as cations.[17–22] However, there is no zinc component in Li-Ion batteries and the largest share of impurities such as iron, aluminium and copper (due to casing and electrodes) can be removed in a first recycling step.

Based on a thorough study which allowed us to assess the reactivity of various imidazole linkers in a mixed solution of cobalt, nickel and manganese, we propose here an original pathway to selectively precipitate cobalt in an hybrid compound by smartly selecting the organic ligand. [23]

2. Materials and methods

Selectivity experiments in methanol:

14.9 mmol of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 14.9 mmol of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 14.9 mmol $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ are dissolved in 600 mL of methanol. The resulting solution is submitted to magnetic stirring at room temperature. 356.7 mmol of an organic linker (Im, 2-Melm, 4-Melm or blm) are added to the solution. The solution is aged for 24h and the reaction product is then recovered by filtration. The resulting material is washed thoroughly with methanol and water.

Selectivity experiment in spent batteries solution:

The spent batteries solution is obtained by leaching a NMC cathode-based black mass from SNAM with a solution of sulfuric acid (1M) and 10% of hydrogen peroxide. To perform the experiment, 60 g of 4-Melm are added to 100 ml of the spent batteries solution. The solution is aged for 24h and the reaction product is then recovered by filtration. The resulting material is washed thoroughly with methanol and water.

LiCoO₂ synthesis:

300 mg of ZIF-67 are intimately mixed with 52.6 mg of lithium carbonate (Li₂CO₃) and the mixture is calcinated at 850 °C during 24 h.

Characterisation:

Purities of all products are controlled by X-ray diffraction using a Brüker AXS D8 diffractometer, equipped with a Cu anticathode.

Morphology of the products is determined by scanning electron microscopy using a LEO 1530 FE-SEM microscope equipped with a field electron gun.

The chemical analysis is performed by using ICP-OES (Agilent Technologies 700 Series ICP-OES).

The electrochemical characterizations are achieved using CR2032 coin-cells type that consist of a cathode and a lithium foil anode separated by a Celgard® 2400 porous polypropylene film and a Viledon® separator. Cathodes are fabricated by coating a slurry of 80 wt% active materials, 10 wt% carbon and 10 wt% PVDF in N-methyl-2-pyrrolidone on aluminium foil. The electrolyte is 1 mol/L LiPF₆ in EC/PC/DMC in a volume ratio of 1/1/3. Coin cells are assembled in an argon-filled glove box and are cycled on an Arbin® tester in galvanostatic mode. Charge and discharge tests are performed at the current discharge of 14 mA/g (C/10) in the voltage range of 3.0 V - 4.3 V at room temperature. All the potentials in this study are given versus Li⁺/Li.

3. Results and discussion

Several imidazole linkers are screened by mixing them with reference equimolar solutions of cobalt, manganese and nickel nitrates in methanol. Benzimidazole (blm), Imidazole (Im), 2-Methylimidazole (2-Melm) and 4-Methylimidazole (4-Melm) are tested (Fig. 1).

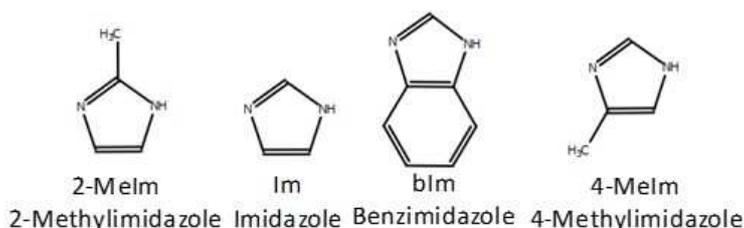


Fig. 1. Imidazole linkers used in the study

In a conventional test, the organic linker, in its solid form, is directly mixed with the metal-based solution while stirring at room temperature. A purple-based precipitate instantly appears (Fig. 2).

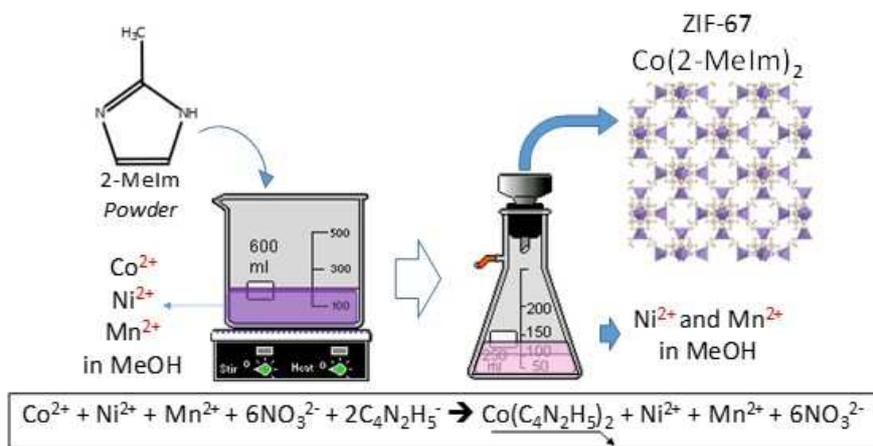


Fig. 2. Experiment and corresponding reaction with 2-Melm linkers

After one day, the purple precipitate is recovered by filtration and is finely characterized by XRD, SEM and ICP-AES (Fig. 3). XRD reveals that blm and 2-Melm respectively precipitate in the well-known ZIF-9-III and ZIF-67 structures.[17,24] The compound obtained with Im and 4-Melm could not be identified and is still being characterised. SEM reveals that small particles between 50-200 nm are obtained, certainly due to the use of a low synthesis temperature. ICP-AES results confirm our assumption: synthesized materials are made of more than 90% of cobalt (molar based on metal elements). A purity of 99% in Co is obtained by using imidazole as a ligand (detailed results of ICP-AES are summarized in Table.S1.). It is now clear that Imidazole linker's family can selectively react with cobalt and lead to high cobalt content ZIFs. This last result confirms that imidazole linkers are promising materials for cobalt extraction or recycling.

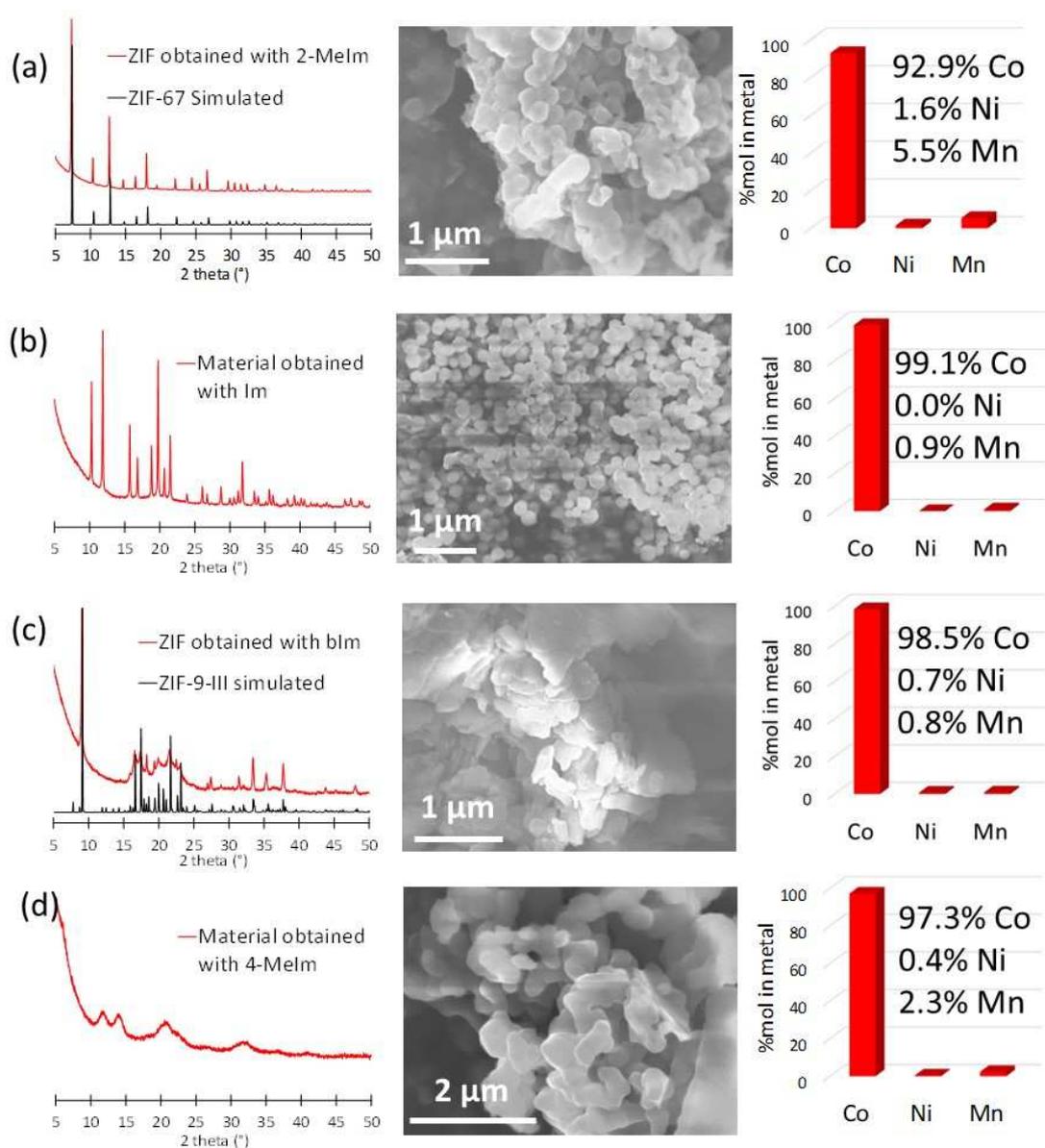


Fig. 3. Results obtained in XRD, SEM and ICP-AES (molar ratios) with (a) 2-Melm, (b) Im, (c) blm and (d) 4-Melm linkers

We believe that this reaction may find many applications in several industrial fields like cobalt extraction, purification, depollution or recycling. As an example, we investigated this selective mechanism for cobalt recycling from a real spent battery leaching solution. As ever, there is a strong difference between model and reality, namely between a model solution using nitrate salts and methanol only, and a real spent batteries solution directly obtained from recycling processes. In such a solution several species are mixed, which come from the active material but also from the current collectors and from the batteries casing. The use of various acids and

oxidative solutions to dissolve batteries parts usually raise also some other issues such as an acidic pH. The spent batteries solution used in this example is obtained by leaching a NMC (lithium layered oxide materials) cathode-based black mass from the SNAM company with a solution of sulfuric acid (1M) and 10% of hydrogen peroxide. The solution is treated with the 4-Melm ligand at room temperature. After one day of precipitation, the purple precipitate is recovered by filtration (results are shown in Fig. 4). We focus on the 4-Melm ligand because this imidazole molecule is already used at large industrial scale as a chemical intermediate for several applications (pharmaceutics, photography, agriculture, dyes, rubber...).[25–28]

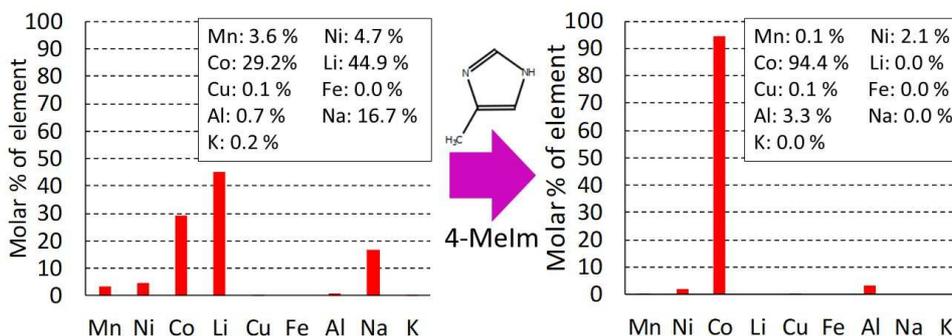


Fig. 4. Analysis of a spent batteries solution: ICP-AES analysis (molar ratios) of left/ the solution before treatment and right/ the material recovered after treatment with 4-Melm

By using 4-Melm linkers, it is possible to extract more than 80% of the cobalt contained in the solution and the recovered material contains more than 94.4% of cobalt (detailed results of ICP-AES are summarized in Table.S2.). However, one may notice that the material concentrates aluminum species. It may reveal useful to remove aluminum before the reaction with imidazole linkers. After drying one night under vacuum, the recovered compound is characterised by XRD and SEM (Fig. S1). By contrast with the results achieved with methanol, the XRD pattern of the material obtained from a spent battery solution shows an amorphous structure. Several MOFs materials are not stable in water-based solutions, and it is difficult to conclude whether an amorphous hybrid compound directly precipitates, or whether a ZIF precipitates, that presents a water sensitive structure.[29,30] In any case, the resulting material is highly pure in cobalt. Surprisingly, SEM reveals slab with beautiful spiral dislocations. The growing mode of such crystals was explained by Burton, Cabrera and Frank in 1951 (BCF mechanism).[31] Several scientists observe and work on this complex phenomenon.[32,33]

Another important aspect of a recycling process is the financial value of the recovered materials. Of course, ZIFs are well known to be good catalysts or adsorbents and materials could be directly used as made, but the carbon framework of this material family also allows using ZIFs as

precursors for material synthesis (glass, stainless steel or supercapacitor...).[23,34–49] In the present paper, we focus on using ZIFs as precursors for the synthesis of a cathode material, thus allowing the design of a full, closed loop process. We use our cobalt-based ZIFs as a starting material to produce the well-known LiCoO_2 material (LCO).[50] This uncommon phase reaction is illustrated in Fig.5.(a,b). Materials obtained with 2-Melm/Co (ZIF-67) and 4-Melm/Co are calcinated with lithium carbonate at 850°C . XRD patterns of the final calcinated powders reveal that the expected layered structure is obtained, able to be directly used as a cathode active material in a lithium-ion battery Fig.5.(c,d).

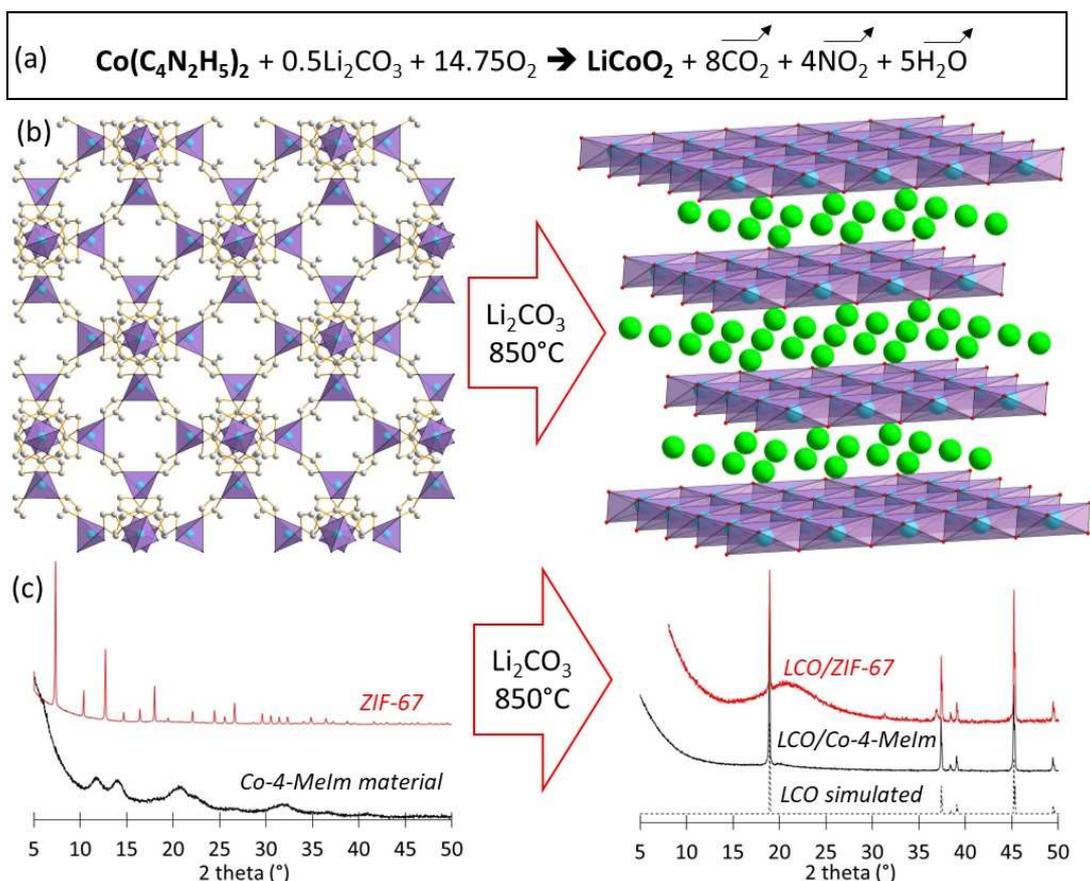


Fig. 5. (a) calcination reaction, (b) structure evolution and (c) XRD change of ZIF-67 with Li_2CO_3 at 850°C

To confirm our proof of concept, the LiCoO_2 materials are used as cathode material in coin cells, which are tested in galvanostatic mode in the voltage windows of 4.3 V – 2.7 V in order to assess the electrochemical performances. Despite a non-optimized synthesis, the electrochemical results show a classic dq/dV signature of a half-cell assembled with LiCoO_2 (Fig.6.(c)).[51-53] In terms of performances, 120 mAh/g are recovered with the LCO synthesized

using ZIF-67 as precursor and 154 mAh/g with the material synthesized using the 4-Melm/Co material (Fig.6.(a) and Fig.6.(c)).

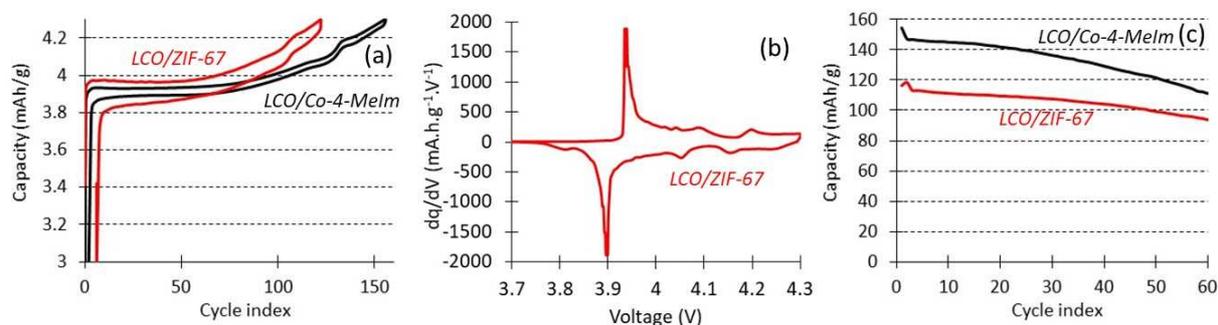


Fig. 6. (a) Galvanostatic curve (first cycle), (b) dq/dV plot of a charge/discharge curve and (c) cycle life at 1C obtained with LiCoO_2 synthesized using ZIF-67 and using Co-4-Melm

4. Conclusions

We demonstrate in this study that cobalt reacts selectively with imidazole to produce hybrid materials such as ZIFs and that the recovered materials contain more than 99 % of cobalt (based on metal element ratio). Our group is currently prolonging this work to identify the selectivity mechanism of this system. To our belief, this discovery paves the way for a very efficient, easy, and affordable route to recycle spent batteries and to recover critical materials. It also opens new perspectives to recover cobalt from waste/mine with an easy and efficient process. Moreover, the resulting product (ZIF) is a high value product that can be directly used as a precursor or an adsorbent. In a more specific application, imidazole linkers allow removing cobalt from a spent battery solution and the resulting product can be directly re-used in a closed-loop process to produce a fresh cathode material. This article only focuses on one application of this selective reaction (recovery of cobalt from spent battery solution) but we assume that applications of this discovery could reveal numerous (e.g. cobalt extraction, cobalt decontamination...). As an example, the resulting Co-ZIFs materials can be also used as a precursor for stainless steels, glasses, catalysts, adsorbents...

CRedit authorship contribution statement

D. Peralta had the idea and designed the research. A-C. Lavergne-Bril and D. Peralta performed all syntheses and characterisation experiments (SEM, XRD and electrochemical tests). E. Billy supplied the battery-spent solution. D. Peralta wrote the manuscript. All authors discussed the results and commented on the manuscript.

Declaration of competing interest

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.

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References

- [1] Publications Office of the E. Union, Study on the review of the list of critical raw materials, (2017), <http://op.europa.eu/en/publication-detail/-/publication/08fdab5f-9766-11e7-b92d-01aa75ed71a1/language-en>.
- [2] Global EV Outlook 2018, IEA Webstore, <https://webstore.iea.org/global-ev-outlook-2018>.
- [3] D. Bloch, G. Lefebvre, Les matériaux requis par les batteries Li-ion, REE 2019-4 (2019), <https://www.see.asso.fr/node/93448/landing> (accessed November 18, 2019).
- [4] X. Zheng, Z. Zhu, X. Lin, Y. Zhang, Y. He, H. Cao and Z. Sun, A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries, Engineering. 4 (2018) 361–370. <https://doi.org/10.1016/j.eng.2018.05.018>.
- [5] W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang and Z. Sun, A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries, ACS Sustain. Chem. Eng. 6 (2018) 1504–1521. <https://doi.org/10.1021/acssuschemeng.7b03811>.
- [6] L. Li, X. Zhang, M. Li, R. Chen, F. Wu, K. Amine and J. Lu, The Recycling of Spent Lithium-Ion Batteries: a Review of Current Processes and Technologies, Electrochem. Energy Rev. 1 (2018) 461–482. <https://doi.org/10.1007/s41918-018-0012-1>.
- [7] F. Wang, R. Sun, J. Xu, Z. Chen, M. Kang, Recovery of cobalt from spent lithium ion batteries using sulphuric acid leaching followed by solid–liquid separation and solvent extraction, RSC Adv., 6 (2016) 85303-85311. <https://doi.org/10.1039/C6RA16801A>.
- [8] G. Alviaal-Hein, H. Mahandra, A. Ghahreman; Separation and recovery of cobalt and nickel from end of life products via solvent extraction technique: A review, Journal of Cleaner Production 297 (2021) 1265922. <https://doi.org/10.1016/j.jclepro.2021.126592>.
- [9] J. C.-Y. Jung, P.-C. Sui, J. Zhang, A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments, Journal of Energy Storage 35 (2021) 102217. <https://doi.org/10.1016/j.est.2020.102217>

- [10] S. Anwani, R. Methekar, V. Ramadesigan, Resynthesizing of lithium cobalt oxide from spent lithium-ion batteries using an environmentally benign and economically viable recycling process, *Hydrometallurgy* 197 (2020) 105430. <https://doi.org/10.1016/j.hydromet.2020.105430>
- [11] L. J. Wang, H. Deng, H. Furukawa, F. Gándara, K. E. Cordova, D. Peri and O. M. Yaghi, Synthesis and Characterization of Metal–Organic Framework-74 Containing 2, 4, 6, 8, and 10 Different Metals, *Inorg. Chem.* 53 (2014) 5881–5883. <https://doi.org/10.1021/ic500434a>.
- [12] E. Perez, R. Navarro Amador, M. Carboni and D. Meyer, In-situ precipitation of Metal–Organic Frameworks from a simulant battery waste solution, *Mater. Lett.* 167 (2016) 188–191. <https://doi.org/10.1016/j.matlet.2015.12.129>.
- [13] E. Perez, M.-L. Andre, R. Navarro Amador, F. Hyvrard, J. Borrini, M. Carboni and D. Meyer, Recovery of metals from simulant spent lithium-ion battery as organophosphonate coordination polymers in aqueous media, *J. Hazard. Mater.* 317 (2016) 617–621. <https://doi.org/10.1016/j.jhazmat.2016.06.032>.
- [14] E. Lagae-Capelle, M. Cognet, S. Madhavi, M. Carboni and D. Meyer, Combining Organic and Inorganic Wastes to Form Metal–Organic Frameworks, *Materials*. 13 (2020) 441. <https://doi.org/10.3390/ma13020441>.
- [15] M. Cognet, J. Cambedouzou, S. Madhavi, M. Carboni and D. Meyer, Targeted removal of aluminium and copper in Li-ion battery waste solutions by selective precipitation as valuable porous materials, *Mater. Lett.* 268 (2020) 127564. <https://doi.org/10.1016/j.matlet.2020.127564>.
- [16] M. Cognet, J. Condomines, J. Cambedouzou, S. Madhavi, M. Carboni and D. Meyer, An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks, *J. Hazard. Mater.* 385 (2020) 121603. <https://doi.org/10.1016/j.jhazmat.2019.121603>.
- [17] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe and O. M. Yaghi, High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture, *Science*. 319 (2008) 939–943. <https://doi.org/10.1126/science.1152516>.
- [18] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe and O. M. Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, *Proc. Natl. Acad. Sci.* 103 (2006) 10186–10191. <https://doi.org/10.1073/pnas.0602439103>.
- [19] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet and G. D. Pirngruber, Synthesis and adsorption properties of ZIF-76 isomorphs, *Microporous Mesoporous Mater.* 153 (2012) 1–7. <https://doi.org/10.1016/j.micromeso.2011.12.009>.

- [20] Y.-X. Tan, F. Wang, and J. Zhang, Design and synthesis of multifunctional metal–organic zeolites, *Chem. Soc. Rev.* 47 (2018) 2130. <https://doi.org/10.1039/c7cs00782e>
- [21] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe, O. M. Yaghi, Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks, *Acc. Chem. Res.* 43 1 (2010) 58–67. <https://doi.org/10.1021/ar900116g>
- [22] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, Ligand-Directed Strategy for Zeolite-Type Metal–Organic Frameworks: Zinc(ii) Imidazolates with Unusual Zeolitic Topologies, *Angew. Chem. Int. Ed.* 45 (2006) 1557 –1559. <https://doi.org/10.1002/anie.200503778>
- [23] D. Peralta, Process for extracting cobalt from a solution comprising, in addition to cobalt, one or more other metal, FR1855348-WO2019243728, 2018.
- [24] P. Zhao, G. I. Lampronti, G. O. Lloyd, M. T. Wharmby, S. Facq, A. K. Cheetham and S. A. T. Redfern, Phase Transitions in Zeolitic Imidazolate Framework 7: The Importance of Framework Flexibility and Guest-Induced Instability, *Chem. Mater.* 26 (2014) 1767–1769. <https://doi.org/10.1021/cm500407f>.
- [25] P. C. Chan, G. D. Hills, G. E. Kissling and A. Nyska, TOXICITY AND CARCINOGENICITY STUDIES OF 4-METHYLIMIDAZOLE IN F344/N RATS AND B6C3F1 MICE, *Arch. Toxicol.* 82 (2008) 45–53. <https://doi.org/10.1007/s00204-007-0222-5>.
- [26] M. Norizadeh Tazehkand, M. Topaktas, M. B. Yilmaz, O. Hajipour and E. Valipour, Delineating the antigenotoxic and anticytotoxic potentials of 4-methylimidazole against ethyl methanesulfonate toxicity in bone marrow cell of swiss albino mice, *Bratisl. Lek. Listy.* 117 (2016) 290–294. https://doi.org/10.4149/bl_2016_057.
- [27] IARC, Some Chemicals Present in Industrial and Consumer Products, Food and Drinking-water <http://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Some-Chemicals-Present-In-Industrial-And-Consumer-Products-Food-And-Drinking-water-2012>.
- [28] F. Mehri, M. Faizi, A. Salimi, E. Seydi and J. Pourahmad, Toxicity of 4-methylimidazole on isolated brain mitochondria: using both in vivo and in vitro methods, *Toxicol. Environ. Chem.* 97 (2015) 663–673. <https://doi.org/10.1080/02772248.2015.1058054>.
- [29] N. C. Burtch, H. Jasuja and K. S. Walton, *Chem. Rev.*, 2014, 114, 10575–10612.
- [30] J. Canivet, A. Fateeva, Y. Guo, B. Coasne, D. Farrusseng, Water adsorption in MOFs: fundamentals and applications, *Chem. Soc. Rev.* 43 (2014) 5594–5617. <https://doi.org/10.1039/C4CS00078A>.

- [31] W.K. Burton, N. Cabrera, F.C. Frank, N.F. Mott, The growth of crystals and the equilibrium structure of their surfaces, *Philos. Trans. R. Soc. Lond. Ser. Math. Phys. Sci.* 243 (1951) 299–358. <https://doi.org/10.1098/rsta.1951.0006>.
- [32] T. Surek, G.M. Pound, J.P. Hirth, Spiral dislocation dynamics in crystal evaporation, *Surf. Sci.* 41 (1974) 77–101. [https://doi.org/10.1016/0039-6028\(74\)90297-0](https://doi.org/10.1016/0039-6028(74)90297-0).
- [33] J.B. Hannon, V.B. Shenoy, K.W. Schwarz, Anomalous Spiral Motion of Steps Near Dislocations on Silicon Surfaces, *Science*. 313 (2006) 1266–1269. <https://doi.org/10.1126/science.1129342>.
- [34] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, C. Chizallet, A.-A. Quoineaud, G.D. Pirngruber, Comparison of the Behavior of Metal–Organic Frameworks and Zeolites for Hydrocarbon Separations, *J. Am. Chem. Soc.* 134 (2012) 8115–8126. <https://doi.org/10.1021/ja211864w>.
- [35] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, G.D. Pirngruber, Separation of C6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A, *Ind. Eng. Chem. Res.* 51 (2012) 4692–4702. <https://doi.org/10.1021/ie202995g>.
- [36] L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Metal–Organic Frameworks for Heterogeneous Basic Catalysis, *Chem. Rev.* 117 (2017) 8129–8176. <https://doi.org/10.1021/acs.chemrev.7b00091>.
- [37] J. Gascon, A. Corma, F. Kapteijn, F.X. Llabrés i Xamena, Metal Organic Framework Catalysis: Quo vadis?, *ACS Catal.* 4 (2014) 361–378. <https://doi.org/10.1021/cs400959k>.
- [38] D. Li, H.-Q. Xu, L. Jiao, H.-L. Jiang, Metal-organic frameworks for catalysis: State of the art, challenges, and opportunities, *EnergyChem.* 1 (2019) 100005. <https://doi.org/10.1016/j.enchem.2019.100005>.
- [39] K.M. Choi, H.M. Jeong, J.H. Park, Y.-B. Zhang, J.K. Kang, O.M. Yaghi, Supercapacitors of Nanocrystalline Metal–Organic Frameworks, *ACS Nano.* 8 (2014) 7451–7457. <https://doi.org/10.1021/nn5027092>.
- [40] Y. Jiao, J. Pei, D. Chen, C. Yan, Y. Hu, Q. Zhang, G. Chen, Mixed-metallic MOF based electrode materials for high performance hybrid supercapacitors, *J. Mater. Chem. A.* 5 (2017) 1094–1102. <https://doi.org/10.1039/C6TA09805C>.
- [41] S. Gao, Y. Sui, F. Wei, J. Qi, Q. Meng, Y. He, Facile synthesis of cuboid Ni-MOF for high-performance supercapacitors, *J. Mater. Sci.* 53 (2018) 6807–6818. <https://doi.org/10.1007/s10853-018-2005-1>.

- [42] D.-G. Wang, Z. Liang, S. Gao, C. Qu, R. Zou, Metal-organic framework-based materials for hybrid supercapacitor application, *Coord. Chem. Rev.* 404 (2020) 213093. <https://doi.org/10.1016/j.ccr.2019.213093>.
- [43] H. N. Abdelhamid, Dehydrogenation of sodium borohydride using cobalt embedded zeolitic imidazolate frameworks, *Journal of Solid State Chemistry* 297 (2021) 122034. <https://doi.org/10.1016/j.jssc.2021.122034>
- [44] H. M. El-Bery, H. N. Abdelhamid, Photocatalytic hydrogen generation via water splitting using ZIF-67 derived $\text{Co}_3\text{O}_4@\text{C}/\text{TiO}_2$, *Journal of Environmental Chemical Engineering* 9 (2021) 105702. <https://doi.org/10.1016/j.jece.2021.105702>
- [45] H. N. Abdelhamid, Zeolitic imidazolate frameworks (ZIF-8, ZIF-67, and ZIF-L) for hydrogen production, *Appl Organomet Chem.* (2021) 35:e6319. <https://doi.org/10.1002/aoc.6319>
- [46] S. Zheng, Q. Li, H. Xue, H. Pang, Q. Xu, A highly alkaline-stable metal oxide@metal-organic framework composite for high-performance electrochemical energy storage, *Natl Sci Rev*, 7, (2020) 305–314. <https://doi.org/10.1093/nsr/nwz137>
- [47] M. D, Q. Li, Y. Zhao, C.-S. Liu, H. Pang, A review of electrochemical energy storage behaviors based on pristine metal-organic frameworks and their composites, *Coordination Chemistry Reviews* 416 (2020) 213341. <https://doi.org/10.1016/j.ccr.2020.213341>
- [48] K.-B. Wang, Q. Xun, Q. Zhang, Recent progress in metal-organic frameworks as active materials for supercapacitors, *EnergyChem* 2, (2020) 100025, <https://doi.org/10.1016/j.enchem.2019.100025>
- [49] Z. Liang, R. Zhao, T. Qiu, R. Zou, Q. Xu, Metal-organic framework-derived materials for electrochemical energy applications, *EnergyChem* 1, (2019) 100001. <https://doi.org/10.1016/j.enchem.2019.100001>
- [50] D. Peralta, Method for producing a lithium-containing metal oxide that can be used as an active material for a positive electrode, FR3082513A1-WO2019243729A1, 2018.
- [51] H. Xia, L. Lu, Y. S. Meng, and G. Ceder, Phase Transitions and High-Voltage Electrochemical Behavior of LiCoO_2 Thin Films Grown by Pulsed Laser Deposition, *J. Electrochem. Soc.* 154 (2007) A337-A342. <https://doi.org/10.1149/1.2509021>.
- [52] B. Shen, P. Zuo, P. Fan, J. Yang, G. Yin, Y. Ma, X. Cheng, C. Du, Y. Gao, Improved electrochemical performance of NaAlO_2 -coated LiCoO_2 for lithium-ion batteries, *J. Solid State Electrochem.* 21 (2017) 1195–1201. <https://doi.org/10.1007/s10008-016-3475-1>.
- [53] M. Yoon, Y. Dong, Y. Yoo, S. Myeong, J. Hwang, J. Kim, S.-H. Choi, J. Sung, S. J. Kang, J. Li, J. Cho, Unveiling Nickel Chemistry in Stabilizing High-Voltage Cobalt-Rich Cathodes for

Lithium-Ion, Batteries. Adv. Funct. Mater. 30 (2020) 1907903.
<https://doi.org/10.1002/adfm.201907903>.