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Review Article

Recent advances in reactor design and control for lithium recovery by means of electrochemical ion pumping

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Abstract

The necessity to tap new natural lithium sources worldwide has pushed in recent years the research in alternative methods for lithium recovery. Among them, electrochemical ion pumping is showing interesting performances, especially when addressing diluted sources. In this review, we summarize the recent advances in materials' and reactors' design for lithium recovery by means of electrochemical ion pumping. We discuss simulations and modeling studies as a tool to study limitations and to provide improved engineering designs. In addition, we provide parameters based on lithium removal and energy consumption for a fair comparison among different ion pumping strategies. Accordingly, we stress the importance to report not only on lithium removal metrics, but also purity and energy-related parameters to provide an optimal assessment of this technology. Finally, remaining challenges and perspectives guidelines are included for future ion-pumping developments.

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Keywords

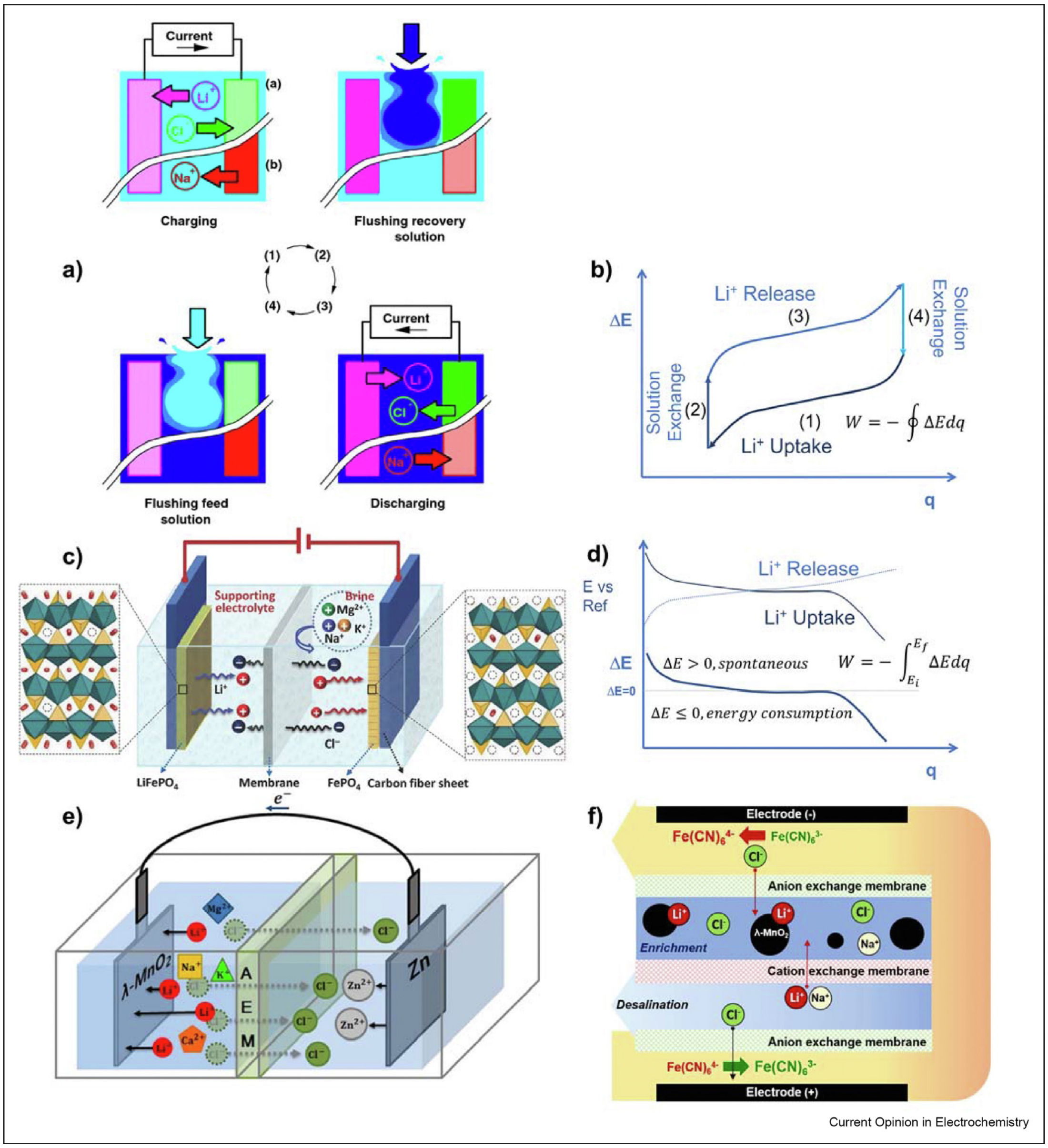
Lithium recovery, Mixing entropy batteries, Electrochemical ion pumping, Metal recovery, Water resources.

Introduction

Lithium-ion batteries have a major role in the world market of batteries, and they are nowadays entering in the automotive and renewable energy market. However, lithium is identified as a critical metal in regard to supply (uneven distribution of the worldwide lithium deposits), demand and import as well as market factors such as production and use [1]. As an example, for battery-grade lithium carbonate (Li_2CO_3) the annual average price of lithium doubled from 2020 to 2021 [2]. To cope with the need of lithium, its extraction from natural aqueous sources would be an eco-friendly and feasible alternative to current ore mining or evaporation processes. For instance, lithium is present in seawater brines at low concentrations (0.19–0.30 mg L^{-1}) in a mixture with other ions such as sodium (Na), magnesium (Mg), or calcium (Ca) [3]. Therefore, there are two main challenges to extract Li^+ from aqueous resources: the low concentration of Li^+ and the selective separation from other dominant ions (e.g., Mg:Li ratio in brines or geothermal waters ranges from 1 to 500). Additionally, purity is a critical requirement to produce Li_2CO_3 suitable for battery application. In this context, selective electrochemical ion pumping (EIP) [4–9] has attracted significant attention as green solution to meet the overwhelming demand for lithium. The main advantages with respect to other methods is the low energy consumption and the high lithium recovery rate, as well as the high Li^+ selectivity obtained without the use of membranes nor the production of chemical waste [10–13].

EIP is based on the transfer of ions from the feed to the recovery (product) solution (see Figure 1) by a selective reaction with the targeted species. The working principle behind a complete cycle is based on four steps (see Figure 1(a),(b)) [14,15]. After dipping the battery-like electrodes in the feed solution, a current, driving the reversible capture of both cations and anions, is applied to the cell. To recover Li^+ ions, the electrolyte is exchanged to a recovery solution and an opposite current is applied to the cell, such that the captured ions are released. It is worth mentioning that ion pumping methods for the recovery of lithium have also been tested coupled to membrane-based architectures (Figure 1(c),(d)), metallic zinc electrode (Figure 1 e), or redox mediated reactions (Figure 1 f) [16–20]. The one evaluated the most is the membrane-based architecture, which uses an anion exchange membrane (AIM) and two Li^+ intercalation electrodes of the same kind but with different states of charge [21–28].

Figure 1



Current Opinion in Electrochemistry

Schematic representation of EIP working principle. (a) Original ion pumping technique. Part (1): salt capturing electrodes. Part (2): ion exchange electrodes. Reproduced with permission [29]. Copyright 2017, IOP Publishing; (b) Cell voltage (ΔE) vs. charge (q) profile in the original EIP device, showing the required energy. Adapted with permission [15]. Copyright 2012, RSC; (c) Membrane-based EIP: Rocking chair mechanism working in a double LFP experiment with AIM. Reproduced under the terms of the CC-BY license [21]. Copyright 2018, The Authors, published by Wiley; (d) Evolution of both electrode potential and cell voltage vs. charge of a rocking chair-based EIP. Adapted with permission [4] Copyright 2021, The Author, published by American Chemical Society; (e) Electrochemical lithium recovery process with the MO-Zn system. Reproduced with permission [18]. Copyright 2018, Wiley; (f) Redox mediated Li^+ removal. Reproduced with permission [20]. Copyright 2021, Elsevier.

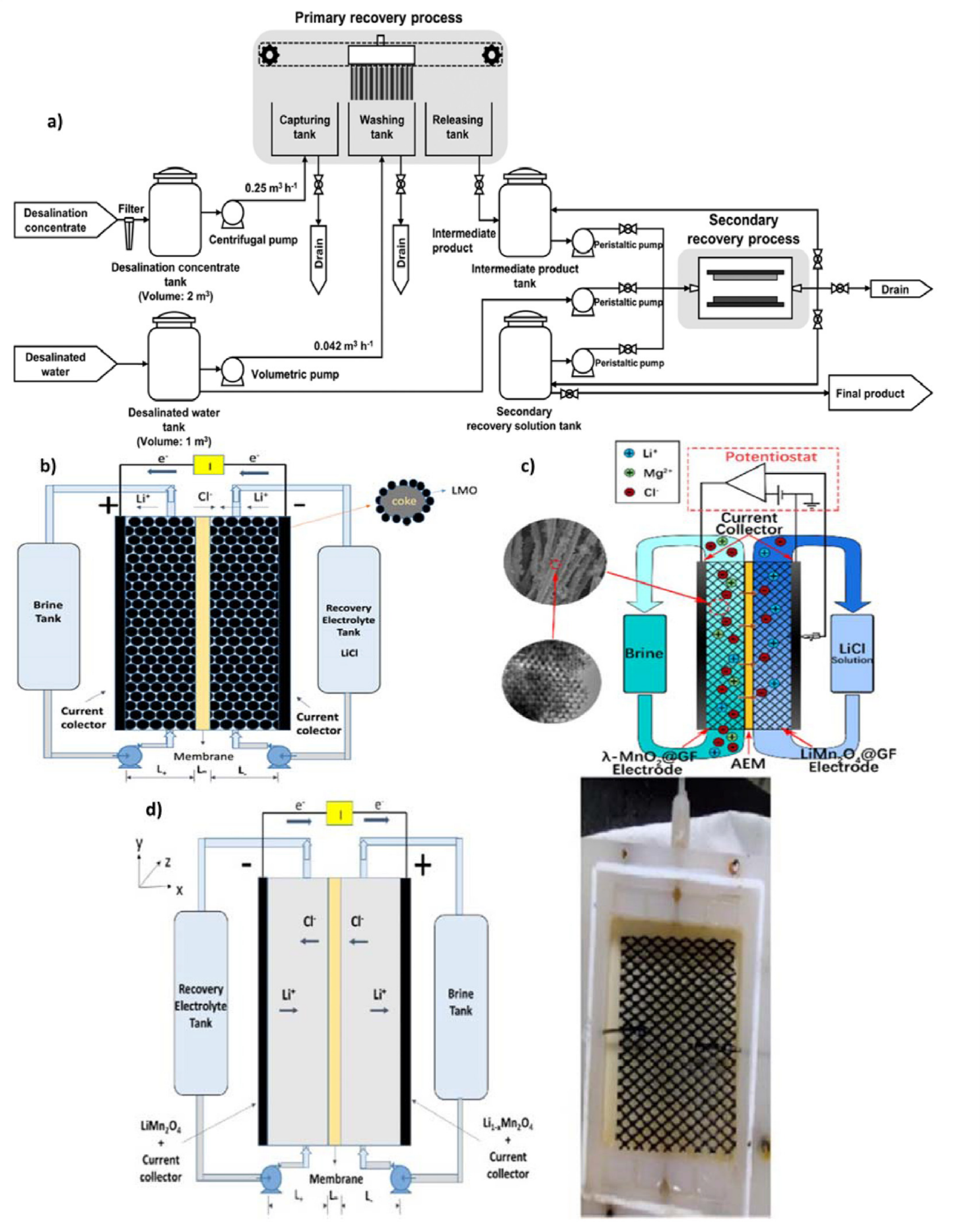
The most studied lithium-selective materials are $LiMn_2O_4$ (LMO) and $LiFePO_4$ (LFP) and their delithiated forms [24–26,30–38]. As counter electrodes, several alternatives, such as conversion electrodes [31,37,39–42], Li^+ exclusion electrodes [29,34,43–46] and electroactive polymers [35,38,47–50], have been proposed. Further detailed information on counter electrodes for electrochemical Li^+ removal have been reported by Trócoli [9]. In this review we will discuss the cell reactor design and the metrics for the evaluation of its performances.

Reactors and their operational modes

Several authors reported that the mass transfer overpotential is one of the main limitations occurring during lithium recovery with EIP [46,49,51]. Furthermore, brine's concentration changes during the operation time.

These phenomena are strongly affected by the cell design, which has a noticeable impact on the production rate and net energy consumption, as consequence. Operating EIP devices under flow conditions promotes convective mass transport and minimizes the diffusion overpotential. However, we have estimated that more than 40% of recent publications studied EIP reactors in static conditions (batch) (Figure 2 (a)) [18,22,27,37,40,41,52]. On the

Figure 2



Current Opinion in Electrochemistry

Schematic representation of different electrochemical cell designs. **a**) Batch. Reproduced with permission [40]. Copyright 2020, RSC; **b**) Packed-bed. Reproduced with permission [23]. Copyright 2020, IOP Publishing; **c**) Flow-through. Reproduced with permission [25]. Copyright 2021, Elsevier; **d**) Flow-by. Reproduced under the terms of the CC-BY license [24]. Copyright 2021, The authors, published by Elsevier.

opposite, there are three main flow reactor configurations discussed in literature: packed-bed, flow through and flow-by reactors (see Figure 2 (b-d)).

The EIP packed-bed reactor is based on static porous electrodes composed by particles of active materials and conductive agent, through which the electrolyte flows (Figure 2 (b)). This design aims to overcome mass transport limitations thanks to increasing the interface between electroactive particles and electrolyte. Since 2018, Romero et al. have been developing and studying 3D EIP packed-bed reactors [23,48,49]. Using simulations for identifying the main limitations of the packed-bad design, they have optimized the operational parameters for this reactor, such as: working/counter electrode mass ratio, flow rate and current density. Their studies, together with the one of Joo et al. [53], emphasize the importance of simulations and modeling for optimizing cell design.

In the flow-through reactors the brine flows through the 3D porous electrodes in the same direction of the current lines (See Figure 2 (c)). As shown by Palagonia et al. [29,45], the electrodes should be designed in order to guarantee a proper trade-off between macropores, to enable reasonable electrolyte flow conditions (flow pressure, hydraulic pressure drop) and mesopores with high-electroactive area to ensure optimal Li^+ insertion. Despite their compact design, one of the disadvantages of these reactors is the restricted choice in suitable current collectors. Only carbon cloth and graphite felt current collectors have been studied in this type of reactors [25,29,45,46].

Flow-by configurations (Figure 2(d)), where the electrolyte circulates between the electrodes, were also proposed EIP [24,26,28,31,34]. Flow-by cells show good performance due to their simple structure and the hydraulic losses are small in comparison to flow-through cells [24,26,31]. Flow-by reactors use a separator that prevents short circuits and acts as flow distributor and turbulence promoter. Complementarily, its thickness must provide mechanical stability versus deformation. Comparing setups, the flow-by configuration is not as compact as the flow-through one due to the need of an electrolyte flow channel. In contrast, ageing of the electrodes in the flow-by setup would not be as fast as in flow-through cells, where it could be important to remove dissolved oxygen. The principal drawback of flow-by EIP cells is the low mass loading of the electrodes, the less compact design, and the worse accessibility of the electrolyte to the electroactive surface, which cause lower recovery rates. Recently, Pérez-Antolin et al. have shown the proof-of-concept of injectable semi-solid electrodes as an alternative solution to regenerate the flow-by cell after reaching its end-of-life [28].

In addition to cell architectures, the lithium recovery performances are determined by the operational parameters. The most relevant are discussed below while in Table 1 we summarized experimental conditions and main results of publications since 2018.

Working under constant current (CC) conditions seems to be the preferred operation mode accounting for ca. 65% of publications. Operating in this mode typically increases the cyclability of the electrodes and decreases the energy consumption, with respect to voltage steps. A novel pulsed electrochemical method, based on the application of CC for short periods of times that is, 1–10 s, showed lower overpotentials and favoured intercalation without damaging the morphology of electrode particles [30]. Current densities in the range of 10–1000 μA cm^{-2} were studied. During the capturing step, a reduction of the current density resulted in better lithium removal performance and higher purity, due to a decrease in the diffusion overpotential [45]. In the case of constant voltage (CV) modes, high extraction capacities (avg. $>$ 15 mg g^{-1}) at cost of a higher energy consumption were shown [17,20,25,52].

The feed composition has a clear impact on the cell performance [21,26,30,34,40,46,48], however also the recovery solution is an important factor, which is often ignored. It is important to define the composition of the electrolyte in which Li^+ is released, because this can influence the energy consumption, the purity of the recovered lithium, and the regeneration of the electrodes as well as their stability. As a result of the moderate capacity of electroactive materials (30–40 $mg_{Li+}\cdot g^{-1}$), cycling is a common strategy to increase the final concentration.

Another aspect to consider is the relative direction of the mass flow with respect to the one of the current. In a flow-through configuration, the mass flow and the current flow are in the same direction, thus allowing the extraction of a significant amount of lithium even in diluted sources, for example, 1 mM LiCl [46]. When the two flows are not in the same direction, mass transport limitation is already significant at circa 10 mM LiCl. In this case, flow rates of 0.1–100 mL min^{-1} were reported, showing an increase in lithium removal capacity with the increase in flow rate. This effect is based on the shrinking of the Nernst layer at the surface of the electrode [29,46,49].

The importance of an accurate evaluation: Metrics

Having highlighted the strong influence of cell architectures on the overall EIP performance [44], it is

Table 1

Summary of the electrochemical EIP methods reported in literature since 2018.

Feed solution ($mg_{Li}.L^{-1}$)	Electrodes	Recovery solution (mM)	Reactor type operational mode	Uptake ($mg_{Li}.g^{-1}$)	$[Li^{+}]_{final}$ (mM)	Energy ($Wh \cdot mol_{Li}$)	References
1260	LMO/PPy	50 mM LiCl	3D packed bed CC	10	70	N.R.	[48]
1322	MnO_2/LMO	100 mM KCl	3D packed bed + AIM CC	28	30	2,8	[23]
1260	LMO/PPy	50 mM LiCl	3D packed bed CC	36	2000	N.R.	[49]
1360	MnO_2/LMO	100 mM KCl	Flow-by + AIM CC	23	9	2,2	[24]
35	LMO	10 mM KCl	Flow-by + CEM AIM CV REDOX $_{Mediated}$	3	27	38,9	[20]
35	$FePO_4$/LFP	N.R.	Flow-by + AIM CC	21	N.R.	3,0	[26]
207	LMO/NiHCF	30 mM KCl	Flow-by + TO-TREC CC	3	23	4,8	[34]
7	LMO/NiHCF	N.R.	Flow through CC	16	N.R.	N.R.	[45]
7	LMO/NiHCF	120 mM KCl	Flow through CC	78	100	6,1	[46]
150	MnO_2/LMO	14 mM LiCl	Flow through CV	13	145	23,4	[25]
670	LMO/Ag	10 mM LiCl	Batch CC	N.A.	25	4,1	[41]
435	LMO/Ag	30 mM KCl	Batch CC	7	190	21,2	[39]
98	LFP/LFP	500 mM NaCl	Flow-through CV 0,2V	8	552	N.R	[21]
1620	NCM/Ag	30 mM LiCl	Batch CC	11	12	2,8	[37]
1449	LMO/Zn	0,1 M $CaCl_2$	Batch CC	N.A.	42	6,3	[18]
26	$FePO_4$/LFP	200 mg_{Na+}/L	Batch CV	17	7	N.R.	[22]
26	LFP/KNHCF	200 mg_{Na+}/L	Batch CV	15	N.R.	60,8	[52]
162	LSNMC/Bi	10 mM LiCl	Flow-by CC	13	11	4,6	[31]
694	LMO/BiOCl-PPy	10 mM HNO_3	Batch short-circuit + CV	2	N.R.	1,0	[42]
694	MnO_2/NiHCF	N.R.	Flow-by CC	16.2‡	N.R.	15.6	[28]

N.R. Not Reported. * Some parameters were estimated from the info provided in the reference. ‡ Amount of lithium removed per mass of NiHCF.

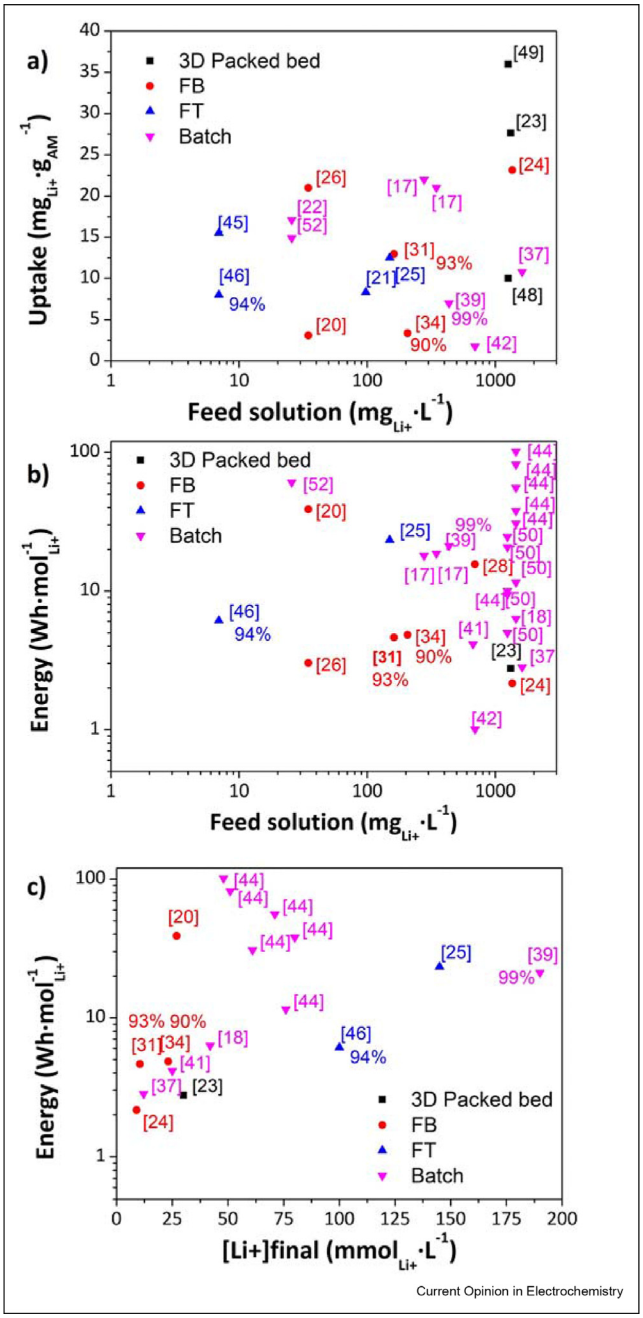
important to provide an adequate evaluation of the lithium recovery performance.

Cell Characteristics: Different solutions (i.e., feed and recovery) are flowing through the reactor during the lithium recovery, therefore special attention must be given to the cell design in order to minimize both dead volume of the cell and possible back-mixing effects [29]. Furthermore, at a given current density, the cell voltage loss is determined by the contact resistance between particles, the ohmic drop of the electrolyte, and the concentration overpotential for lithium capturing. Accordingly, detailed cell characterization must be provided (i.e., resistance, mass loadings, electrodes' mass ratio, electrodes distances). Moreover, current density, as well as current rate, have a strong influence on the performances [29,45].

Li^{+} removal metrics: In literature, there is the tendency to maximize one metric at the expense of the others. Whereas the maximization of the lithium removal capacity ($mg_{Li} \cdot g^{-1}$) is an objective in almost every new study, energy consumption and purity of the recovered lithium are often ignored. The risk of establishing the lithium removal capacity as the major selection criterion is that such parameter is a metric that depends not only on the electrodes but also on the feed salinity and composition. Nevertheless, this metric would be insightful if comparing novel materials or different electrodes configuration at given standard composition of the feed solution.

Lithium removal is also strongly affected by side reactions, such as co-ions intercalation and oxygen reduction. Side reactions imply that not all the current

Figure 3



Figures of merit of different configurations. a) Lithium uptake vs. concentration of the feed solution; Energy consumption b) vs. concentration of the feed solution and c) vs. final Li concentration of the recovery solution. Available purity values are reported as percentage (%) close to the reference.

flowing through the cell is invested in Li^+ removal, resulting in a Coulombic efficiency lower than unity. Recently, Wang et al. proposed strategies for dealing with the loss of performance in LFP-based electrodes due to the presence of co-ions competition effects and dissolved oxygen in the electrolyte [26].

Energy-related metrics: Pump energy consumption is not considered in the energy-related calculations; however, it is a key parameter in flow reactors. It has been discussed that the energy consumption of the pumping is not negligible [29,45,46] representing the largest energy required by the process in feed solutions with low lithium concentration (ca. 2 $kWh \cdot mol^{-1}$ in diluted brines 1 mM LiCl) [46]. Therefore, it is advised to always include an estimation of the pumping and/or stirring energy when working on a new reactor design. Furthermore, energy is frequently reported for a single cycle and thus its variation upon cycling is often not considered. Results reporting the average gravimetric energy consumption ($Wh \cdot mol_{Li^+}^{-1}$ or $Wh \cdot g_{salt}^{-1}$) are more practical.

Recovery solution metrics: The final product of EIP for Li removal is most often a recovery solution, which means that lithium concentration of the recovery and purity-based performance measures are more directly relevant to practical applications. Figure 3 shows the figures of merits gathering main results of the latest publications. Purity was only reported in four publications.

Finally, in literature often the experimental conditions are not specified with a level of details, which permits a proper evaluation of the metrics and reproducibility of the experiments. Unfortunately, this leads to a lack of reliable data and to a misinterpretation of the results. Here, we propose a nominal standard separation of removing ≥10 mM from the feed (e.g., natural, or simulated brines, geothermal or seawater, avoiding the use of equimolar multi-ions solutions), $\Delta[Li^+]_{final,\ recovery}$ ≥15–20 mM and a purity ≥85% referred to the recovery (product) solution. We highly encourage to state the recovery solution used. We refer the reader to the review of Battistel et al. for further details on how to evaluate accurately lithium recovery parameters [8].

Conclusions and perspectives

EIP reactors for lithium recovery are in their initial developing stage, which gives them high flexibility for future advancements. Different strategies require different cell designs. On one hand, cell architectures using membranes imply higher investment and maintenance costs, due to scaling/fouling effects. On the other hand, in packed-bed and flow-through designs, particles clogging, and large pressure losses could be cause increasing maintenance and operational costs. A trade-off between Li^+ uptake performance and practical feasibility of a large industrial-scale production is needed. Simulation would provide a proper evaluation of the EIP reactors' viability in short-medium term scenarios.

The importance of the Li release step—regeneration of the electrodes is often overlooked. Studies to identify key-aspects of the release step, to produce Li^+ rich solution with high purity minimizing the energy consumption, are required. Side reactions and their effect on the Li^+ removal performance remain also unknown. Flowing conditions might have a relevant impact during prolonged operation. We conclude that lithium removal performances need to be clearly defined and rationally discussed. Also, studies on the cycle life of the EIP reactors are scarce and in future they will be necessary to evaluate their industrial feasibility.

In this short-review, our proposal for an objective evaluation of EIP reactors is based on four metrics: average gravimetric energy consumption, Li removal capacity, final concentration, and purity of the recovery solution. Each of them should be obtained starting from a well-defined source solution (natural brines, geothermal, sea water) and current density. This protocol will help the comparisons between different reactors and their further development.

Declaration of competing interest

The authors declare the following financial interests/personal relationships that may be considered as potential competing interests. Cleis Santos reports financial support was provided by European Union.

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