



Electrochemical extraction of lithium by ion insertion from natural brine using a flow-by reactor: Possibilities and limitations

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ABSTRACT

Experimental results on the sustainable extraction of lithium chloride from natural brine (Salar de Hombre Muerto, Argentina) using a flow-by electrochemical reactor at constant applied current are presented. The maximum applied current, the current efficiency and the lithium recovery per mass of lithium ion insertion material are evaluated and the flow-by vs. flow-through configurations are compared.

Lithium extraction by ion pumping in entropic electrochemical cells was introduced by La Mantia and co-workers [1]. Following that, several groups have reported the extraction of lithium from natural and artificial brines, sea water and geothermal fluids using electrochemical methods [1-17], a topic that has recently been reviewed [18-22].

Lithium extraction by ion intercalation in battery-type materials can be accomplished either by selective ion capture [1] or by ion exchange [6]. The selective ion capture method uses a Li⁺ ion intercalation electrode coupled to a chloride-selective electrode, such as Ag/AgCl, for the extraction of LiCl from aqueous solution in an undivided cell [1]. The cation exchange mode employs two identical lithium intercalation electrodes in different states of charge (different lithium content), one in contact with natural brine and the other in the recovery electrolyte; the electrodes are separated by an anion exchange membrane [10,11,14,16]. Alternatively, Trocoli and co-workers reported the selective capture of Na⁺ or K⁺ by a K[NiFe(CN)₆] anode and Li⁺ capture by a lithium-deficient LiMn₂O₄ cathode [8,23].

A lithium-selective intercalation battery cathode material, LiMn₂O₄ (LMO), has been employed in the extraction of lithium in combination with different auxiliary electrodes: platinum [2,3,24], carbon [25,26], zinc [27], Ag [28], polypyrrole [29], hydrogen electrode (PtH₂) [30], and polyaniline [31].

Electrochemical reactors for the extraction of lithium have been described in recent years, using both flow-through [32-36] and flow-by [37,38] configurations. We have recently published a report on a flow-through cation-exchange electrochemical reactor consisting of two

Li_{1-x}Mn₂O₄ (0 ≤ x ≤ 1) /LiMn₂O₄ electrodes for the capture and release, respectively, of lithium from brine into a recovery electrolyte [35]. Unlike the configuration reported by Palagonia et al. [34], the flow of electrolyte through the Li⁺ exchanger was parallel to the electric field (current collectors).

In the present communication we report experimental results on lithium chloride extraction from natural brine using a flow-by electrochemical reactor based on the intercalation of lithium ions in Li_{1-x}Mn₂O₄ and de-intercalation in LiMn₂O₄ electrodes. These electrodes have different states of charge (different lithium ion content (0 ≤ x ≤ 1) in the tetrahedral sites of the cubic spinel lattice).

The electrodes consist of thin porous layers of LiMn₂O₄ deposited on a titanium mesh from a slurry of LiMn₂O₄, Vulcan carbon XC.72 and PVDF binder (80:10:10).

The flow-by reactor comprised two compartments, one containing natural brine and the other 0.1 M KCl recovery electrolyte, separated by an anion-selective membrane, as depicted in Scheme 1. The lithium-deficient Li_{1-x}Mn₂O₄ electrode was the cathode and the fully lithiated LiMn₂O₄ electrode was the anode.

LiMn₂O₄ was de-lithiated with 0.12 M (NH₄)₂S₂O₈ by flowing the solution for 48 h through the cathode material, resulting in 55% de-lithiation from the lithium concentration in the leached electrolyte. The degree of de-lithiation was measured by ICP analysis and followed qualitatively by the shift in the LiMn₂O₄ XRD reflections, as shown in the inset of Fig. 2.

A constant current was applied to the cell, which resulted in the

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insertion of lithium ions at the cathode and their release at the anode, while the transport of chloride anions takes place from the brine compartment, through the anion-selective membrane, to the dilute KCl recovery electrolyte, completing the charge circulation. Both electrolytes, natural brine and the recovery solution, were circulated through their respective compartments in a flow-batch mode [39]. Re-circulation of the electrolytes resulted in the depletion of LiCl concentration in the brine while a concentration build-up occurred in the recovery electrolyte.

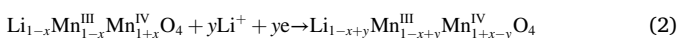
The equilibrium potential difference of the cell depends on both the state of charge difference between the LiMn_2O_4 electrodes and the difference in LiCl activity between the brine and the recovery electrolyte [15]:

$$\Delta E = \frac{RT}{F} \ln\left(\frac{1-x}{x}\right) + f(x) + \frac{RT}{F} \ln\left(\frac{a_{\text{LiCl,brine}}}{a_{\text{LiCl,recovery}}}\right) \quad (1)$$

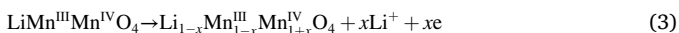
$f(x)$ describes the interactions in the solid that result in two plateaus in the potential-charge curve.

As the electrolysis proceeds, with uptake of lithium from the brine and its release into the recovery electrolyte, the electrode potential of the cathode decreases while the anode potential increases, so that the overall cell voltage is their difference, ΔE [18].

As in previous publications, we consider a concerted electron-ion transfer process [17,35,36,40]. The electrode reactions, which involve the simultaneous transfer of lithium ions and electrons at the LiMn_2O_4 /electrolyte interfaces, are:



at the negative electrode (cathode) with ($0 \leq x \leq 1$, and $y \leq x$), and:



at the positive electrode (anode).

The maximum insertion of lithium ions from the brine and maximum release into the recovery electrolyte takes place for $y = x$, with the overall reaction:



Fig. 1 depicts the evolution over time of the cell potential difference ΔE when a constant current of 20 mA was applied to the flow reactor while circulating 250 mL of natural brine in the cathodic half-reactor and 250 mL of 0.1 M KCl recovery electrolyte in the anodic compartment at a flow rate of 55 mL min^{-1} . The open circuit potential of the reactor was 0.310 V and the initial potential drop corresponds to an uncompensated resistance of 9 Ω in the full reactor.

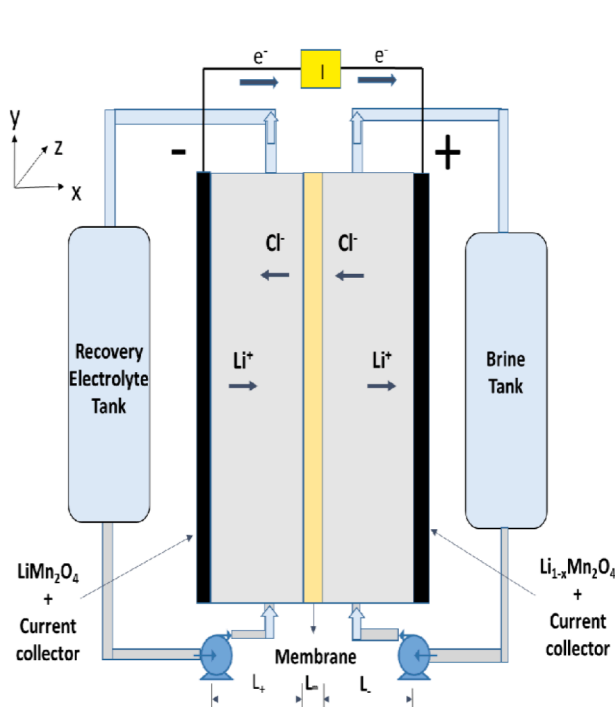
Natural brine from the Hombre Muerto salt flats, (GPS: 25°25'9"S, 67°4'0"W, Minera Santa Rita, Salta, Argentina) was employed. The brine composition was: Na^+ 114.000 ppm (4.96 M); K^+ 15.700 ppm (0.40 M); Mg^{2+} 3100 ppm (0.13 M); Li^+ 1360 ppm (0.19 M); boron 1520 ppm; calcium 630 ppm (15 mM); chloride 182.000 ppm (5.1 M); and sulphate 11.370 ppm (118 mM).

During operation of the flow-by reactor at room temperature (25 °C), the lithium chloride concentration in the recovery electrolyte was followed with a potentiometric lithium ion-selective electrode (Mettler-Toledo DX207-Li). The potentiometric response to the LiCl concentration build-up is depicted in Fig. 1 and the evolution of LiCl concentration over time was obtained using the potentiometric response and the calibration curve of the Li^+ ion-selective electrode vs. LiCl activity shown in Fig. 2.

For a constant current (I) applied to the cell, the mass of lithium extracted from brine and released into the recovery electrolyte should increase linearly with time (t): $m = Mf\frac{It}{F}$ where f is the current efficiency factor, F the Faraday constant and M the molar mass. The linear response of the mass of lithium extracted from natural brine into the recovery electrolyte as a function of the charge consumed in the process is shown in Fig. 3, revealing a slope of 0.22 mg of Li per mAh.

From the experimental slope, the theoretical 148 mAh/g LiMn_2O_4 and the 38.2 mg Li/g LiMn_2O_4 , we find that the process has a current efficiency of 85%.

In this experiment the total mass of lithium extracted was 16.2 mg at 20 mA – this was limited by the mass of the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ cathode (0.70 g) and not by the amount of lithium available in the 250 mL of natural



Scheme 1. Reactor scheme showing the electrolyte flow direction, electron current and ion fluxes. Right: Photo of a half compartment of the reactor.

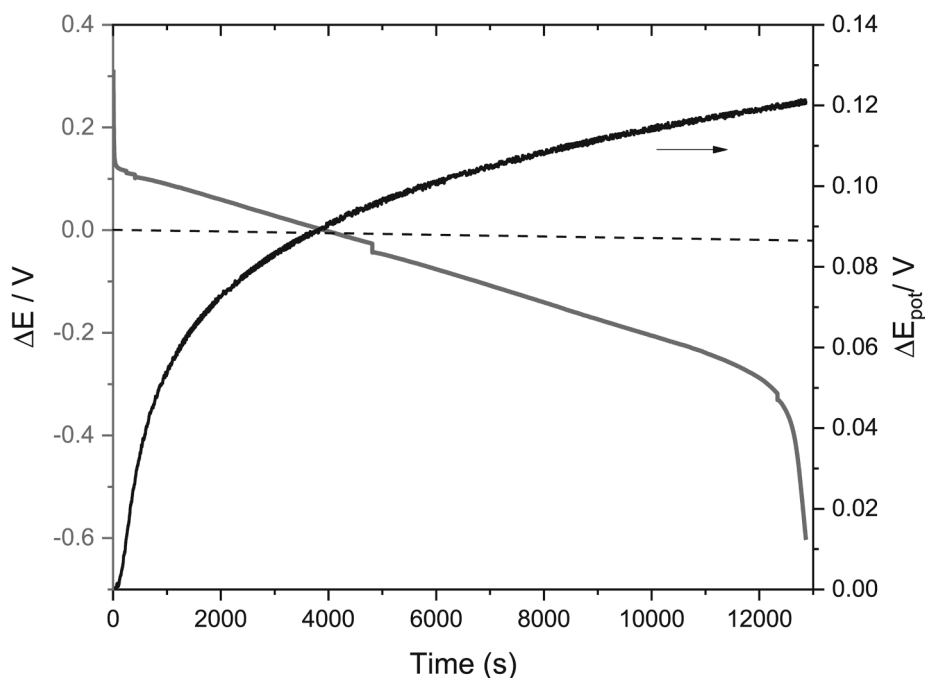


Fig. 1. Time evolution of the potential difference between lithium intercalation electrodes at constant current of 20 mA and the simultaneous potentiometric response of lithium ion-selective electrode (ΔE_{pot}). Mass of LiMn_2O_4 0.78 g and mass of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($x = 0.45$) 0.84 g. The dashed line indicates $\Delta E = 0$.

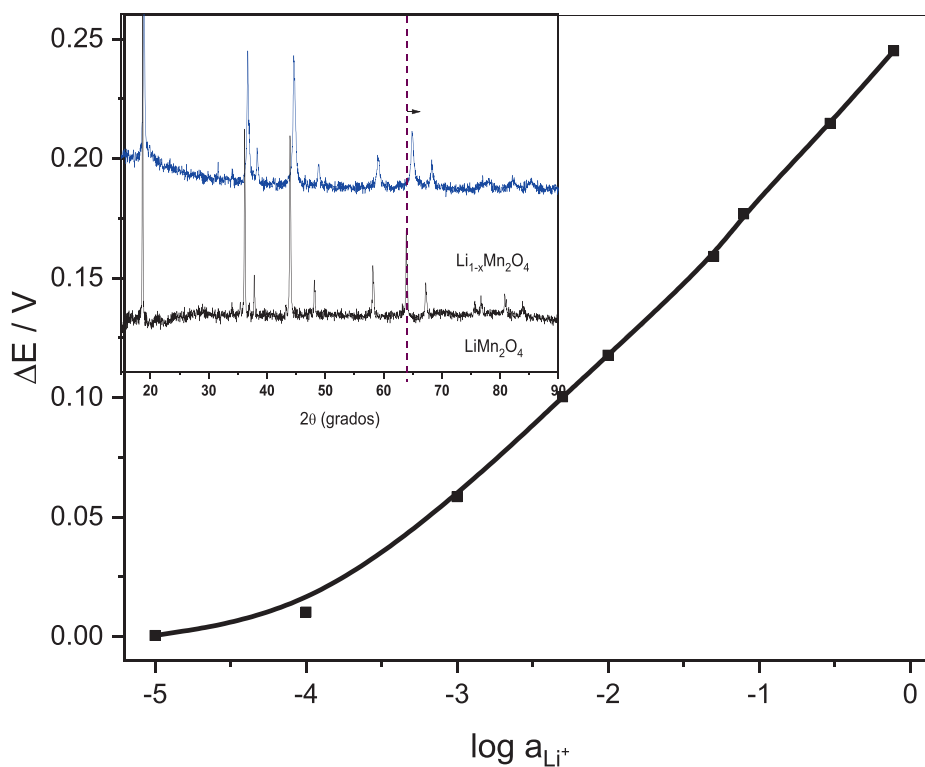


Fig. 2. Lithium potentiometric calibration curve with a potentiometric lithium ion selective electrode (Mettler-Toledo DX207-Li) and an Ag/AgCl; 3 M KCl reference electrode. Inset: XRD pattern for $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ with $x = 1$ and $x = 0.45$.

brine (0.33 g). The maximum extraction capacity of the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ cathode (at $x = 1$) is 38.2 mg per gram of LiMn_2O_4 , and therefore the mass of LiMn_2O_4 in the electrode is critical for large-scale extraction. The flow-by configuration with axial electrolyte flow and a thin electroactive film with a small mass of LiMn_2O_4 (as employed in the present study) can extract less LiCl than a flow-through configuration with a larger mass of active material and larger mass to volume ratio [35].

The time needed to accomplish this extraction, 3.57 h, was determined by the total applied current, $I = 20$ mA, since the lithium charge is given by $q = It$. However, if one wishes to avoid any side reactions, the maximum total applied current is also limited by the electroactive surface area of the intercalation LiMn_2O_4 , since the local current density at the particles/electrolyte interface is determined by the Butler-Volmer equation:

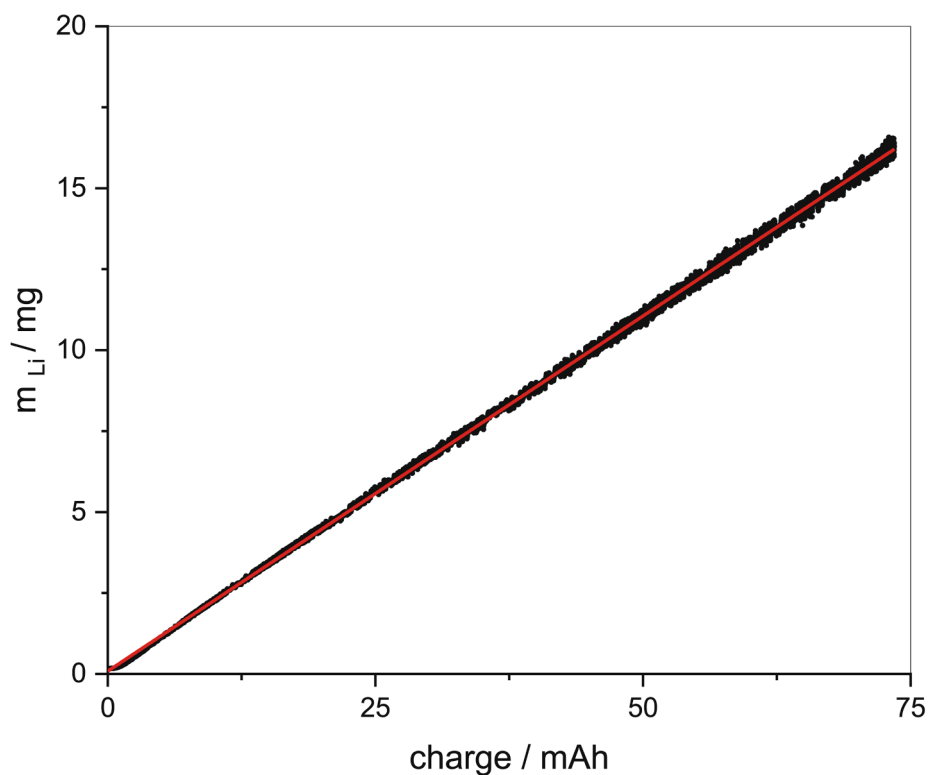


Fig. 3. Mass of lithium extracted from potentiometric measurement vs. charge circulated in the experiment described in Fig. 1.

$$i_{LOC} = Fk_0^0(1-\theta)^{\alpha_a}(\theta)^{\alpha_c} \left(\frac{c_{Li}}{c_{Li,ref}} \right)^{\alpha_a} \left[e^{\left(\frac{\alpha_c F \eta}{RT} \right)} - e^{\left(\frac{\alpha_a F \eta}{RT} \right)} \right] \quad (5)$$

with $c_s/c_{s,max} = \theta$, $k_0^0 = k_c^{\alpha_a} k_a^{\alpha_c} c_{s,max}^{(\alpha_a + \alpha_c)}$, the reference lithium concentration $c_{Li,ref} = 1 \text{ mol m}^{-3}$, $\alpha_a = \alpha_c = 0.5$, c_s is the lithium particle surface

concentration and $c_{s,max} = 25 \text{ M}$ is the maximum lithium concentration in the LiMn_2O_4 crystal.

It should be noted that the local current density (i_{LOC}) depends on the Li^+ concentration in the electrolytes, the state of charge of the intercalation electrode and the electrode potential [41]. Typical values of i_{LOC} are a few microamperes per square centimeter [41], therefore the total

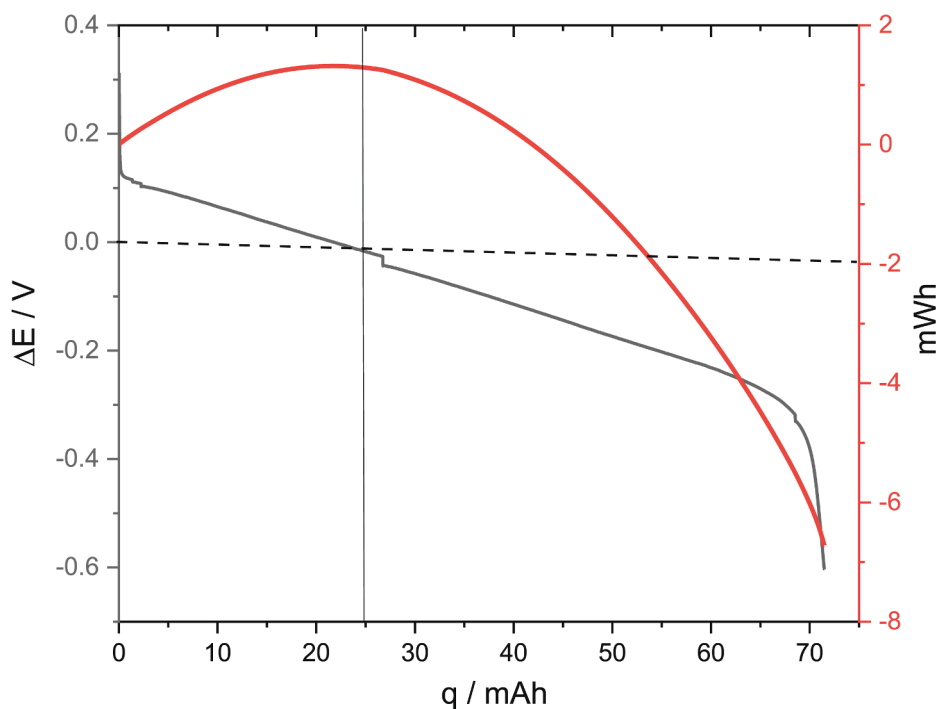


Fig. 4. Experimental energy balance for a double LMO ion exchange flow-by experiment, with 0.78 g LiMn_2O_4 anode and 0.70 g of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($x = 0.45$) cathode, at 20 mA.

current that can be applied cannot exceed $I \leq i_{\text{LOC}} \times S_f \times V_{\text{LMO}}$, where S_f is the specific electroactive area of the particles per unit volume (cm^{-1}) and V_{LMO} (cm^3) is the volume of the intercalation active material in the surface film. An important parameter in the reactor design is the specific surface area per volume; for spherical particles this is $S_f = 3\varepsilon_s/r_p$, where ε_s is the solid volume fraction and r_p is the particle radius [42]. Therefore, the total electrochemically active area should be $S_f \times V_{\text{LMO}} \geq 2 \times 10^4 \text{ cm}^2$ to sustain a total applied current of 20 mA. In the present case this is satisfied with $r_p = 2.2 \times 10^{-5} \text{ cm}$ and $\varepsilon_s = 0.75$, so that $S_f = 10^5 \text{ cm}^{-1}$ and the electrode film volume is 0.17 cm^3 with $V = m_{\text{LMO}}/\rho_{\text{LMO}}$, $m_{\text{LMO}} = 0.70 \text{ g}$ and $\rho_{\text{LMO}} = 4.02 \text{ g cm}^{-3}$.

Another aspect of interest is the specific energy consumed during LiCl extraction and recovery (Wh mol^{-1}), which can be calculated from the following equation (see Fig. 4) [35]:

$$W = - \left[\int_{0.2}^{E=0} \Delta E \cdot dq + \int_{E=0}^{-0.4} \Delta E \cdot dq \right] \quad (6)$$

The first term is the energy obtained from the spontaneous process at $\Delta E_{\text{R}} > 0$, which increases the larger the difference between the states of charge of the anode and the cathode (ΔSOC), but decreases with the ohmic drop in the reactor. The second term in eqn. (6) represents the energy supplied to the reactor in order to continue the extraction of lithium at $\Delta E < 0$.

The total cell voltage ΔE under operation at a given applied current, and thus the energy consumed, is determined by the overpotentials at each electrode and the ohmic drop in the electrolyte (9Ω from the initial ohmic drop in the present experiment):

$$\eta = \Delta\phi_{s/1} - \Delta\phi_{s,\text{film}} - E_{\text{eq}} + \frac{RT}{F} \log \frac{c_{\text{Cl,m}}}{c_{\text{Cl}}} - \frac{RT}{F} \ln \frac{c_{\text{Li}}(t)}{c_{\text{Li}}(t=0)} \quad (7)$$

where $\Delta\phi_{s/1}$ is the potential difference at the LMO/electrolyte interface, $\Delta\phi_{s,\text{film}}$ is the potential drop caused by the electrode material film resistance, $\Delta\phi_{\text{Donnan}} = \frac{RT}{F} \log \frac{c_{\text{Cl,m}}}{c_{\text{Cl}}}$ is the Donnan membrane potential (with $c_{\text{Cl,m}}$ the concentration of fixed charges in the membrane). The last term in Eq. (7) corrects the equilibrium potential (E_{eq}) for the change in concentration due to LiCl concentration decrease (in brine) and increase (in recovery solution) as the extraction/recovery proceeds.

Integration of the experimental ΔE vs. charge curve in Fig. 1 at 20 mA yields a total energy difference of 5 mW for the extraction of 16.2 mg of lithium (Fig. 4), so the specific energy consumed is 2.16 Wh/mole Li, in good agreement with previous data obtained using the same method and material [35,38]. Note that the specific energy consumed depends on the initial difference in the state of charge, ΔSOC , between the electrodes, and thus on the degree of delithiation of the cathode.

An important factor to consider in reactor performance is the flow rate of the electrolytes in the reactor, since the diffusion concentration gradients at the electrodes should be minimized by fluid circulation [40]. Axial flow rates above 1 mL/minute break the diffusion concentration gradients in the direction of the electric field [35].

In a flow-by reactor, even with a high electrode surface to electrolyte volume ratio [37] the mass of the intercalation electrode material per unit surface of current collector is very small compared to the mass of the same material in a flow-through reactor [32-36,40] and consequently the amount of lithium extracted is limited by the small amount of intercalation material since only 38.6 mg can be intercalated/deintercalated per gram of LiMn_2O_4 . Therefore, a flow-by reactor is not likely to be a suitable configuration for the extraction of lithium on a large scale. The mass of LiMn_2O_4 electrode material can be maximized in a flow-through configuration with the flow direction parallel [32-34] or perpendicular to the electric field [35,36]. Each gram of lithium to be extracted from brine requires 26.1 g of LiMn_2O_4 in the cathode, and the time required to extract 1 g of Li depends on the total current applied to the reactor, since the charge circulated, $q = I \times t$, and 148 mAh of charge is needed to recover 7 g of lithium if 100% efficiency is achieved. However, the local current density at the LiMn_2O_4 crystal is of the order

of microamperes per square centimeter, and therefore the electroactive surface of the electrodes needs to be increased significantly, which is easier with a flow-through reactor rather than with a thin LMO deposit in a flow-by configuration.

In conclusion, in spite of the benefits of LMO electrodes, namely high selectivity for lithium ions, low energy cost, the environmental benefits of electrochemical extraction, and faster extraction compared to evaporation methods, the flow-by configuration with a small mass of intercalation material is not suited for large-scale lithium extraction from brine, while a flow-through configuration lends itself to industrial scale-up with moderate flow rates.

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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