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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Manuscript number: NCOMMS-24-16096-T

Title : Electro-driven direct lithium extraction from geothermal brines to generate battery-grade lithium hydroxide

Recommendation: major revisions

Summary

The paper presents results of an electrochemical process aiming the selective lithium extraction from a synthetic geothermal brine. Using the results obtained, the authors also carried out a technical and economic study. The present work is highly topical and provides valuable data and findings. However, the structure of the manuscript is still in need of considerable improvement and is therefore not yet ready for publication. I therefore suggest a structural revision of the manuscript.

General Comments

- 1) For better comprehensibility, I recommend structuring the manuscript according to the introduction, methods, results, and discussion sections.
- 2) The introduction should be shortened.
- 3) The technical-economic assessment of the extraction process should be separated from the series of experiments. A tabular overview of the relevant parameters would add further valuable information to the manuscript.
- 4) The discussion section is short compared to the other chapters and does not meet scientific standards. The authors emphasize the positive results of their work. However, critical appraisal (optimization potential of the method, open questions / research subjects, etc.) is completely missing.
- 5) The authors speak very generally of geothermal fluids without mentioning a regional reference or geological context and generalize their chemical properties. I recommend that the authors refer precisely to the Salton Sea geothermal site, whose brines are the subject of the research.

Specific comments

Line 27: „geothermal brine“... should be limited to Salton Sea geothermal brine

Line 30: LCOL... here and generally in the manuscript abbreviations should be introduced before they are used.

Line 92: Reference is missing.

Line 95: The subheading is very long and should be shortened. This also applies to other subheadings in the manuscript. Please check.

Line 100: ...“capturing only lithium and leaving” ... It should be added that this is a theoretical assumption. Various on-site tests on lithium extraction from geothermal brines worldwide show that the very complex chemical fluid composition shows significant differences in practice compared to laboratory tests with synthetic waters.

Line 116: ...geothermal brine ... has a pH around 5.5... This statement is not generally valid. Please specify which waters are involved. Salton Sea?

Line 193: ...brine A and e,... please check. Current wording is confusing for the reader.

Line 215: Please specify what "little magnesium" means.

Fig. 3: Inscription on the legend (right) missing.

Line 224-246: Not a generally valid statement! Please narrow down to a specific geothermal site.

Reference is also missing.

Line 257: Headline too long.

Line 260: Abbreviation not introduced.

Line 357: "ultrahigh" ...please define.

Line 379: "using harsh acid". This statement is not true. There are sorbents (LDH) that can be regenerated with water.

Line 373-385: The chemical composition of the geothermal brines has a significant influence on the extent of lithium extraction and the purity of the products. The authors have so far examined synthetic waters in their study. Redox-sensitive parameters have not yet been taken into account. The same applies to the fact that heavy metals and naturally occurring radionuclides are also dissolved in the Salton Sea geothermal brine (e.g. Zukin et al. 1987). Due to the far more complex chemical composition of real geothermal brines (compared to synthetic brines), the potential impact of foreign ions on the present results should be discussed at more detail.

Line 387: "...using electricity as the input"... The present work implies that the required electricity is supplied by existing geothermal plants. Otherwise, this would have an enormous impact on the economic viability of the process presented.

Reviewer #2 (Remarks to the Author):

In the present work, titled: Electro-driven direct lithium extraction from geothermal brines to generate battery-grade lithium hydroxide, the authors propose an experimental strategy that coupled two technologies: Li intercalation and electrodialysis with bipolar membranes. The objective is to produce battery-grade lithium hydroxide from Geothermal Brine as a feed solution.

In my opinion, for a better understanding of the work it could be interesting to change the structure of the manuscript and describe the Materials and Methods before the discussion of the results. In addition, the results section has a bit mixed-up the descriptions that correspond to Materials and Methods and results. This makes it difficult to connect the ideas.

Concerning the content of the presented work I have some suggestions:

1. I do not agree with the use of the term unconventional to describe a Geothermal Brine as a source of lithium. This does not correspond to an unknown and unexploited source, several works are focusing on this type of lithium source and it is being exploited on an industrial level (e.g. USA). Thus, a geothermal brine represents a source of lithium with a lower lithium content than continental brines (salars), but it is not an unconventional source.

2. I suggest to reinforce the references in the Introduction section.

3. At line 86 in which authors list the elements that are present in the brine, it would be more appropriate to write ions: Li^+ instead of Li, Na^+ instead of Na...
4. I suggest increasing the size of the ions in Figure 1 for a better understanding.
5. Authors confirmed by DRX the lithiation or delithiation of the host material (line 133), I suggest the incorporation of a cyclic voltammetry or an XPS study for a better characterization.
6. Authors discuss the performance of lithium extraction from graphs presented in Figure 2. All represented values are percentages, instead of absolute values. For example, it is important to know how much lithium is being captured from the feed solution and which is the ratio between this quantity and the lithium content in the recovery solution. A percentage of 90% for lithium in the solution of release implies that other ions are present in a minor concentration, but it does not imply that the majority of the initial lithium was captured and then released. In addition, the authors report a value of 0.18 for lithium extraction efficiency (Table S5), however, the amount of lithium in moles in both solutions is not reported.
7. In Figure 3 authors show TEM images and an elemental mapping for Fe, Na, and Li. This is complemented by table S2 which lists the atomic composition. In that table, lithium (the target element) is not present. The brightness obtained for Figure 3B is not conclusive as Na also is detected by EELS.
8. In line 292, the authors conclude that from the results obtained from the simulation, the selectivity of the host material for lithium over other cations is confirmed. It might be interesting to compare or match these calculations with empirical data obtained from the system studied.
9. In line 384 authors mentioned that membrane-based technologies struggle to achieve high lithium selectivity over monovalent cations. That technology requires steps of lithium concentration and separation of other cations by precipitation (for example), the selectivity is not reached by a cation exchange membrane. The recovery of lithium salts implies the conjunction of more than one step, as in the presented work where first lithium is concentrated and converted to LiCl , then the product is purified and finally it is converted to LiOH .
10. The authors make a good techno-economic assessment and highlight the fact that their technology does not involve the use of additional reagents and that it could be coupled with renewable energy sources, which is a great point to highlight. For completeness, it would be interesting to calculate the deionized water needed per liter of treated brine. The cell is washed with water three times after lithium capture and before lithium release (data taken from their previous work, Ref.7).

Response to Reviewers' Comments and List of Changes Made in the Manuscript

Electro-driven direct lithium extraction from geothermal brines to generate battery-grade lithium hydroxide

Reviewer 1

General: We are grateful to the reviewer for the comments and interest in the paper.

Our specific responses to the reviewer's comments are listed below.

1. **Reviewer:** The paper presents results of an electrochemical process aiming the selective lithium extraction from a synthetic geothermal brine. Using the results obtained, the authors also carried out a technical and economic study. The present work is highly topical and provides valuable data and findings. However, the structure of the manuscript is still in need of considerable improvement and is therefore not yet ready for publication. I therefore suggest a structural revision of the manuscript.

Reply: We thank the reviewer for the encouraging comments and suggestions. We address the reviewer's comments below.

2. **Reviewer:** General Comments 1) For better comprehensibility, I recommend structuring the manuscript according to the introduction, methods, results, and discussion sections.

Reply: We thank the reviewer for the suggestions, and we move the Methods section after Introduction section in the revised manuscript.

3. **Reviewer:** 2) The introduction should be shortened.

Reply: We appreciate the reviewer's suggestion on shortening the introduction.

Change in text: We shortened the second paragraph on Page 3 of the revised manuscript to read:

"Considering energy consumption and extraction cost, several alternative aqueous sources containing relatively high lithium concentration are considered potential lithium sources, including geothermal brine, oil and gas produced water, and reject brines from desalination^{1,2}. Geothermal brines are a particularly promising candidate for lithium sources,

especially the Salton Sea in California. Minalable lithium resource in the Salton Sea area is estimated at 600,000 tons annually, far exceeding U.S. annual lithium consumption³. There are also detected lithium-rich geothermal brine in deep tectonic sedimentary basins in Germany and France and in volcano-sedimentary environment in Italy⁴ and also Qinghai-Tibet Plateau in China⁵. There is an urgent need to develop robust, economic, environment-friendly technologies to extract lithium from geothermal brines.”

Change in text: We shortened the first paragraph on Page 4 of the revised manuscript to read:

“Inspired by Li-ion batteries, Li intercalation materials like lithium iron phosphate (LiFePO_4) have been demonstrated as promising electrodes for selective lithium extraction from high salinity brines^{6,7} due to their unique lattice structure^{8,9}. However, several key research gaps remain.”

4. **Reviewer:**3) The technical-economic assessment of the extraction process should be separated from the series of experiments. A tabular overview of the relevant parameters would add further valuable information to the manuscript.

Reply: We appreciate the reviewer’s suggestion on reorganizing the TEA section. We separated TEA from experimental results and made it a standalone subsection in the Results section, please see the revised manuscript. As the reviewer suggested, we have also included two tables of the relevant parameters for the TEA analysis, as shown below and also included in our revised manuscript and supporting information.

Table 1. Important parameters for the techno-economic assessment

Financial parameters	Variable	Value	Unit	Source/Note
Plant service life	L_{pl}	20	Year	¹⁰
IEM lifespan	L_{IEM}	8	years	¹¹
Electrode lifespan	L_{elec}	0.5	years	²
Activated carbon	C_{car}	10	\$/kg	Kuraray
BPM cost	C_{BPM}	1350	\$/m ²	¹²
IEM cost	C_{IEM}	60	\$/m ²	^{13,14}
Electricity cost	$VC_{electri}$	0.07	\$/kWh	U.S. EIA
Discount rate	i	7	%	¹⁵
Case specifications	Variable	Value	Unit	Source/Note
Brine Li concentration	c_{in}	232	mg/L	¹⁶
Brine flow rate	Q_{out}	37.85	m ³ /day	
Brine recovery ratio	R_w	80	%	This work
Li Extraction efficiency	α	18	%	Experimental Data
Li Conversion rate	β	25	%	Experimental Data
Specific extraction	SEC_{extr}	4	kWh/kg Li+	Experimental

energy consumption				Data
Specific pumping energy	SPE	0.1	kWh/m ³ water pumped	
Specific conversion energy consumption	SEC_{BMED}	2.45	kWh/ kg LiOH·H ₂ O	Experimental Data

Table S5. Other parameters used for the techno-economic assessment

Financial parameters	Variable	Value	Unit	Source/Note
Total capital cost factor	F_{TCC}	2.0	(Total capital cost/equipment cost)	17,18
Maintenance & labor factor	F_{ML}	2	% of initial total capital cost/year	19,20
Chemical factor	F_C	1	% of initial total capital cost/year	19
Peripherals Factor	F_P	1.5	(Peripherals cost/membrane stack cost)	12
Plant Load Factor	η_{LF}	90	%	19,21
Spacer cost	C_{SP}	10	\$/m ²	12
System parameters	Variable	Value	Unit	Source/Note
Electrode mass of active LFP	$M_{(LFP,ex\ pr)}$	65.6	mg	This work
Cycle length	τ	16	h	This work
Electrode density	ρ	0.75	g/cm ³	
Operating current	I	0.892	mA	This work
The number of treatment trains	n_{train}	1		
BMED Operating Voltage	v	2	A	Experimental Data
BMED Cross sectional area of	A_{BMED}	0.25	m ²	22
BMED Flowrate	Q_{BMED}	0.0025	m ³ /s	22
The number of IEMs in a cell	n_{IEM}	4	/	This work
The number of BPMs in a cell	n_{BPM}	3	/	This work
The number of spacers in a cell	n_{SP}	8	/	This work

5. **Reviewer:** The discussion section is short compared to the other chapters and does not meet scientific standards. The authors emphasize the positive results of their work. However, critical appraisal (optimization potential of the method, open questions / research subjects, etc.) is completely missing.

Reply: We appreciate the reviewer's suggestion on adding contents into Discussion section. We added more discussion about the optimization potential of the method and open questions on page 32 of the revised manuscript:

"To further commercialize electrochemical direct lithium extraction technologies, there are barriers needed to overcome for scaling up. First, electrode fabrication needs to be optimized for industrial-scale manufacturing. The drop casting method used in the lab is only capable of producing electrodes in the centimeter size range; for manufacturing electrodes with larger areas in the meter range, more scalable methods including roll-to-roll coating²³ and slot-die coating²⁴, or spray coating²⁵ should be employed. Second, the Li extraction cells need to have the ability to handle high-temperature brines for long periods of time, and automated control systems need to be added to maximize system efficiency. Third, the geothermal brine and other alternative lithium sources have complex water composition, containing foulants and mineral scalants which might cause deterioration of electrode performance over extended cycling. Further improving the capacity retention of the electrode while maintaining high Li selectivity through the optimization of electrode fabrication and device operation will be critical to enhancing the economic competitiveness of electrochemical Li extraction from geothermal and other alternative lithium brine sources."

6. **Reviewer:** The authors speak very generally of geothermal fluids without mentioning a regional reference or geological context and generalize their chemical properties. I recommend that the authors refer precisely to the Salton Sea geothermal site, whose brines are the subject of the research.

Reply: We appreciate the reviewer's suggestion on clarifying the Salton Sea geothermal brine as the research subject. Change in text: We added the followings on Page 4:

"In this work, for the first time, we report an economically viable battery-grade lithium production system by integrating electrochemical system to extract lithium from Salton Sea geothermal brines in Imperial Valley, California and directly produce battery-grade (99.5% purity) lithium hydroxide as the final product²⁶."

7. **Reviewer:** Specific comments: Line 27: „geothermal brine“... should be limited to Salton Sea geothermal brine

Reply: We appreciate the reviewer's suggestion on clarifying the Salton Sea geothermal brine. Change in text: We added "Salton Sea" on Page 2:

"In this work, we design an economically feasible electrochemical process that achieves selective lithium extraction from Salton Sea geothermal brine and purification of lithium chloride using intercalation materials,"

8. **Reviewer:** Line 30: LCOL... here and generally in the manuscript abbreviations should be introduced before they are used.

Reply: LCOL is the abbreviation of levelized cost of LiOH•H₂O (Capital letters of each word). Change in text: To avoid further confusion we deleted “produced” on Page 2:

“We conducted techno-economic assessments using a parametric model and estimated the levelized cost of LiOH•H₂O (LCOL) as 4.6 \$/kg LiOH•H₂O, which is over 3 times lower than the current market price.”

9. **Reviewer:** Line 92: Reference is missing.

Reply: Change in text: We added the following citation as market price reference on Page 5:

“Finally, we conducted techno-economic analysis (TEA) to evaluate the economic competitiveness of this technology and estimated the levelized cost of produced LiOH•H₂O (LCOL) as 4.6 \$/kg LiOH•H₂O which is about 3 times lower than the market price^{27,28}.”

10. **Reviewer:** Line 95: The subheading is very long and should be shortened. This also applies to other subheadings in the manuscript. Please check.

Reply: We shortened the subheadings from “Design of the integrated lithium extraction and refining system.” to “Design of the direct lithium extraction system”. And we also shortened the other subtitles. Change in text on Page 9, 13, 20, 26:

“Design of the direct lithium extraction system”

“High selectivity of Li extraction from brines”

“Mechanisms of Li selectivity revealed by DFT calculations”

“Techno-economic assessment of the process”

11. **Reviewer:** Line 100: ...”capturing only lithium and leaving” ... It should be added that this is a theoretical assumption. Various on-site tests on lithium extraction from geothermal brines worldwide show that the very complex chemical fluid composition shows significant differences in practice compared to laboratory tests with synthetic waters.

Reply: We thank the reviewer for the suggestion. We added “theoretically” on Page 9. Change in text:

“The brine undergoes a lithium extraction and refinement process, theoretically capturing only lithium and leaving all other elements in the bulk solution,”

12. **Reviewer:** Line 116: ...geothermal brine ... has a pH around 5.5... This statement is not generally valid. Please specify which waters are involved. Salton Sea?

Reply: We added “around Salton Sea area” on Page 10. Change in text:

“Salton Sea geothermal brine for lithium extraction has a pH of around 5.5,”

13. **Reviewer:** Line 193: ...brine A and e,... please check. Current wording is confusing for the reader.

Reply: To avoid confusion, we changed the caption “Metal ion concentration percentage with d, synthetic geothermal brine A and e, synthetic geothermal brine B feed solution”
Change in text:

“d-e, metal ion concentration percentage with synthetic geothermal brine A (d) and synthetic geothermal brine B feed solution (e)”

14. **Reviewer:** Line 215: Please specify what "little magnesium" means.

Reply: We thank the reviewer for specifying the Mg concentration. Change in text on Page 17:

“since Salton Sea geothermal brine contains only 0.4% magnesium,”

15. **Reviewer:** Fig. 3: Inscription on the legend (right) missing.

Reply: The right legend for counts is comparable for all the three panels for Li element. We have added the following clarification in the Fig. 3 caption:

“and Li EELS elemental mapping (the color bar legend is only for Li elements).”

16. **Reviewer:** Line 224-246: Not a generally valid statement! Please narrow down to a specific geothermal site. Reference is also missing.

Reply: We thank the reviewer for pointing this out. We added “around Salton Sea area” in Line 244 and citations. Change in text on Page 19:

“Geothermal brine produced from the reservoir (generally at a temperature of 230°C to 370°C for Salton Sea) is first used for power generation in a geothermal power plant using high-temperature steam and would cool down to 80°C to 110°C prior to direct lithium extraction²⁹⁻³³.”

17. **Reviewer:** Line 257: Headline too long.

Reply: We shortened the subheading “Mechanisms of ultrahigh Li selectivity of LFP in aqueous solutions revealed by DFT calculations.” Change in text on Page 20:

“Mechanisms of Li selectivity revealed by DFT calculations.”

18. **Reviewer:** Line 260: Abbreviation not introduced.

Reply: We moved the Methods after Introduction section. The abbreviation is introduced there.

19. **Reviewer:** Line 357: “ultrahigh”...please define.

Reply: To avoid confusion, we changed “ultrahigh” to “high”. We opt not to specify the selectivity values, which has been reported in Figure 2 and vary with different cation pairs (Li/Na, Li/K, etc).

Change in text on Page 32:

“1) high selectivity for Li over monovalent and multivalent competing cations in geothermal brines;”

20. **Reviewer:** Line 379: “using harsh acid”. This statement is not true. There are sorbents (LDH) that can be regenerated with water.

Reply: We thank the reviewer for pointing this out. Indeed, some adsorbents can be regenerated with freshwater. However, freshwater is a scarce resource in remote and arid locations where many geothermal brines are found, and the use of large amounts freshwater for regeneration is still undesirable. We have highlighted this in the revised manuscript.

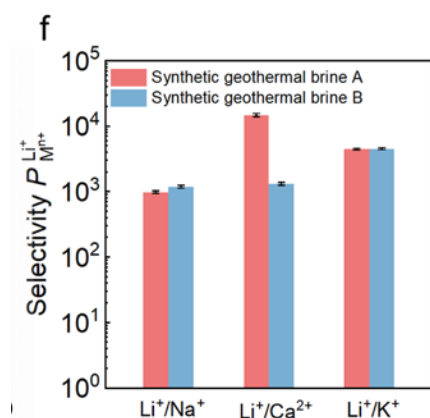
Change in text on Page 33:

“Lithium sorbents/ion exchangers and some organic solvents have a high affinity for Li⁺, but suffer from drawbacks of using harsh acid for regeneration and the potential release of organic solvents to the environment, respectively³⁴⁻³⁷. Some lithium sorbents like layered double hydroxide can be regenerated by freshwater³⁸, which, however, is a scarce resource in remote and arid locations where many lithium brines are found.”

21. **Reviewer:** Line 373-385: The chemical composition of the geothermal brines has a significant influence on the extent of lithium extraction and the purity of the products. The authors have so far examined synthetic waters in their study. Redox-sensitive parameters have not yet been taken into account. The same applies to the fact that heavy metals and naturally occurring radionuclides are also dissolved in the Salton Sea

geothermal brine (e.g. Zukin et al. 1987). Due to the far more complex chemical composition of real geothermal brines (compared to synthetic brines), the potential impact of foreign ions on the present results should be discussed at more detail.

Reply: We thank the reviewer's suggestions on considering redox-sensitive parameters. From our DFT simulation results, metal ions with larger dehydrated radii than K^+ will not be able to intercalate into the $FePO_4$ host, and therefore will not affect the selectivity. Because the concentrations of these heavy metals and naturally occurring radionuclides is lower than 10 mM (see the table below), we didn't study them in this project. In this study, the synthetic geothermal brine B includes Fe^{2+} and Mn^{2+} , also are redox active ions and have relatively high concentrations (>30 mM). From Figure 2f as shown below, the presence of these redox active ions did not appear to have a significant impact on Li selectivity.



We agree with the reviewer that these foreign redox sensitive ions can have unexpected impacts on the electrode performance over extended cycling, due to the precipitation of metal (hydr)oxides. In our future work on authentic brine samples, we will evaluate how those elements impact the electrode lifespan.

Change in text: We added the detailed composition of other metal elements in real geothermal brine in Table S1c and also shown below.

Composition of the Simbol Feed Brine (SFB; 2022 Report of Analysis)

Analyte	Concentration (mM)
Lithium	34
Sodium	2700
Calcium	940
Potassium	460
Manganese	38
Iron	30
Barium	4
Strontium	6

Lead	0.5
Copper	0.1
Magnesium	2
Aluminum	0.1
Antimony	<0.005
Arsenic	0.01
Silver	<0.01

22. **Reviewer:** Line 387: ...”using electricity as the input”... The present work implies that the required electricity is supplied by existing geothermal plants. Otherwise, this would have an enormous impact on the economic viability of the process presented.

Reply: We calculated the total electricity consumption in TEA based on the electricity price from the grid (\$0.07 per kWh), and our results show that the electricity cost takes a small portion (<10%) of the total cost of lithium extraction. The geothermal source of electricity is highlighted to demonstrate that utilizing green electricity makes the whole lithium extraction process more environmentally sustainable. The electricity could be sourced from other renewables or conventional power sources.

Reviewer 2

General: We are grateful to the reviewer for the interest in the paper and for the comments to help us improve the manuscript.

Our specific responses to the reviewer’s comments are listed below.

1. **Reviewer:** In the present work, titled: Electro-driven direct lithium extraction from geothermal brines to generate battery-grade lithium hydroxide, the authors propose an experimental strategy that coupled two technologies: Li intercalation and electrodialysis with bipolar membranes. The objective is to produce battery-grade lithium hydroxide from Geothermal Brine as a feed solution.

Reply: We thank the reviewer for the constructive comments to help us improve our manuscript. We have addressed the reviewer’s comments below.

2. **Reviewer:** In my opinion, for a better understanding of the work it could be interesting to change the structure of the manuscript and describe the Materials and Methods before the discussion of the results. In addition, the results section has a bit mixed-up the descriptions that correspond to Materials and Methods and results. This makes it difficult to connect the ideas.

Reply: We thank the reviewer for the suggestions, and we move the Methods section after Introduction section.

3. **Reviewer:** Concerning the content of the presented work I have some suggestions: 1. I do not agree with the use of the term unconventional to describe a Geothermal Brine as a source of lithium. This does not correspond to an unknown and unexploited source, several works are focusing on this type of lithium source and it is being exploited on an industrial level (e.g. USA). Thus, a geothermal brine represents a source of lithium with a lower lithium content than continental brines (salars), but it is not an unconventional source.

Reply: We appreciate the reviewer's comments on clarifying geothermal brine as a lithium source. In response, we have revised our terminology, changing "unconventional" to "alternative" to better describe geothermal brine as an emerging lithium source that stands as an alternative to the traditional sources such as salt flats and hard rocks.

Change in text:

on Page 2:

"Extracting lithium from alternative aqueous sources such as geothermal brines plays an important role in meeting this demand."

on Page 2:

"The results demonstrate the potential of our technology for electro-driven, chemical-free lithium extraction from alternative sources."

on Page 3:

"This projected lithium deficit calls for technological advancements to extract lithium from alternative sources to help meet the rapidly growing lithium demand and prevent the depletion of continental Li resources^{2,39}."

on Page 3:

"Considering energy consumption and extraction cost, several alternative aqueous sources containing relatively high lithium concentration are considered potential lithium sources,"

on Page 34:

"but also holds promise in lithium extraction from continental salt flat brines as well as alternative lithium sources like oil/gas produced water and desalination brines."

on Page 34:

"So, further improving the capacity retention of the electrode while maintaining high Li selectivity through the optimization of electrode fabrication and device operation will be critical to

enhancing the economic competitiveness of electrochemical Li extraction from geothermal and other alternative lithium brine sources.”

4. **Reviewer:** 2. I suggest to reinforce the references in the Introduction section.

Reply: We appreciate the reviewer’s comment on reinforcing the references in the Introduction section. We added the following citations:

“The electrification of the transportation sector drives the rapid growth of electric vehicles (EVs) and increasing demand for Li-ion batteries⁴⁰⁻⁴². ”

“This projected lithium deficit calls for technological advancements to extract lithium from alternative sources to help meet the rapidly growing lithium demand and prevent the depletion of continental Li resources^{2,39,43,44}. ”

“Conventional Li mining from brines relies on solar evaporation followed by slow chemical precipitation methods, which waste large amounts of water resources. Recent developments of direct lithium extraction have focused on Li sorbent materials⁴⁵⁻⁴⁸, Li selective membranes⁴⁹⁻⁵⁴, and electrochemical technologies^{6,55-59}. ”

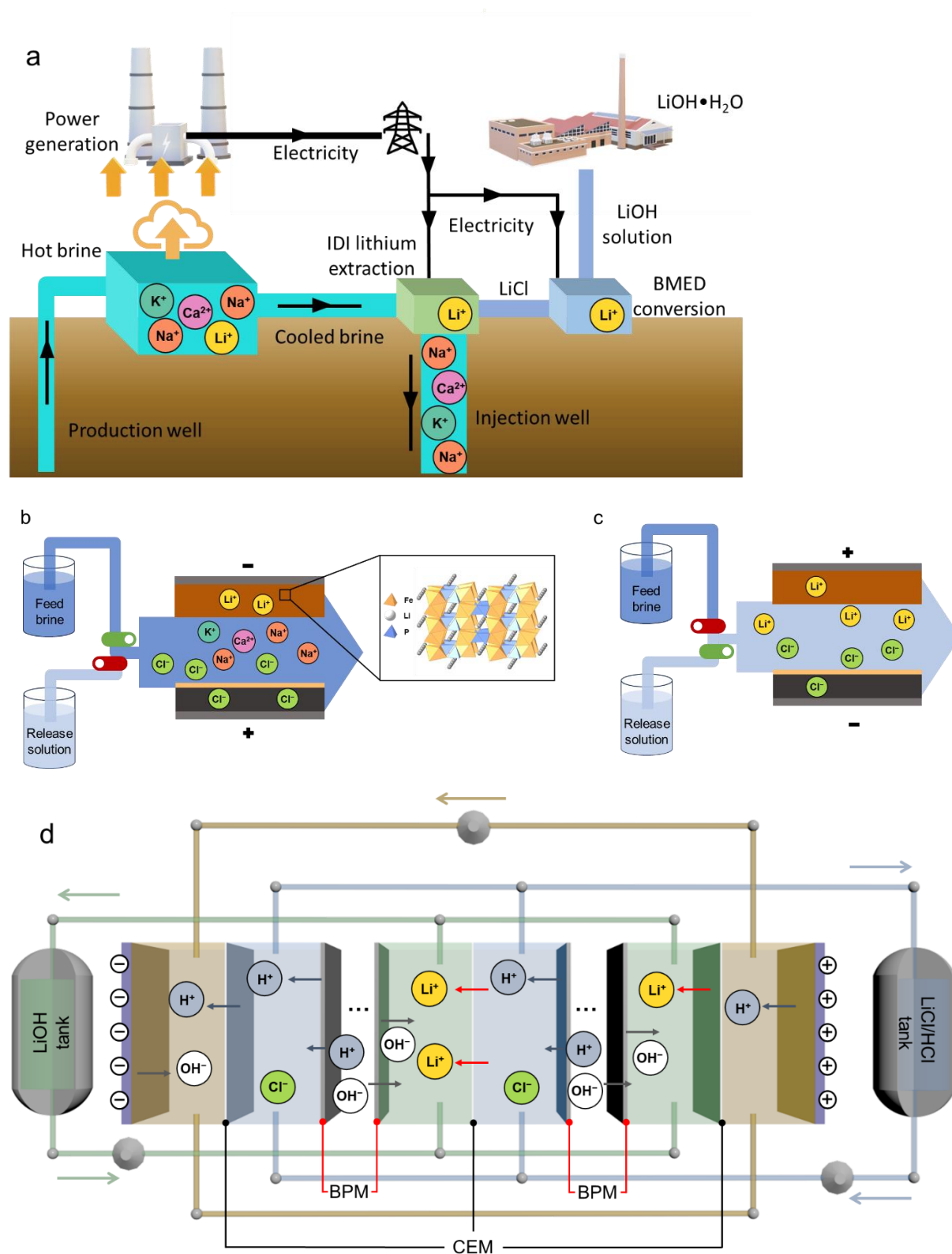
5. **Reviewer:** 3. At line 86 in which authors list the elements that are present in the brine, it would be more appropriate to write ions: Li⁺ instead of Li, Na⁺ instead of Na...

Reply: We added the valence to all mentioned metal ions. Change in text on Page 5:

“We achieved 91.2% ± 0.9% Li molar purity in released solution from a synthetic geothermal brine containing Li⁺, Na⁺, Ca²⁺, K⁺, Fe²⁺, and Mn²⁺. ”

6. **Reviewer:** 4. I suggest increasing the size of the ions in Figure 1 for a better understanding.

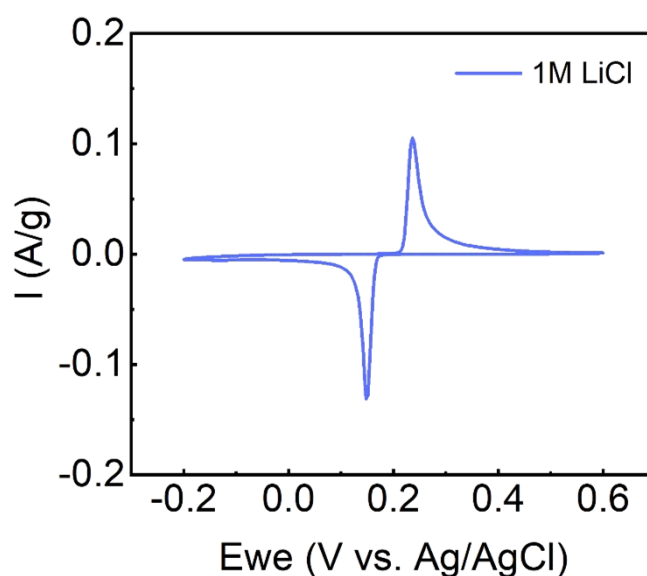
Reply: We appreciate the reviewer’s comment on making the ion size larger in Fig. 1. We increased the ion size in Fig.1. Change in Fig. 1, see the revised manuscript and also shown below.



7. **Reviewer:** 5. Authors confirmed by DRX the lithiation or delithiation of the host material (line 133), I suggest the incorporation of a cyclic voltammetry or an XPS study for a better characterization.

Reply: We appreciate the reviewer's suggestion on confirming the crystal structure. A cyclic voltammetry is reported in Fig. S3 in our original submission. The CV curve clearly shows the reversible lithiation and delithiation processes in the LFP electrode. We also have the following discussion of the CV results in our original manuscript:

"Fig. S5 shows the cyclic voltammetry (CV) results for FePO_4 in 1 M LiCl solutions under 1 mV/s scan rate. The CV curve shows a pair of symmetric redox peaks indicating lithium capture and release. The theoretical potential plateau of lithiation and delithiation for FePO_4 is about 3.5 V versus Li metal⁶⁰, which is 0.26 V versus Ag/AgCl. The half-wave potential ($E_{1/2} = 0.20$ V vs. Ag/AgCl) is close to the theoretical thermodynamic values⁶⁰."



"Fig. S2. CV curve of FePO_4 in 1 M lithium chloride aqueous solution at a 1 mV/s scan rate."

8. **Reviewer:** 6. Authors discuss the performance of lithium extraction from graphs presented in Figure 2. All represented values are percentages, instead of absolute values. For example, it is important to know how much lithium is being captured from the feed solution and which is the ratio between this quantity and the lithium content in the recovery solution. A percentage of 90% for lithium in the solution of release implies that other ions are present in a minor concentration, but it does not imply that the majority of the initial lithium was captured and then released. In addition, the authors report a value of 0.18 for lithium extraction efficiency (Table S5), however, the amount of lithium in moles in both solutions is not reported.

Reply: We appreciate the reviewer's suggestion on clarifying the Li concentration in release solution and the amount of Li ion captured from the brine. We have made the following changes to clarify the Li concentrations in the feed and released solution.

Change in text on Page 17:

“Lithium molar fraction was around 0.9% in the feed solution and increased to about $92.3\% \pm 1.0\%$ in the released solution. The concentration of Li^+ in the feed and released solution was 30 mM and 9.6 mM, respectively. Note that a 5 mM LiCl solution was used as the release solution; after accounting for this, 4.6 mM Li^+ was released from the electrode.”

In addition, we have performed additional experiments to increase the extraction efficiency to 85%. We have also added the following paragraph on Page 19 to clarify this.

“The Li extraction process needs to recover $>80\text{--}90\%$ Li in the geothermal brine to make the process economically viable. One technical barrier to achieving such a high extraction efficiency is that a sudden concentration change of over 50% will cause the electrochemical potential for Li intercalation to change abruptly, based on the Nernst equation. Therefore, to maintain a stable potential, the Li concentration change in the brine in each pass must be well controlled. To maximize the extraction efficiency while also maintaining stable electrical potential, we designed a stepwise extraction system with cells arranged in series (See Fig. S8). The brine with partial lithium extracted in the series 1 cell goes through the next series 2 extraction cell until most of the lithium in the brine is extracted. Using this design, we successfully achieved an extraction efficiency of over 85% in six cells in series (Fig. S9). Note that further improving the extraction efficiency to $>90\%$ is possible by including more cells, but the energy consumption will also increase due to the low concentration of Li left in the brine. Therefore, we opt to keep our extraction efficiency at 85% to maintain a good balance between high Li recovery and low energy consumption.”

We have also added Figure S9 (also shown below) to show that 85% extraction efficiency was achieved using six cells in series design. The lithium concentrations before and after extraction are specified in the figure caption: The initial lithium concentration in the brine is 42 mM; after extraction in six cells in series, the lithium concentration remaining in the brine is 6.2 mM.

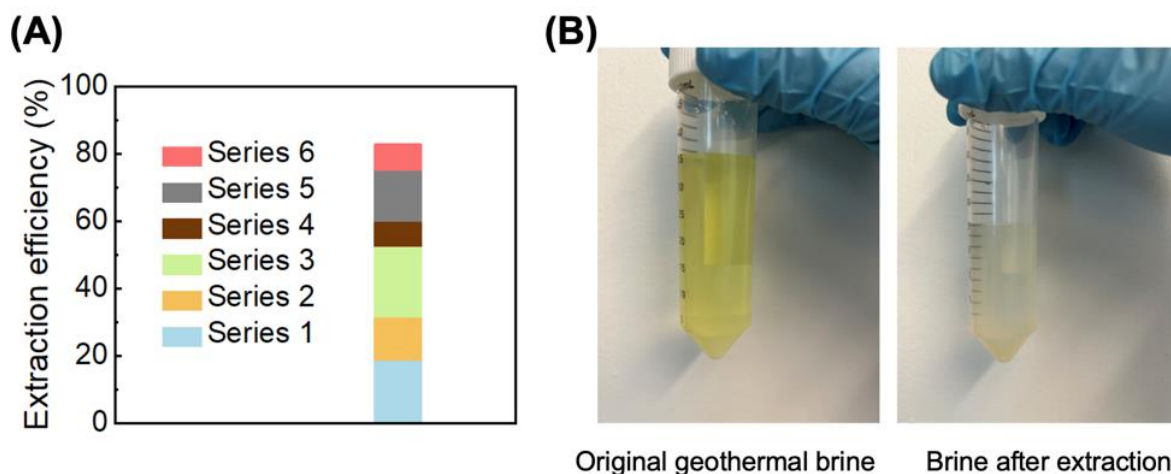


Fig. S9 (A) Extraction efficiency in six series of extraction. The initial lithium concentration in the brine is 42 mM; after extraction in six cells in series, the lithium

concentration remaining in the brine is 6.2 mM. (B) Photos of brine before and after extraction.

9. **Reviewer:** 7. In Figure 3 authors show TEM images and an elemental mapping for Fe, Na, and Li. This is complemented by table S2 which lists the atomic composition. In that table, lithium (the target element) is not present. The brightness obtained for Figure 3B is not conclusive as Na also is detected by EELS.

Reply: We thank the reviewer for the comment. First of all, we would like to clarify that Li was measured using the EELS technique, while Na, Fe, O, and P were measured with the EDS technique with the corresponding compositions listed in Table S2. The color legend on the right only applies to the Li elemental mapping by EELS. It is widely known that EDS has not been traditionally used for characterizing light elements such as Li due to long acquisition times, weak interaction between X-rays and such light elements, and significant overlapping with background noise^{61,62}. The detected Na on the electrode by EDS can be due to the background signals from the detector or the amount of Na being below the detection limit, which is too small to give exact values. It is hard to directly quantify Li/Na using EELS/EDS different techniques, since the measurement sensitivity and background intensity may be different. For a more accurate determination of Li/Na amount in the released solution, we used ICP-OES (Refer to ICP results) to measure out the corresponding amounts.

To clarify that the color legend is only for Li elemental mapping in EELS, we revised the figure caption the read:

"Li EELS elemental mapping (the color bar legend is only for Li elements)."

10. **Reviewer:** 8. In line 292, the authors conclude that from the results obtained from the simulation, the selectivity of the host material for lithium over other cations is confirmed. It might be interesting to compare or match these calculations with empirical data obtained from the system studied.

Reply: We appreciate the reviewer's suggestion on matching the simulation results with empirical data. As shown in Table S3, our DFT simulations revealed a much smaller diffusion activation energy for Li^+ than Na^+ , which in turn is smaller than Ca^{2+} . Moreover, Li^+ is the only cation that exhibited a negative enthalpy change upon diffusion. Thus, our predicted order of extraction efficiency for these three cations, i.e., $\text{Li}^+ > \text{Na}^+ > \text{Ca}^{2+}$, is consistent with our experimental selectivity, as illustrated in Fig. 2f.

We have revised the sentence on Page 22 to include comparison with the experimental data reported in Figure 2 to read:

"Taken all together, our simulation results confirmed the exceptional extraction selectivity of Li^+ over other common cations (Na^+ , K^+ , and Ca^{2+}) in aqueous solutions by FePO_4 observed in Fig. 2."

11. **Reviewer:** 9. In line 384 authors mentioned that membrane-based technologies struggle to achieve high lithium selectivity over monovalent cations. That technology requires steps of lithium concentration and separation of other cations by precipitation (for example), the selectivity is not reached by a cation exchange membrane. The recovery of lithium salts implies the conjunction of more than one step, as in the presented work where first lithium is concentrated and converted to LiCl , then the product is purified and finally it is converted to LiOH .

Reply: We appreciate the reviewer's comment on the comparison between technologies. We agree with the reviewer that selectivity between monovalent ions (such as between Li^+ and Na^+) is not required if lithium carbonate is produced via precipitation. However, as we mentioned in the introduction, LiOH has becoming a more desirable raw material for manufacturing NMC batteries which are needed for long range electric vehicles. To produce LiOH with high purity, selectivity between monovalent ions (Li^+ vs Na^+ , and Li^+ vs K^+) is required, since the presence of other monovalent ions will interfere the production of LiOH . As both $\text{LiOH}\cdot\text{H}_2\text{O}$ and NaOH are highly soluble in water, it is challenging to separate $\text{LiOH}\cdot\text{H}_2\text{O}$ from NaOH simply by precipitation. In this study we focus on LiOH as the end product, so we highlight the mining process of capturing Li from brine sources to provide a LiCl solution for LiOH generation. The LiOH production process is indeed a conversion process, but a pure LiCl solution is required to obtain high purity LiOH .

To clarify the need for Li/Na selectivity to produce LiOH , we have revised the manuscript on Page 33 to read:

"While most membrane-based lithium extraction technologies show selectivity for lithium over multivalent cations, they often struggle to achieve high selectivity (>5) for lithium over monovalent cations such as Na^+ and K^+ (see Table S7), which is needed to produce high purity lithium hydroxide monohydrate."

12. **Reviewer:** 10. The authors make a good techno-economic assessment and highlight the fact that their technology does not involve the use of additional reagents and that it could be coupled with renewable energy sources, which is a great point to highlight. For completeness, it would be interesting to calculate the deionized water needed per liter of treated brine. The cell is washed with water three times after lithium capture and before lithium release (data taken from their previous work, Ref.7).

Reply: We appreciate the reviewer's suggestion on considering the consumption of DI water. In this work, the system is not disassembled between lithium capture and release. Only a fixed volume of DI water is circulating into the flow system for washing. We

analyzed freshwater consumption in our TEA analysis. Freshwater consumption is estimated as 24.8 L/kg LiOH•H₂O, and the cost of freshwater contributes to 0.04 \$/kg LiOH•H₂O which is less than 1% of total cost.

Change in text on Page 29:

“Considering the freshwater usage for washing the flow cell system between the extraction and release processes, the water cost could be calculated by followings:

$$r_{wash} = flowrate_{wash} t_{wash} / mass_{Li+_{cycle}} \quad (19)$$

$$V_{wash_year} = r_{wash} mass_{Li+_{year}} \quad (20)$$

$$LCOL_{water} = \frac{V_{wash_year} price_{water}}{mass_{LiOH_year}} \quad (21)$$

$LCOL_{water}$ is the levelized cost for washing in this process, in \$/kg

Freshwater consumption is estimated as 24.8 L/kg LiOH•H₂O, and the cost of freshwater contributes to 0.04 \$/kg LiOH•H₂O which is less than 1% of total cost.”

We again thank the reviewers’ comments, which greatly helped us improve the manuscript.

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REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have restructured the manuscript and addressed the reviewer comments. This has significantly improved the readability and quality of the manuscript, which is why I no longer have any reservations about publishing the manuscript.

Reviewer #2 (Remarks to the Author):

I would like to thank the authors for the great work they have done in improving the organisation and quality of the manuscript. They have responded in a detailed way to all suggestions made and have reinforced the discussion of results with the requested calculations.