Novel method of lithium production from brines combining battery material and sodium sulphite as a cheap and environmentally friendly reducing agent

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Abstract

The growing increase in the global demand for lithium for the production of lithium batteries demands for the development of alternative, fast, environmental-friendly and cost-effective technologies for lithium production. Most lithium resources are in the form of brines, which are concentrated saline solutions containing lithium in the presence of an excess of other cations (primarily, sodium, magnesium and potassium). The use of lithium battery materials has been shown to be highly advantageous for the selective sequestration of lithium from brines, thus achieving the efficient separation of lithium from other cations and, with this, facilitating the production of the highly pure Li_2CO_3 required for the battery industry. The sequestration of lithium by battery material can be driven by electricity or redox agents, and the later has advantages in terms of the simplicity of the reactor design for large scale production. A critical aspect in the use of redox agents is the cost and environmental compatibility. Here we demonstrate the use of a novel redox reagent, sodium sulphite, that is cheap, non-toxic and induces fast lithium sequestration reactions.

Key words: lithium production, sodium sulphite, chemical lithium extraction, brines, lithium-ion batteries, lithium iron phosphate.

INTRODUCTION

The demand for lithium production worldwide has experienced a dramatic increase in recent years, mainly due to the growth of the rechargeable lithium battery market, and an even higher increase is expected in coming years due to the expansion of lithium battery applications in electric vehicles, portable devices and grid storage.[1–5] Consequently, the development of alternative methods of lithium production is urgently needed to cope with the increasing demands.[6–9]

Around 60% of the global lithium resources are in the form of highly saline solutions, called lithium brines, which contain cations such as Na^+, K^+ and Mg^{2+} in much higher concentrations than that of Li^+.[6,8] Unfortunately, current methods of lithium production can only be applied to a narrow range of brine compositions,[6] and hence, it is necessary to develop new methods able to extract lithium ions selectively, in the presence of a vast excess of other cations, since that would enable a massive increase in the lithium production. Several methods for lithium sequestration from brines have been explored and the use of lithium battery materials to enable the selective lithium extraction from brines appears particularly promising, as illustrated in table 1.

Table 1. Studies of lithium sequestration from brines using battery host materials.

Battery material	**Methodology for lithium recovery**	**Brine**	**Quantification of lithium sequestration**	**Experimental conditions**	**Ref.**
$LiMn_2O_4$	Electrochemical	Geothermal water	Li uptake in solid = 11 mg g^{-1} [a]	10 cycles of lithium capture (from 1.0 to 0.2 V vs SCE[e]) and release (from 0.2 to 1.0 V vs. SCE[e]) at 0.1 mV s^{-1} using a Pt/λ-MnO_2 electrode and a Pt wire as counter electrode.	10
		Salar de Atacama	$\Delta[Li^+]_{recovery\ solution}$ = 18 mM [b]	4 cycles of lithium capture from brine (reduction) and release in 1st recovery solution (oxidation) followed by 4 cycles of lithium capture from 1st recovery solution (reduction) and release in 2nd recovery solution (oxidation) in a λ-MnO_2/Ag cell, ±0.5 mA cm^{-2}, 30 min.	11
		Salar de Atacama	$\Delta[Li^+]_{recovery\ solution}$ = 60 mM [b]	3 cycles of lithium capture from brine (reduction) and release in 1st recovery solution (oxidation) followed by 3 cycles of lithium capture from 1st recovery solution (reduction) and release in 2nd recovery solution (oxidation) in a λ-MnO_2/activated carbon cell, containing an anion exchange membrane, ±0.5 mA cm^{-2}, 30 min.	12
		Salar de Atacama	$\Delta[Li^+]_{recovery\ solution}$ = 45 mM [b]	3 cycles of lithium capture (reduction, cut-off = 1.38 V) and release (oxidation, cut-off = 1.93 V) in a λ-MnO_2/Zn cell containing an anion exchange membrane, ±0.5 mA cm^{-2}.	13
		Desalination brine	Li purity in recovery solution = 99% [c]	1 cycle of lithium capture from brine (-0.01 mA cm^{-2}) and release in 1st recovery solution (0.2 mA cm^{-2}) followed by 1 cycle of lithium capture from 1st recovery solution (-0.1 mA cm^{-2}) and release in 2nd recovery solution (0.1 mA cm^{-2}) in a λ-MnO_2/Ag cell. Reduction current cut-off = 0.2 V. Oxidation current cut-off = 0.9.	14
		Salar de Olaroz	$\Delta[Li^+]_{recovery\ solution}$ = 16 mM [b]	1 cycle of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/polypyrrole cell, ±2.5 mA cm^{-2}, 16 h.	15
		Salar de Atacama	Li purity recovery solution = 61% (λ-MnO_2/NiHCF), 96% (λ-MnO_2/Ag) [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/NiHCF or λ-MnO_2/Ag cell, ±148 mA g^{-1}, 60 min.	16
		Salt lake brine	Li uptake in solid = 35 mg g^{-1} [a]	1 cycle of lithium capture (reduction, -0.2 V vs Ag/AgCl) and release (oxidation, 1 V vs Ag/AgCl), each step for 2 h using a λ-MnO_2/polypyrrole/polyninylsulfonate electrode and a Pt wire as counter electrode.	17
		Simulated brine concentrated seawater	Li uptake in solid = 21-22 mg g^{-1} [a]	1 cycle of lithium capture (reduction, at -0.6 V) and release (oxidation, at 0.6 V), each step for 120 min, in a $LiMn_2O_4$/$Li_{1-x}Mn_2O_4$ cell containing an anion exchange membrane.	18
		Salt lake brine	$\Delta[Li^+]_{recovery\ solution}$ = 18 mM (film electrode), 25 mM (powder electrode) [b]	100 cycles of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/Ag cell, ±50 mA g^{-1},30 min.	19
		Taijinair lake	$\Delta[Li^+]_{recovery\ solution}$ = 35 mM [b]	4 cycles of lithium capture (reduction, cut-off = 0.15 V) and release	20

				(oxidation, cut-off = 0.7 V) in a polyaniline/$Li_xMn_2O_4$ cell, ±0.5 mA cm^{-2}.	
		Salt lake brine	Li uptake in solid = 14 mg g^{-1} [a]	5 cycles of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/Ag cell, ±50 mA g^{-1}, 30 min.	21
$LiFePO_4$		Sodium rich brine	Li uptake in solid = 8 mg g^{-1} [a] Li purity in recovery solution = 85% [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/Ag cell, ±0.5 mA cm^{-2}, 120 min.	22
		Salar de Atacama	Li purity in recovery solution = 98% [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/Ag cell, ±0.5 mA cm^{-2}, 60 min.	23
		Salar de Atacama	Li purity in recovery solution = 74% [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a λ-MnO_2/NiHCF, ±108.5 mA g^{-1}, 40 min.	24
		West Taijnar salt lake	Li uptake in solid = 29-33 mg g^{-1} [a]	1 cycle of lithium capture (reduction, at -1 V) and release (oxidation, at 1 V), each step for 10 h, in a $LiFePO_4$/$FePO_4$ cell containing an anion exchange membrane.	25
		Salt lake brine	Li uptake in solid = 39 mg g^{-1} [a]	1 cycle of lithium capture (reduction, at -0.25 V) and release (oxidation, at 0.25 V), each step for 10 h, in a $LiFePO_4$/ $FePO_4$ cell containing an anion exchange membrane.	26
		West Taijnar salt lake	Li uptake in solid = 25 mg g^{-1} [a]	1 cycle of lithium capture (reduction, at -0.2 V) and release (oxidation, at 0.2 V), each step limited to a current cut-off = 0.05 mA cm^{-2}, in a $LiFePO_4$/$FePO_4$ cell containing an anion exchange membrane.	27
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$		Salar de Uyuni	Li uptake in solid = 11 mg g^{-1} [a] Li purity in recovery solution = 97% [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$/Ag cell, ±0.5 mA cm^{-2}, 20 min.	28
$LiNi_{0.5}Co_{1.5}Mn_{1.5}O_2$		Salar de Uyuni	Li uptake in solid = 9 mg g^{-1} [a] Li purity in recovery solution = 98% [c]	1 cycle of lithium capture (reduction) and release (oxidation) in a $Li_{1-x}Ni_{0.5}Co_{1.5}Mn_{1.5}O_2$/Ag cell, ±0.44 mA cm^{-2}, 20 min.	29
$LiFePO_4$	Redox agents	Central Altiplano	Li uptake in solid = 46 mg g^{-1} [a]	$Na_2S_2O_3$ as reducing agent, [$Na_2S_2O_3$] = 0.3 M, 24 h.	30
		Central Altiplano	Li uptake in solid = 44-45 mg g^{-1} [a] Li purity in solid = 94-96% [d]	Na_2SO_3 as reducing agent, [Na_2SO_3] = 0.3 M, 24 h.	This work

[a] The Li uptake is defined as the amount of recovered lithium per gram of solid (mg g^{-1}). [b] Increase in lithium concentration in the recovery solution. [C] The lithium purity in the recovery solution defined as the relation between the lithium concentration in solution and the total concentration of all cations in solution (including lithium). [d] The lithium purity in the solid is defined as the relation between the lithium uptake in the solid and the total uptake of all cations in the solid (including lithium). [e] SCE = Saturated calomel Electrode.

Within the methods using battery materials, the use of redox agents to induce the reaction is particularly well suited to be scaled-up for industrial lithium production. We first demonstrated the suitability of the use of redox agents combined with battery materials by employing sodium thiosulfate ($Na_2S_2O_3$) to drive the lithium sequestration reaction into a $FePO_4$ host battery structure, thus producing $LiFePO_4$ as the reaction product.[30] As illustrated in figure 1, once lithium is selectively sequestrated in the battery host structure (in the form of $LiFePO_4$), then the $LiFePO_4$ powder is removed from the reaction mixture, and lithium is released using an oxidising agent thus recovering the battery material (as $FePO_4$) and producing a lithium salt (e.g. Li_2CO_3) as the overall product of the whole process. Therefore, the battery material can be used in many cycles of lithium sequestration and release, and only the redox agents are consumed for the production of the lithium salt. In this work, we report the use of an advantageous alternative redox agent, sodium sulfite (Na_2SO_3), which is cheaper, induces a higher amount of lithium insertion per mole of reactant, is non-toxic and the product of the reaction (Na_2SO_4) is completely inert. The reactions of lithium sequestration are as follows:

$Li^+ + FePO_4 + e^- \rightleftharpoons LiFePO_4$ (E^0 = 0.40 V vs. SHE)[30] (1)

$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$ (E^0 = 0.08 V vs. SHE)[31] (2)

$2Li^+ + 2FePO_4 + 2S_2O_3^{2-} \rightleftharpoons 2LiFePO_4 + S_4O_6^{2-}$ (ΔG^0 = -62 kJ/mol) (3)

$SO_3^{2-} + H_2O \rightleftharpoons SO_4^{2-} + 2H^+ + 2e^-$ (E^0 = -0.52 V vs. SHE, pH = 7)[31] (4)

$2Li^+ + 2FePO_4 + SO_3^{2-} + H_2O \rightleftharpoons 2LiFePO_4 + SO_4^{2-} + 2H^+$ (ΔG^0 = -178 kJ/mol) (5)

where E^0 stands for the standard potentials and the driving force for the lithium sequestration reactions are the lower values of standard potentials of the reducing agents ($Na_2S_2O_3$ and Na_2SO_3) compared to the $LiFePO_4/FePO_4$ redox potential.

Na_2SO_3 is a cheap and accessible reagent used in different applications, such as pulp and paper industry,[32] water treatment[33] or in the textile industry.[34] Additionally, it is also used in chemical manufacturing as a sulfonation agent and in the production of $Na_2S_2O_3$.[35] Na_2SO_3 has also been proposed as a cost-effective alternative for battery recycling.[36,37] On the other hand, the use of Na_2SO_3 instead of $Na_2S_2O_3$ seems to be favourable considering the stoichiometry of the reactions (reactions 3 and 5). Indeed, reaction 5 has a stoichiometric molar ratio $Li^+/Na_2SO_3 = 2/1$, while the stoichiometric molar ratio of $Li^+/Na_2S_2O_3 = 1/1$ suggests that a higher amount of reducing agent would be required to induce the Li intercalation using $Na_2S_2O_3$ (reaction 3). Additionally, the reaction product of the sequestration reaction induced by Na_2SO_3 is Na_2SO_4, which is inert and innocuous, and Na_2SO_3 itself is also non-toxic.[38] In this work, the use of Na_2SO_3 to induce the sequestration of lithium into a $FePO_4$ host structure is fully characterised and compared with the use of $Na_2S_2O_3$, concluding that the selectivity and kinetics of lithium sequestration reactions are similar with both reagents, thus confirming the suitability of Na_2SO_3 as an advantageous alternative reagent for the production of lithium from brines.

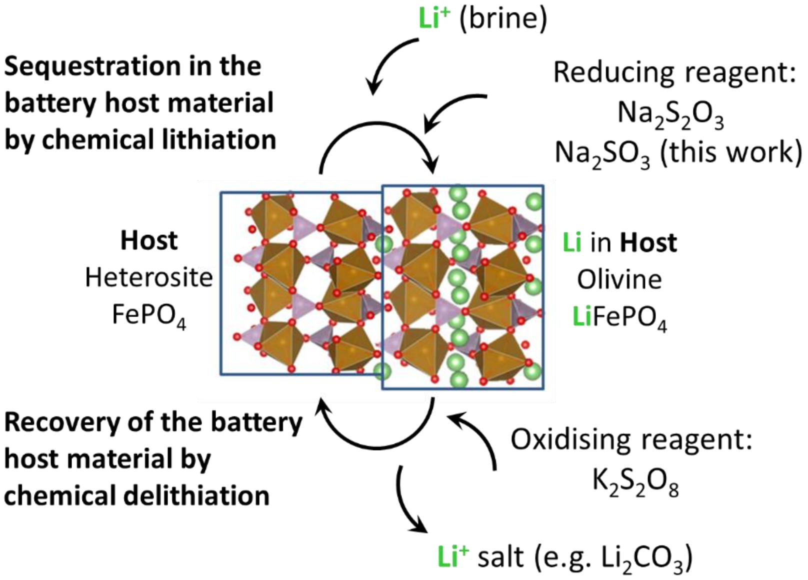

Figure 1. Methodology for the production of lithium using $LiFePO_4$ battery material as sequestering agent and redox reagents to drive the reactions.

MATERIALS AND METHODS

Chemical delithiation of lithium iron phospate

Commercial $LiFePO_4$ (LFP, provided by Tatung, battery grade) was used for all the experiments. $LiFePO_4$ was chemically delithiated using $K_2S_2O_8$ (Sigma Aldrich, ACS grade, ≥ 99%) as an oxidizing agent following the methodology reported previously.[30,39] Briefly, $LiFePO_4$ (0.2 M) and $K_2S_2O_8$ (0.1 M) were mixed in ultrapure water (18.2 MΩ cm, Suez, Select). The reaction was held for 24 hours at room temperature under continuous stirring. The resultant solid was filtered, washed and dried overnight at 80 ºC. These conditions led to the complete delithiation of $LiFePO_4$ (LFP), obtaining $FePO_4$ (FP) as the reaction product.[30,39]

Chemical lithiation of iron phospate

Delithiated $LiFePO_4$ ($FePO_4$ or FP, obtained as described above) was chemically lithiated using $Na_2S_2O_3$ ($Na_2S_2O_3 \cdot 5H_2O$, Sigma Aldrich, ACS grade, ≥ 99.5 %) or Na_2SO_3 (Sigma Aldrich, ACS grade, ≥ 98%) as reducing agents and Li_2SO_4 ($Li_2SO_4 \cdot H_2O$, Sigma Aldrich, ACS grade, ≥ 99 %) as the lithium source. In a typical experiment, a known amount of $FePO_4$ (around 1 g), the reducing agent ($Na_2S_2O_3$ or Na_2SO_3) and Li_2SO_4 were dissolved in 35 mL of ultrapure water under continuous stirring at room temperature. The initial molar concentrations of the reagents in the mixture were 0.375 M $FePO_4$, 0.75 M Li_2SO_4 and 1.5 M $Na_2S_2O_3$ or Na_2SO_3. Thus, the molar ratio of $FePO_4 : Li^+ :$ reducing agent in the initial mixture was 1:4:4. The reaction was stopped after 20 min, 1 hour or 24 hours. The resultant solid was filtered, washed and dried overnight at 80 ºC. The solid reaction product was characterized by XRD, galvanostatic cycling in Li-half cells, and ICP measurements of the digested solid.

Chemical extraction of lithium from artificial brines

Chemical extraction of lithium was also performed in two different artificial brines. The molar compositions are listed in Table 2. These experiments were carried out in the presence of 0.3 M Na_2SO_3. For brine 1, 0.03 M $FePO_4$ was employed, and for brine 2, 0.1 M $FePO_4$.

Therefore, the molar ratio of $FePO_4$: Li^+ : reducing agent in the initial mixture was 1:2:10 for brine 1 and 1:2:3 for brine 2. These initial compositions were selected so that, throughout the process of lithium sequestration, lithium ions and the reducing agent are both in excess with respect to $FePO_4$ for both brine compositions. The reactions were carried out at room temperature for 24 h. The solid reaction product was characterized by XRD, galvanostatic cycling in Li-half cells, and ICP measurements of the digested solid.

Chloride salts, LiCl, NaCl, KCl and $MgCl_2 \cdot 6H_2O$ (Sigma Aldrich, ACS grade, ≥ 99%), were used for the preparation of the brines with the exception of the potassium source in brine 2, where K_2SO_4 (Sigma Aldrich, 99%) was used. These artificial brines represent two typical compositions in the lithium reserves in Central Altiplano (Bolivia),[40] and they were used in our previous study using $Na_2S_2O_3$ as reducing agent.[30]

Table 2. Molar compositions of the artificial brines studied in this work.

Brine	**LiCl**	**NaCl**	**KCl**	**K_2SO_4**	**$MgCl_2$**
1	0.06 M	4.0 M	0.2 M	-	0.3 M
2	0.2 M	2.4 M	-	0. 3 M	1.3 M

X-ray diffraction characterization

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker D2 Phaser diffractometer equipped with a 300 W (30 kV-10 mA) Cu Kα radiation source with a Bragg-Brentano configuration. Scans were done at 5.3 ° min^{-1} for 2θ values from 10° to 50°.

Electrochemical characterisation in Li-half cells

Li_xFePO_4 electrodes were prepared by mixing the active material ($LiFePO_4$ as received or as obtained from the lithiation reaction of $FePO_4$), carbon black (Timcal SUPER C65) and polyvinylidene fluoride (PVDF, Solef® 5130) in a weight ratio of 80:10:10. Slurry inks were prepared using N-methyl-2-pyrrolidone (NMP) as solvent. The slurry was mixed under 2000 rpm for 5 minutes with a planetary mixer (THINKY ARE-250). This last process (2000 rpm for 5 minutes) was repeated three times to obtain a homogeneous mixture. Subsequently, the resultant slurry was hand coated on an aluminum foil (Advent Research Materials, thickness = 0.125 mm, 99%) with a K-bar to a wet thickness of 200 µm. Prior to the coating, the aluminum foil was roughened with a P1200 sandpaper to improve adhesion. The electrodes were dried in a vacuum oven at 80 ºC overnight and then, punched (precision punch, Nogami) with a 11 mm diameter die and calendaring to 10 tonnes (Specac). The active material mass loading was ≈ 3-4 mg cm^{-2}.

The electrochemical tests were performed in PFA Swagellok® type cells, previously dried at 80 ºC overnight. The cells were assembled in an argon glove box (≤ 0.1 ppm H_2O; ≤ 0.1 ppm O_2), using the Li_xFePO_4 electrodes as working electrodes and a lithium foil (Rockwood Lithium, 100 µm thickness, cut in 12 mm diameter discs) as both counter and reference electrode. The electrolyte was 150 µL of 1.0 M lithium hexafluorophosphate solution ($LiPF_6$) in ethylene carbonate (EC) and dimethyl carbonate DMC with a volume ratio EC/DMC =1/1 (LP57, PuriEL). Two glass fibers (Whatman®, grade GF-F, 12 mm diameter) were used as separators. Aluminium current collectors were used for the Li_xFePO_4 electrodes, whereas copper collectors were used on the lithium side. Li_xFePO_4 electrodes and GF-F separators were dried under vacuum at 120 ºC for 48 hours in a Büchi tube oven before being introduced in the glovebox.

The cells were placed in a Memmert climatic chamber set to 25 °C and electrochemical measurements were done with a VMP2 multichannel potentiostat (BioLogic). Galvanostatic cycling with potential limitations (GCPL) between 2.7 and 4.1 V vs Li^+/Li were performed at a C-rate of C/10 corresponding to a specific current (normalized by the mass of Li_xFePO_4 active material) of 17 mAh g^{-1}.

Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS analysis were performed on a Thermo Scientific X-Series II spectrometer to determine the amounts of Li^+, Na^+, K^+ and Mg^{2+} present in the Li_xFePO_4 solids. Samples were digested in 2 ml of a solution of 20 wt.% of HCl (Sigma Aldrich, ACS grade, 37%) and 20 wt.% HNO_3 (Sigma Aldrich, ACS grade, 70%) in ultrapure water (18.2 MΩ cm, Suez, Select). The mixture was stirred at 60 °C for 2 hours. PFA volumetric flasks with screw caps were used for the digestions. The flask and stirrer were washed with ultrapure water previously to each experiment.

RESULTS AND DISCUSSION

Kinetics of lithium sequestration by $FePO_4$ induced by Na_2SO_3 or $Na_2S_2O_4$

The reaction of sequestration of lithium onto a $FePO_4$ battery host driven by Na_2SO_3 (reaction 5) or $Na_2S_2O_3$ (reaction 3) produces $LiFePO_4$ as a reaction product. The reaction was characterised by mixing $FePO_4$ power (FP, as obtained after de-lithiation of $LiFePO_4$, LFP), the reducing agent (Na_2SO_3 or $Na_2S_2O_3$) and a lithium salt (Li_2SO_4), with initial concentrations of 0.375 M $FePO_4$, 1.5 M Na_2SO_3 or $Na_2S_2O_3$ and 0.75 M Li_2SO_4. Under these conditions, the initial concentration of reducing agent and Li^+ are 4 times higher than that of $FePO_4$, thus ensuring that the reaction of lithium sequestration does not produce a significant change in the concentrations of reducing agent and Li^+, while enabling the full conversion of $FePO_4$ into $LiFePO_4$. The reaction was stopped after 20 minutes, 1 hour or 24 hours, and the solid powder reaction product was filtered, dried and characterised by XRD, electrochemical measurements in Li-half cells and ICP measurements of the digested solid. Table 3 shows the result of the evaluation of the lithium molar content on the Li_xFePO_4 powder sample using these three techniques. The kinetics of the lithium sequestration reaction are fast, since almost full lithiation is achieved in one hour for both reducing agents.

Table 3. Lithium molar content, x, of Li_xFePO_4 samples obtained by lithiation of $FePO_4$ from the reaction product of 0.375 M $FePO_4$ + 0.75 M Li_2SO_4 + 1.5 M $Na_2S_2O_3$ or Na_2SO_3 after different reaction times, as indicated, as estimated from ICP (a), electrochemical (b) and XRD (c) measurements.

Reducing agent	**20 min**	**1 h**	**24 h**
$Na_2S_2O_3$ ref.[30]	0.29^a 0.25^b 0.22^c	0.86^b 1.00^c	1.02^b 1.00^c
Na_2SO_3	0.78^a 0.74^b	0.92^a 0.90^b 1.00^c	0.98^a 1.00^b 1.00^c

Figure 2 shows some examples of the XRD characterisation, illustrating that nearly full conversion to $LiFePO_4$ is obtained with both reducing reagents after 1 hour of reaction time, since the characteristic diffraction peaks associated to $FePO_4$ have fully disappeared and the diffraction peaks associated to $LiFePO_4$ have appeared after the reaction.[30]

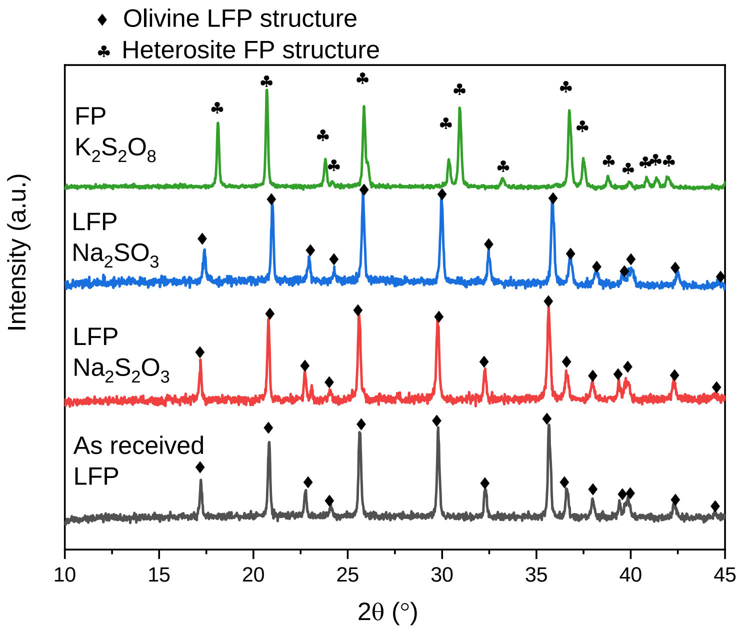

Figure 2. XRD patterns of the Li_xFePO4 solid powders obtained from the reaction product of 0.375 M $FePO_4$ + 0.75 M Li_2SO_4 + 1.5M $Na_2S_2O_3$ or Na_2SO_3 after 1 hour of reaction time. The diffractograms of the as received $LiFePO_4$ (LFP) powder and of $FePO_4$ (FP) obtained from chemical delithiation of LFP using $K_2S_2O_8$ are also shown for comparison.

Electrochemical testing in Li-half cell cells was also performed to quantify the extent of lithium insertion into the $FePO_4$ host. For that purpose, the Li_xFePO_4 reaction product powder was dried and mixed with carbon and binder to produce composite electrodes that were cycled against a lithium metal electrode in Swagelok cells in an organic carbonate electrolyte (LP57). Figure 3 illustrates an example of the galvanostatic removal of lithium from the electrodes prepared with the Li_xFePO_4 reaction product obtained using Na_2SO_3 as the reducing agent at different reaction times. The capacity associated with the first electrochemical extraction of lithium from the Li_xFePO_4 electrode is proportional to the amount of lithium present initially in the electrode, according to the Faradays's law. The lithium content in Li_xFePO_4 was obtained taking into account that the as received, fully lithiated $LiFePO_4$ produces an experimental capacity of 160 mA h g^{-1}.

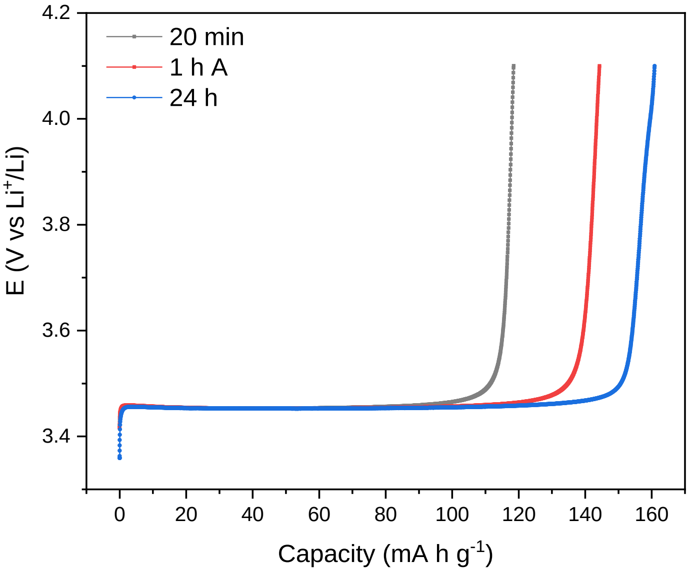

Figure 3. First charge (delithiation) curves of Li_xFePO_4 electrodes obtained from the reaction product of 0.375 M $FePO_4$ mixed with 0.75 M Li_2SO_4 and 1.5 M Na_2SO_3 with different reaction times. Specific current: 17 mA g^{-1} (C-rate of C/10).

Figure 4 shows examples of the galvanostatic cycling done with electrodes made with the Li_xFePO_4 obtained from the chemical insertion driven by $Na_2S_2O_3$ or Na_2SO_3 after 24 hours of reaction time. The electrochemical data in figure 4a shows that full lithiation of $FePO_4$ was obtained with both reducing agents after 24 hours of reaction time, since the first lithium extraction capacities were the same as in the as received $LiFePO_4$. Further cycling of the samples is shown in figure 4b, showing good cycling stability, in good agreement with the measurements with the as received $LiFePO_4$. The good electrochemical performance of the samples obtained after the lithium sequestration reaction indicates that the present approach could also be applied for the direct recycling of battery electrodes.[41,42] For example, the addition of a reducing agent could be used to recover fully lithiated $LiFePO_4$ from a battery containing used Li_xFePO_4 electrodes that could have inhomogeneities in the lithium content (or state of charge), due to, for example, the presence of regions of the electrode with poor or no contact with the current collector as a result of electrode structural degradation.

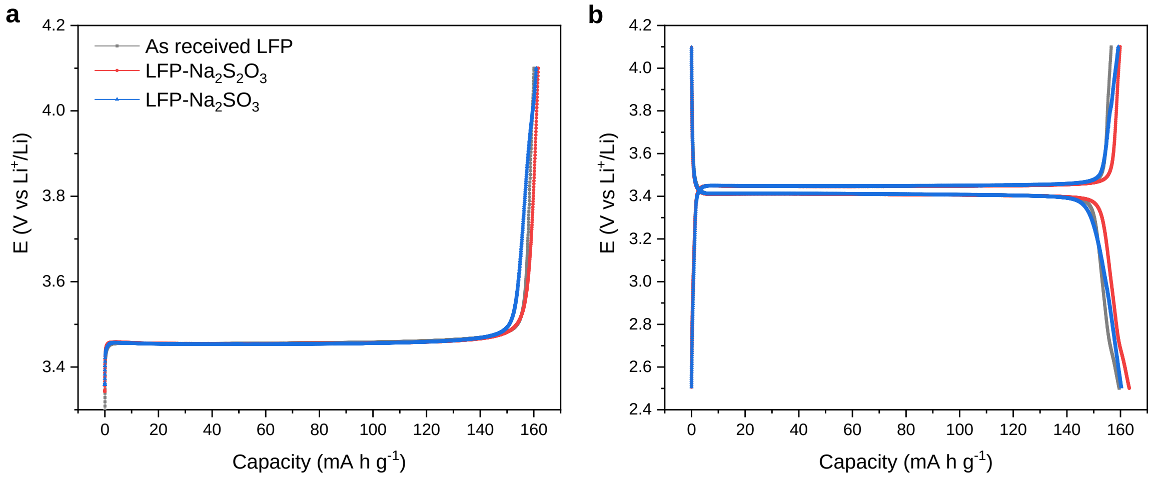

Figure 4. First charge (a) and first discharge and second charge (b) curves of Li_xFePO_4 electrodes obtained from the reaction product of 0.375 M $FePO_4$ mixed with 0.75 M Li_2SO_4 and 1.5 M $Na_2S_2O_3$ or Na_2SO_3 with 24 hours of reaction time. The curve of the as received $LiFePO_4$ (LFP) is also shown for comparison. Specific current: 17 mA g^{-1} (C-rate of C/10).

Selectivity of lithium sequestration from brines induced by Na_2SO_3 or $Na_2S_2O_3$

Critical for the success in the implementation of the novel method of lithium production proposed here is a high selectivity for lithium sequestration from solutions containing other ions. Therefore, the selectivity was studied by performing the lithium extraction experiments in solutions mimicking the composition of natural lithium brines, which typically contain sodium, magnesium and potassium in much higher concentration than lithium, see table 2. Although the electrochemical insertion of sodium into the $FePO_4$ structure obtaining $NaFePO_4$ has been reported by several authors,[43–48] it is kinetically slower than the formation of $LiFePO_4$, [27,48–50] and it has been suggested that the introduction of small amounts of lithium in the $FePO_4$ structure could block the insertion of sodium ions.[51] On the other hand, the insertion of magnesium or potassium into $FePO_4$ seems to be prevented.[27] In order to assess the applicability of the new reducing agent proposed here for commercial applications, two artificial brines were used with similar compositions to those found in lithium reserves in Central Altiplano (Bolivia).[40]

Figure 5 shows the XRD patterns of the solids obtained by reaction of $FePO_4$ in brines in the presence of 0.3 M Na_2SO_3 after 24 hours of reaction. The characteristic peaks of the olivine $LiFePO_4$ structure were the only peaks observed for both artificial brine compositions, indicative of the complete chemical insertion of lithium ions forming $LiFePO_4$ only. The insertion of Na^+ into $FePO_4$ would produce characteristic diffraction peaks associated to olivine $NaFePO_4$,[44] which are not observed experimentally. The insertion of any other cation in the $FePO_4$ structure, including the insertion of protons, would also produce the appearance of diffraction peaks at different reflection positions,[52] and therefore, it can be excluded too. Figure 6 shows the results of the electrochemical characterisation, showing the same behavior as the as-received $LiFePO_4$ sample, which again confirms the formation of fully lithiated $LiFePO_4$ as the reaction product. Similar results were previously reported using the same experimental conditions but with $Na_2S_2O_3$ as reducing agent.[30]

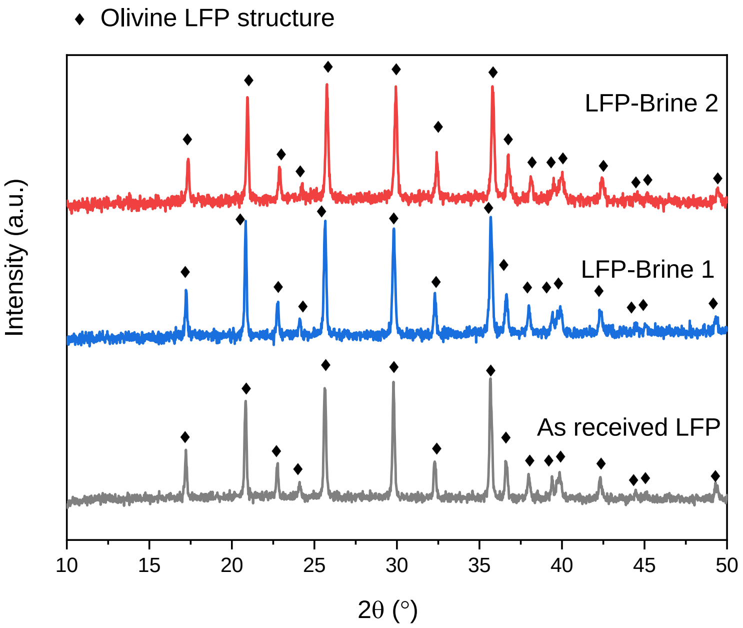

Figure 5. XRD patterns of the Li_xFePO_4 solid powder obtained from the reaction of $FePO_4$ in brines with 0.3 M Na_2SO_3 after 24 hours of reaction. The diffractograms of the as received $LiFePO_4$ (LFP) powder is also shown for comparison.

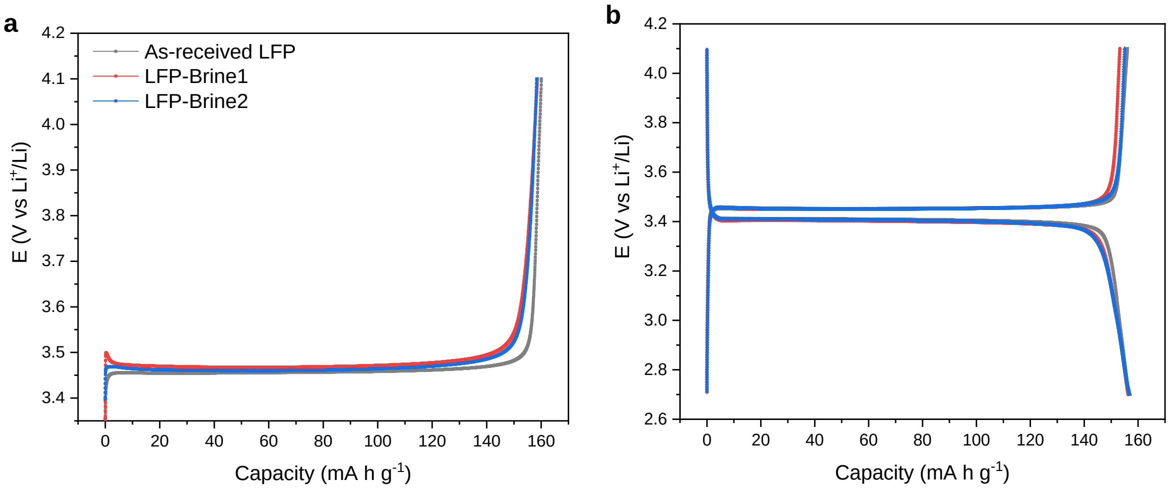

Figure 6. First charge (a) and first discharge and second charge (b) curves of Li_xFePO_4 electrodes obtained from the reaction of $FePO_4$ in brines with 0.3 M Na_2SO_3 after 24 hours of reaction. Curves of the as received $LiFePO_4$ (LFP) are also shown for comparison. Specific current: 17 mA g^{-1} (C-rate of C/10).

Table 4 compares the results of ICP elemental analysis of the digested Li_xFePO_4 obtained with the two different brines using Na_2SO_3 as reducing agent; the results using $Na_2S_2O_3$ are also included for comparison purposes. The values of Li, Na, K and Mg uptake reported here have been defined as the amount of ion, in mg, normalized to the mass, in g, of the absorbing material ($FePO_4$). For full lithiation of $FePO_4$, forming $LiFePO_4$, the Li uptake is expected to be 46 mg g^{-1}. Table 4 shows that, for both reducing agents (Na_2SO_3 and $Na_2S_2O_3$), the Li update is indeed close to 46 mg g^{-1}. Furthermore, it is observed that the uptake of other cations is very small, thus demonstrating the high selectivity for lithium.

From the ICP results, it is useful to calculate the molar ratio of lithium ion and other cations (M = Na^+, K^+ or Mg^{2+}) in the solid ($[Li^+]_{solid}$:$[M]_{solid,}$ see values in table 4). This can, then, be compared to the molar ratio of lithium and other cations in solution ($[Li^+]_{solution}$:$[M]_{solution,}$ see table 4). Clearly, lithium is a minority component in solution (that is, in the artificial brines), because the values of $[Li^+]_{solution}$:$[M]_{solution}$ are very small. But then lithium becomes the majority component in the solid (that is, in Li_xFePO_4) because the values of $[Li^+]_{solid}$:$[M]_{solid}$ are very high. In order to quantify this change in relative abundance of Li with respect to other cations in the solid with respect to the solution, and following our previous work,[30] we have defined the lithium selectivity as the enhancement of the lithium concentration over that of other cations in the solid with respect to the solution:

$$\text{Lithium selectivity} = \frac{[Li^+]_{solid}:[M]_{solid}}{[Li^+]_{solution}:[M]_{solution}} \tag{6}$$

Table 4 shows that the use of Na_2SO_3 produces very high values of lithium selectivity, similar to that with $Na_2S_2O_3$. While the present ICP measurements were done in aqueous solutions, which prevents the evaluation of proton insertion into $FePO_4$, previous experimental and theoretical studies have shown that the insertion of protons or hydrogen into $FePO_4$ is negligible.[52,53]

The ICP results can also be used to calculate the lithium purity in the solid, which equals the uptake of lithium by the solid divided by the sum of the uptakes of all cations. With Na_2SO_3, the lithium purity in the solid equals 94% and 96% for brines 1 and 2, whereas for $Na_2S_2O_3$, it is 90% and 96%. Thus, it is concluded that very high lithium purities in the solid can be achieved by this method: the values of lithium purity compare well with the lithium purity in the recovery solution reported in previous studies (see table 1). Further improvements in lithium purity could be achieved via the optimization of the process and materials. For instance, the $LiFePO_4$ used in this work has been optimized for battery performance in terms of particle size, carbon coating etc., but the properties required are different for lithium production/recycling applications.

Table 4. Li, Na, K and Mg uptakes and lithium selectivity of samples obtained by the reaction of $FePO_4$ with $Na_2S_2O_3$ or Na_2SO_3 in artificial brines 1 or 2 (see table 2) for 24 hours of reaction time.

Reducing agent	**Brine**	**M**	**Uptake (mg g^{-1})**	**$[Li^+]_{solution}$: $[M]_{solution}$**	**$[Li^+]_{solid}$:$[M]_{solid}$**	**Lithium selectivity**
$Na_2S_2O_3$ ref.[30]	Brine 1	Li^+	45.7			
		Na^+	2.5	1:77	61:1	4700
		K^+	1.5	1:3	170:1	510
		Mg^{2+}	0.8	1:5	200:1	1000
	Brine 2	Li^+	46.4			
		Na^+	0.4	1:15	370:1	5550
		K^+	1.4	1:3	180:1	540
		Mg^{2+}	0.2	1:6.5	870:1	5600
Na_2SO_3	Brine 1	Li^+	45.5			
		Na^+	0.9	1:77	164:1	12560
		K^+	0.3	1:3	782:1	2608
		Mg^{2+}	1.9	1:5	84:1	422
	Brine 2	Li^+	44.1			
		Na^+	0.2	1:15	585:1	8773
		K^+	0.2	1:3	1060:1	3181
		Mg^{2+}	1.3	1:6.5	118:1	765

CONCLUSIONS

Na_2SO_3 is shown to be an advantageous reducing reagent to drive the selective sequestration of lithium from natural brines into a $FePO_4$ host battery material, for applications in an alternative and sustainable method of lithium production, as illustrated in figure 1. The kinetics of the lithium sequestration reaction are found to be fast, since full lithiation is achieved in one hour in 1.5 M Na_2SO_3 solutions. The selectivity of the lithium sequestration reaction is found to be outstanding, since in natural brine solutions containing up to 60-fold excess of sodium, 6-fold excess of magnesium and 3-fold excess of potassium, the amount of lithium inserted per gram of solid absorbant is ca. 45 mg/g whereas the uptakes of sodium, potassium and magnesium were below 0.9, 0.3 and 1.9 mg/g, respectively. Consequently, the kinetics and selectivity of the lithium sequestration reactions are comparable to those previously reported using $Na_2S_2O_3$ as reducing agent.[30] However, Na_2SO_3 has advantages in terms of lower cost, reaction stoichiometry that involves less consumption of reagent, non-toxicity and formation of an innocuous reaction product (Na_2SO_4).

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Synopsis: *Selective lithium sequestration from natural brines with a battery material using a novel reducing agent, sodium sulphite, as a sustainable new approach for lithium production.*