Selective Lithium Extraction from Brines by Chemical Reaction with Battery Materials

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ARTICLE TYPE

Selective Lithium Extraction from Brines by Chemical Reaction with Battery Materials

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We demonstrate fast and efficient chemical redox insertion of lithium ions into solid $FePO_4$ from lithium salt solutions contaminated with other cations. The method is illustrated with sodium thiosulfate, $Na_2S_2O_3$, as a reducing agent that is found to have an optimum redox potential for this reaction. The method shows a very high selectivity for lithium extraction; enrichment in lithium concentration *vs.* other ions of more than 500 is achieved under the conditions relevant to lithium extraction from brines.

It is clear the Earth contains enough lithium to supply lithium batteries for widespread use in electric vehicles; what is debateable is which resources can be used and at what cost. Lithium extraction from the largest deposits is currently too complex, slow and inefficient to be economical[1,2]. This is mainly because the high cost of extracting lithium from chloride-based brines, in which lithium is diluted by up to 1:100 by mass in other metal ions such as sodium, magnesium and potassium[3]. Recycling of lithium is an attractive idea that is ripe for research and development. In both cases the requirement is an inexpensive process for concentrating and refining lithium from dilute sources containing other metal cations.

Current lithium extraction from salt lake brines involves pre-concentration by evaporation for 12-24 months, followed by treatment with lime (CaO) to remove magnesium and sodium carbonate (Na_2CO_3) to precipitate out lithium carbonate[2,4,5]. In addition to being slow, the process only recovers around 50% of the lithium, and it is unsuitable in the presence of high concentrations of magnesium and sulphate. Another method based on ion exchange techniques uses manganese dioxide as a lithium-ion absorbent or lithium-ion sieve, but the process is usually not limited to Li^+-H^+ exchange reaction; redox reactions causing the dissolution of manganese ions from the adsorbent during the acid treatment also take place, and hence, the adsorbent is difficult to reuse.[6-10] A few recent studies investigated lithium extraction by application of an electric current between two battery electrodes, but that approach requires large-area electrodes and a small solution volume and it is very time consuming due to the slow diffusion of highly diluted ions.[11-13]

The process investigated here involves the topotactic insertion of lithium cations into heterosite $FePO_4$ from a lithium salt solution, which is the discharge reaction for the well-known lithium iron phosphate rechargeable battery. The product, crystalline $LiFePO_4$ in the olivine phase is more stable than its sodium analogue (sodium insertion takes place at 200 mV less positive potentials[11]), suggesting that the $FePO_4$ lattice may accept lithium in preference to other cations on exposure to lithium salt solutions contaminated with other cations. An enhancement of the proportion of lithium in the structure relative to other mobile cations in solution may also be achieved kinetically because of the high mobility of lithium in the structure, as shown in fast discharge reactions; this suggests that lithium may be selected by controlling the time of exposure of $FePO_4$ to contaminated lithium salt solutions. Indeed, sodium insertion into heterosite $FePO_4$ involves a large volumetric expansion, structural rearrangement and slow kinetics[14-16]. In addition, the presence of a small amount of lithium ions in the $FePO_4$ matrix seems to block the insertion of sodium.[17]

Previous demonstrations of lithium insertion and extraction on $FePO_4$ have been electrochemical, including the case where sodium was deliberately introduced[11,13-16]. In this work, we demonstrate that lithium ions can be selectively extracted from brines by chemical insertion into $FePO_4$. This approach overcomes some of the limitations of the electrochemical method, such as the slow rate of diffusion of lithium cations in solution into an electrode structure at low concentrations, ohmic drop losses and interference of side reactions such as water electrolysis. As we will show below, the chemical approach is a fast and easy one-pot process that appears to be easy to scale up. In this work, we have demonstrated the concept with sodium thiosulfate as a mild, water-stable reducing agent (Reaction 1) that provides the driving force for lithium insertion into $FePO_4$ (Reaction 2). The overall chemical reaction (Reaction 3) is therefore investigated as an alternative to electrochemical lithium insertion into $FePO_4$ as a selective absorbent.

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^- \quad E^0 = 0.08\text{V vs. SHE}^{18} \qquad (1)$$

$$Li^+ + FePO_4 + e^- \rightleftharpoons LiFePO_4 \quad E^0 = 0.4\text{V vs. SHE}^{11} \qquad (2)$$

$$2Li^+ + 2FePO_4 + 2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2\,LiFePO_4 \qquad (3)$$

To complete the process, the lithium is recovered as lithium sulfate solution, using potassium persulfate as the oxidant according to equation (4) as previously described[19]. Alternatively the $LiFePO_4$ product may be used directly in a lithium ion battery. Both approaches are considered in this work.

$$2LiFePO_4 + K_2S_2O_8 \rightleftharpoons 2FePO_4 + Li_2SO_4 + K_2SO_4 \tag{4}$$

The aims of this work are:

1. to determine the rate of lithium extraction from lithium salt solutions as a function of concentration of lithium and thiosulfate.
2. to measure the ratio of lithium to other cations inserted into the structure as a function of the ratio in solution.
3. to demonstrate effective cycling of regenerated $LiFePO_4$ as a positive lithium ion battery electrode.

The kinetics of lithiation of $FePO_4$ from aqueous Li^+

The formation of $LiFePO_4$ by lithium insertion into $FePO_4$ from various solutions was attempted with a 4-fold molar excess of the solution reagent over the solid absorbant. 1g samples of the washed, dried product were taken and characterised by X-ray diffraction (XRD). Fig. 1 is an example of the XRD pattern of a partially lithiated product, showing the presence of both heterosite $FePO_4$ and olivine $LiFePO_4$ structures (Fig. S1). Rietveld refinement of the data provides an estimate of the extent of lithiation, as defined as the phase % of the olivine vs. the heterosite structures (Table 1).

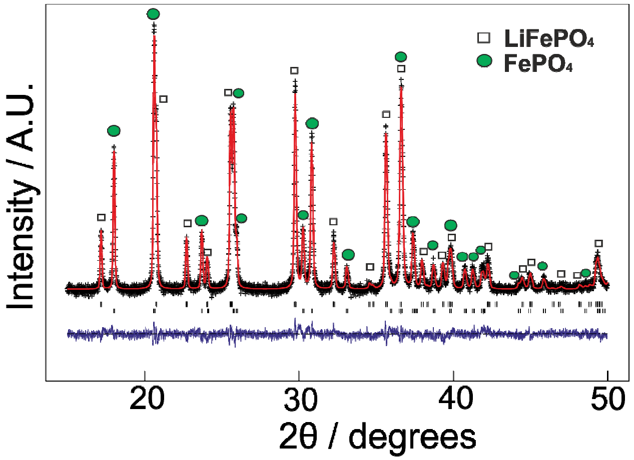

Fig.1. Fit to XRD data of Li_xFePO_4 obtained by lithiation of $FePO_4$ with 0.7M $Na_2S_2O_3$ + 0.35M Li_2SO_4 for 120 minutes. Black line is the experimental data, red line is the fit and blue line is the difference. Upper tick marks and ☐ show the allowed reflection positions for $LiFePO_4$ and lower tick marks and ● for $FePO_4$.

Table 1. Lithium molar content of Li_xFePO_4 samples obtained by lithiation of $FePO_4$ with a 4-fold excess of reagent (Li_2SO_4 + $Na_2S_2O_3$ in molar ratio 1:2) for different times, as indicated, as estimated from XRD (a), electrochemical (b) and ICP (c) measurements.

$[Li_2SO_4]$	5min	20min	60min	120min	240min	600min
1.5M	0.08^a 0.09^b 0.10^c	0.28^a 0.41^b	1.00^a 0.82^b	1.00^a 1.02^b	1.00^a 1.02^b	1.00^a 1.10^b 0.95^c
0.75M	0.00^a 0.02^b	0.22^a 0.25^b 0.29^c	1.00^a 0.86^b	1.00^a 1.00^b	1.00^a 1.00^b	1.00^a 1.02^b
0.35M	0.00^a 0.02^b	0.00^a 0.04^b	0.31^a 0.28^b 0.32^c	0.44^a 0.50^b 0.47^c	1.00^a 1.00^b	1.00^a 1.01^b
0.15M	0.00^a 0.02^b 0.03^c	0.00^a 0.01^b	0.00^a 0.05^b	0.00^a 0.04^b	0.00^a 0.12^b	0.48^a 0.50^b 0.54^c

An independent estimation of the extent of lithiation was obtained by electrochemical measurements. The powder samples were made into lithium ion cathodes by mixing with binder and conductive additive then incorporated into cells with lithium anodes. Electrochemical potentiometric titration was used to determine the molar lithium deficiency with respect to $LiFePO_4$ according to Faraday's law (Fig. S2). This could be done by either oxidative removal of lithium or by the reductive insertion of lithium, both methods providing consisting results. Fig. 2 illustrates an example of the galvanostatic removal of lithium, where higher values of the specific charge are associated with higher molar lithium content, and Table 1 summarizes the resulting values.

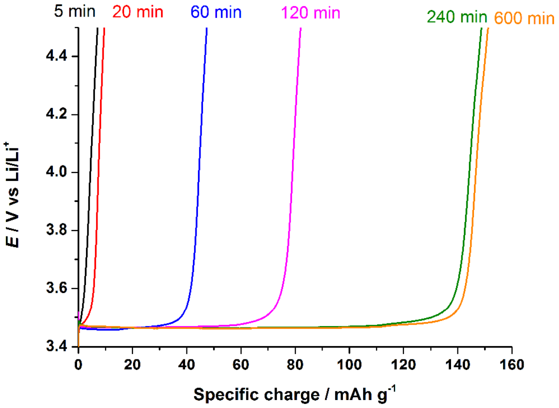

Fig. 2 Potentiometric titration of Li_xFePO_4 electrodes prepared with the reaction product of $FePO_4$ in 0.7M $Na_2S_2O_3$ + 0.35M Li_2SO_4 for different times, as indicated. Specific current: 17 mA/g (C/10).

A third estimation of the lithium content in the Li_xFePO_4 reaction product was obtained by digesting the product with 0.2M HNO_3 + 0.2M HCl in order to dissolve Li_xFePO_4 into $xLi^+ + Fe^{3+} + PO_4^{3-}$. The solution was then diluted and examined by ICP-MS to give the lithium concentration, from which the lithium molar fraction in the solid sample was calculated (Table 1).

Table 1 clearly shows that lithiation $FePO_4$ to form $LiFePO_4$ occurs relatively quickly in aqueous solution. This corresponds to a lithium uptake of 45 mg of Li^+ per gram of $FePO_4$ solid absorbent. This value of the lithium uptake is much higher than that obtained with most other types of absorbents, with the exception of some advanced manganese oxide ion-sieves that absorbed up to 38- 46 mg Li per gram of absorbant.[20-23] In addition, it is clear from Table 1 that consistent values of the lithium content are obtained from all three methods. This strongly indicates that contamination of the sample with other cations (sodium) is only minor, since sodium inserted in $FePO_4$ would contribute to the electrochemical measurements but not to the ICP-MS analysis. Furthermore, olivine $NaFePO_4$ would lead to additional reflection positions in the XRD pattern (Fig. S3). A more quantitative analysis of the lithium selectivity is presented below. From the experiments presented here it can be seen that, for example, complete lithium insertion in less than 3 hours requires $[Li^+]>0.7M$ and $[S_2O_3^{2-}]>0.7M$. The kinetic analysis of the results (Fig. S4) suggests a reaction rate which is first order with respect to both lithium and thiosulfate concentrations with an overall second order rate constant of around 0.03 min^{-1} M^{-2}.

It is also important to point out that the process of lithium insertion and extraction from $FePO_4$ could be repeated several times without noticeable changes in the structural stability of the adsorbant (Fig. S5).

Determination of the lithium selectivity

In the previous section, we have shown that one can form $LiFePO_4$ from $FePO_4$ in lithium-containing solutions. Here, we will analyse the presence of contaminant ions, such as sodium, magnesium and potassium, in the reaction product. For that purpose, we have performed a chemical analysis of the solid products via digestion of the solid followed by ICP-MS analysis. First of all, we studied the contamination by sodium ions from solutions of high sodium concentrations. We performed the lithiation of $FePO_4$ in solutions with $[Li^+]$ to $[Na^+]$ ratios varying between 0.1 and 0.01 with a moderate concentration of reducing agent, $[S_2O_3^{2-}]=0.3M$. Table 2 shows the results of the lithium and sodium uptake, as well as the lithium selectivity, as defined as the ratio of lithium to sodium molar concentrations in the solid vs. that in the solution. As presented in Table 2, the composition of the solid is relatively insensitive to the presence of an excess of sodium cations in solution, resulting in remarkably high lithium selectivities as the sodium concentration in solution increases.

Table 2. Li and Na concentrations of samples obtained by treatment of 1g $FePO_4$ for 24 hours with $[Na_2S_2O_3]=0.3M$ + $[LiCl]=0.06M$ + $[NaCl]=5.4M^a$, $2.4M^b$, or $0M^c$.

$[Li^+]:[Na^+]_{solution}$	Li uptake (mg/g)	Na uptake (mg/g)	$[Li^+]:[Na^+]_{solid}$	Lithium selectivity
$1/100^a$	45.3	3.8	40	4000
$1/50^b$	44.8	3.0	48	2400
$1/10^c$	35.1	3.0	39	390

We then studied the selectivity towards lithium insertion obtained with solutions containing lithium, sodium, potassium and magnesium cations in the concentrations observed in natural brines in one of the largest lithium reserves in the world (Central Altiplano, Bolivia)[3]. Table 3 demonstrates that full lithiation of $FePO_4$ can be achieved under those conditions, with remarkable values of the amount of lithium absorbed (around 46 mg/g). Furthermore, the uptake of other ions is very small, and smaller than that reported for manganese oxide sieves.[20,22-25] In conclusion, the method has a very high selectivity towards lithium, leading to an enrichment in lithium concentration vs. other ions of >500 under the conditions relevant to lithium extraction from brines. Since we have observed that the final composition of the $LiFePO_4$ reaction product is not very sensitive to the concentration of ions in solution, it is expected that the lithium selectivity will only increase as the concentration of lithium in solution is made much smaller than that of other ions. Figs. S6-7 show the XRD pattern and electrochemical characterization of the samples, confirming $LiFePO_4$ formation from natural brines and the absence of detectable contaminants.

Table 3. Li, Na, K and Mg concentrations of samples obtained by: a) 0.6g $FePO_4$ with $[Na_2S_2O_3]=0.3M$ + $[LiCl]=0.06M$ + $[NaCl]=4M$ + $[KCl]=0.2M$ + $[MgCl_2]=0.3M$ for 24 hours; b) 1g $FePO_4$ with $[Na_2S_2O_3]=0.3M$ + $[LiCl]=0.2M$ + $[NaCl]=2.4M$ + $[K_2SO_4]=0.3M$ + $[MgCl_2]=1.3M$ for 24 hours. [M] stands for the molar concentration of the metal cation referred in each row, i.e. Na^+, K^+ or Mg^{2+}.

Me	Uptake (mg/g)	$[Li^+]:[M]_{solution}$	$[Li^+]:[M]_{solid}$	Lithium selectivity
Li^+	45.7^a			
Na^+	2.5^a	1/77	61	4700
K^+	1.5^a	1/3	170	510
Mg^{2+}	0.8^a	1/5	200	1000
Li^+	46.4^b			
Na^+	0.4^b	1/15	370	5550
K^+	1.5^b	1/3	180	540
Mg^{2+}	0.2^b	1/6.5	870	5600

Electrochemical cycling of regenerated electrodes

Finally, we tested the applicability of the method for recycling of battery materials in natural brines. We prepared lithium ion electrodes with $LiFePO_4$ obtained by regenerating $FePO_4$ with brines. Fig. 3 shows the results of the electrochemical cycling at different rates. The difference in the charge delivered by the commercial and the recycled $LiFePO_4$ electrodes is smaller than the reproducibility of these measurements, except for the case of the electrode lithiated in brine type b at fast cycling rates, which provides smaller charges.

Conclusions

We have demonstrated the following:

1. The kinetics of lithium extraction by $FePO_4$ from aqueous salt solutions can be described with an overall second order rate constant of 0.03 min^{-1} M^{-2}.
2. The amount of lithium inserted in $LiFePO_4$ can be as high as 46 mg Li per gram of solid.
3. The uptake of other ions such as sodium, potassium and magnesium is <3 mg per gram of solid.
4. Recycled $LiFePO_4$ was found to give satisfactory performance as a positive lithium ion battery electrode.

These conclusions have important implications for both lithium extraction and recycling. This work demonstrates a low cost route to concentrate and purify lithium salts from diluted and contaminated precursors such as natural brines and products of recycling.

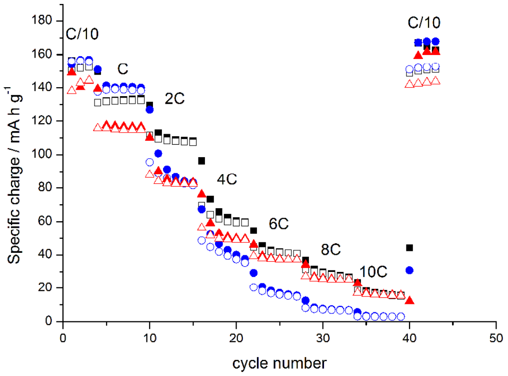

Fig 3. Electrochemical cycling of $LiFePO_4$ at different cycling rates, as indicated. ■ □: electrodes prepared with $LiFePO_4$ (Tatung). ▲ △ : 0.6g $FePO_4$ with $[Na_2S_2O_3]=0.3M$ + brine type a: $[LiCl]=0.06M + [NaCl]=4M + [KCl]=0.2M + [MgCl_2]=0.3M$ for 24 hours. ● ○ : 1g $FePO_4$ with $[Na_2S_2O_3]=0.3M$ + brine type b: $[LiCl]=0.2M + [NaCl]=2.4M + [K_2SO_4]=0.3M + [MgCl_2]=1.3M$. Closed symbols: charge; open symbols: discharge.

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Notes and references:

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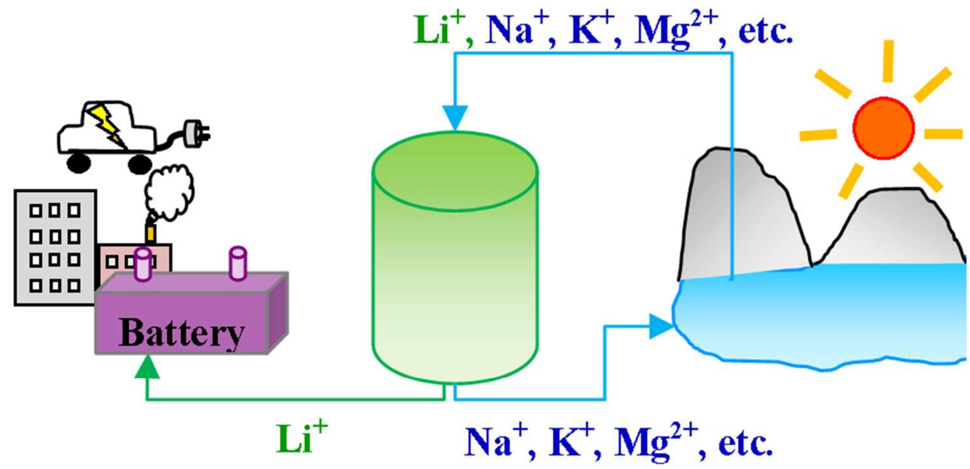

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