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Lithium Extraction from Seawater through Pulsed Electrochemical Intercalation

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HIGHLIGHTS

Li extraction from seawater is demonstrated using electrochemical intercalation

Pulsed electrochemical methods are developed to increase the selectivity of Li to Na

1:1 Li to Na was recovered after the electrochemical extraction from seawater

Pulsed electrochemical methods are developed to realize Li extraction from brines and seawater through intercalation. 1:1 Li to Na is recovered from seawater with Li selectivity of $\sim 1.8 \times 10^4$. The pulse-rest-reverse pulse-rest is also proven to stabilize the electrode structure during co-intercalation, and ten stable extraction cycles are demonstrated.

Article

Lithium Extraction from Seawater through Pulsed Electrochemical Intercalation

Chong Liu,[1,2] Yanbin Li,[1] Dingchang Lin,[1] Po-Chun Hsu,[3,7] Bofei Liu,[1] Gangbin Yan,[2] Tong Wu,[1] Yi Cui,[1,4,*] and Steven Chu[5,6,8,*]

SUMMARY

It is highly attractive to develop efficient methods to directly extract Li from seawater to secure the supply of Li. However, high concentration of Na in the seawater poses a great challenge in Li extraction. Here, we developed pulsed-rest and pulse-rest-reverse pulse-rest electrochemical intercalation methods with TiO_2-coated $FePO_4$ electrodes for Li extraction. The method can lower the intercalation overpotential and successfully boost the Li selectivity. Moreover, the pulse-rest-reverse pulse-rest method can also promote electrode crystal structure stability during the co-intercalation of Li and Na and prolong the lifetime of the electrode. We demonstrated 10 cycles of successful and stable Li extraction with 1:1 of Li to Na recovery from authentic seawater, which is equivalent to the selectivity of $\sim 1.8 \times 10^4$. Also, with lake water of higher initial Li/Na ratio of 1.6×10^{-3}, we achieved Li extraction with more than 50:1 of Li to Na recovery.

INTRODUCTION

The fast development of energy storage technology and electronics has boosted global lithium (Li) demand to ~180,000 tons of Li carbonate equivalent in 2015, with projections as high as 1.6 M tons by 2030[1,2] where 1.4 M tons of the demand will be used in Li-ion batteries for electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs).[3] By 2030, 28% of light-duty vehicles may be EVs and PHEVs, with ~ 80% EVs and by 2040, the majority of new light-duty vehicles sold will be EVs.[4] This switch away from internal combustion engine vehicles is driven, in part, by concerns about climate change due to global greenhouse gas emissions and rising health concerns over particulate matter below 2.5 μm ($PM_{2.5}$) and NO_x emissions from vehicles. Thus, there are a number of incentives to develop cost-effective technology to develop methods to extract Li economically from a wider set of resources.

There are 43.6 M tons of Li on land sources, including 16.7 million tons in ores and 26.9 million tons in brines.[5] The current method to extract Li from brines, which typically have Li concentrations between 100 and 1,000 ppm is based on evaporation and chemical precipitation which is highly time-intensive due to the pre-treatment process to concentrate Li ions. In contrast, there are 5,000 times more Li present in the seawater of above 200 billion tons,[6] but where Li concentration is only 0.180 ppm. More recently, Li obtained from water produced in oil and gas extraction has also been considered.[7] In the US, 2.5 billion gallons of water are produced each year during oil extraction.[8] Assuming a concentration of 100 ppm Li in the produced water, there are 0.350 million tons of Li in the produced water that potentially be recovered each year.

Context & Scale

Li demand will increase dramatically in the coming decades due to global climate change and energy crisis. Seawater contains 5,000 times more Li than the combination of ore and brine-based resources. However, the chemically similar Na is four orders of magnitude more concentrated than Li, which poses a significant challenge in Li extraction selectivity. Here, we develop pulsed-rest and pulse-rest-reverse pulse-rest electrochemical methods using intercalation chemistry to extract Li from seawater with TiO_2-coated $FePO_4$ electrodes. The pulsed electrochemical methods can lower the intercalation overpotential and successfully boost the Li selectivity. Moreover, the pulse-rest-reverse pulse-rest method can also promote electrode crystal structure stability during the co-intercalation of Li and Na and prolong the lifetime of the electrode. We demonstrate successful and stable Li extraction with 1:1 of Li to Na recovery from authentic seawater.

In addition to the refining of Li ores and the evaporation and chemical precipitation of brines, there are research efforts to develop sorbent materials such as MnO_2[9] or H_2TiO_3[10] to adsorb Li. Also, there was work to develop dialysis membranes for Li extraction.[11,12] However, the performance still needs to be improved greatly. Electrochemical Li extraction emerges as an attractive route for Li extraction, which can potentially utilize renewable energy to power the electrochemical processes. In electrochemical Li extraction, Li can be driven by an electric current into electrode materials[13–16] or through Li selective membranes.[17] For most of the study using electrode materials, the focus was on highly concentrated Li brine with Li to Na concentration ranging from 0.001 to 1. Real seawater condition with much lower Li concentration is rarely tested. A more efficient Li extraction technology that directly extracts Li from seawater, or from produced water or brine lake sources without the time-consuming evaporation process would greatly increase the Li production capacity to meet the anticipated demand for Li in the coming decades.

Here, we report the use of the TiO_2-coated $LiFePO_4$ electrode combined with a pulsed electrochemical method to extract Li with high selectivity through intercalation chemistry. The intercalation chemistry naturally provides a high selectivity of Li to Na because Li can provide higher structural stability in $FePO_4$ and has faster ion diffusivity.[18,19] The TiO_2 coating was used to increase the interface contact between the working electrode and seawater. The pulsed electrochemical method lowered the overpotential to drive the intercalation of Li into the $FePO_4$ crystal structure hence increase the selectivity and structural stability. Starting from an authentic seawater sample obtained at Half Moon Bay, California, we have demonstrated 10 cycles of stable Li extraction with 1:1 Li/Na ratio. This is equivalent to a molar selectivity as high as 1.8×10^4. Besides seawater, we also demonstrated the use of electrochemical intercalation method to extract Li from a higher initial Li to Na molar ratio solutions as well as lake water. We achieved 50.2% $\pm$ 0.78%, 94.3% $\pm$ 4.0%, ~100%, and 98.1% $\pm$ 1.0% Li/(Li + Na) recovery from solution which has Li/Na ratio of 5.4×10^{-5}, 5.0×10^{-4}, 4.0×10^{-3}, and natural salt lake water, respectively.

RESULTS

The procedure of extracting Li from seawater using electrochemical intercalation is illustrated in Figure 1. In the first step, a host material was used as the working electrode to allow Li intercalation into the crystal structure. The host material selection must follow the rules that during lithiation and delithiation, its potential should be within the water stable window. Seawater has a pH of 8.2, which sets the water stable window to be −0.48 V versus standard hydrogen electrode (SHE) to avoid H_2 evolution and 0.75 V versus SHE to avoid O_2 evolution (as shown in Figure 1A).[20–22]

In this work, we chose $FePO_4$ from delithiated $LiFePO_4$ as the working electrode. The potential plateau of lithiation and delithiation with 1M Li salt solution for $FePO_4$ is ~3.4 V versus Li metal, which is 0.36 V versus SHE and is stable in seawater.[23] Moreover, there is also selection criteria for the pairing counter electrode during the Li extraction cycle. First, an O_2 evolution electrode needs to be eliminated due to several reasons. (1) It can induce significant pH change to the seawater environment. Li-ion (~25 μM) comparing with hydroxide ion (~1 μM) has a higher concentration in seawater, even if 10% of the Li is extracted, it would induce a significant acidification effect to seawater environment. (2) The dissolved O_2 would diffuse to the negative electrode and get reduced to peroxide species. The O_2 reduction reaction in seawater (0.20 V versus SHE)[20] happens at a slightly higher potential to Li intercalation when considering the real seawater Li concentration of 180 ppb so that the O_2

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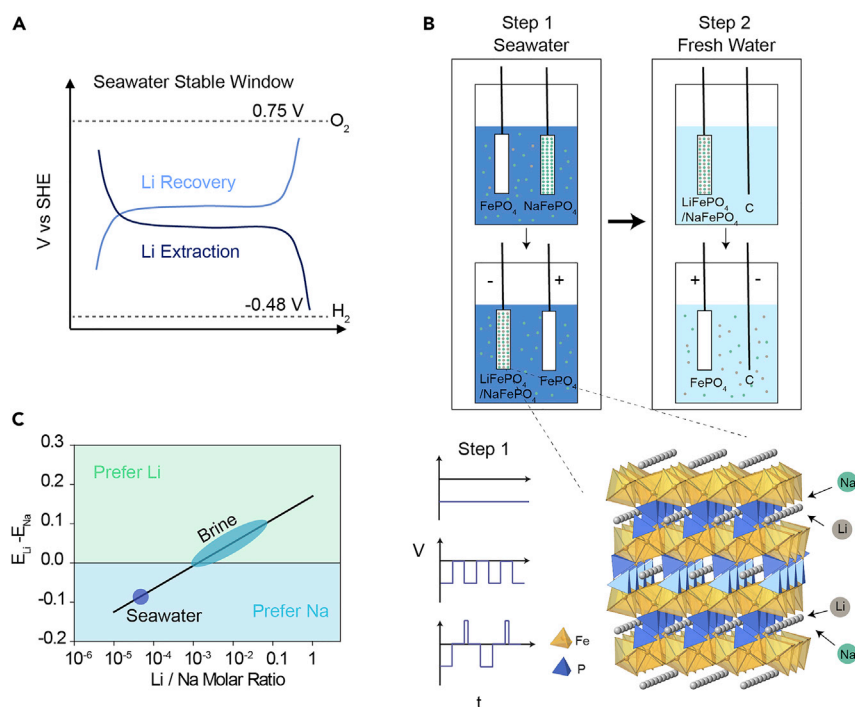*Correspondence: yicui@stanford.edu (Y.C.), schu@stanford.edu (S.C.)

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Figure 1. Li Extraction from Seawater by Electrochemical Intercalation

(A) Schematics showing the water stability window marked by H_2 and O_2 evolution reactions in seawater.

(B) Schematics showing the Li extraction steps. First, $FePO_4$ electrode and $NaFePO_4$ electrode were used as working and counter electrodes in seawater for Li intercalation with a high selective preference for Li over Na. Then, the working electrode was regenerated in a fresh solution to recovery the Li extracted. Voltage profiles used in different electrochemical methods (continuously on, pulsed-rest, and pulsed-rest-reverse pulse-rest) are shown.

(C) Calculation of the Li and Na intercalation potential difference at difference initial Li to Na molar concentration using $FePO_4$ electrode.

reduction reaction would reduce the faradic efficiency of Li extraction on the negative electrode (as shown in Figure S1). (3) The peroxide species would damage the $FePO_4$ electrode permanently.[24]

We chose $NaFePO_4$ as the counter electrode. Na will be released into seawater during the Li extraction cycle. Since the amount of Na released from the electrode is in much less concentration comparing with background Na, this could minimize the environmental impact to seawater. During the Li extraction step, the two electrodes were put into seawater and the system was kept in an N_2 atmosphere (Figure 1B). $FePO_4$ was the negative electrode to allow Li ions to intercalate into the crystal structure. In the second step, the $FePO_4$ electrode filled with Li will be placed into a fresh water-based recovery solution, and Li will be released into the solution by a reverse bias while the $FePO_4$ electrode was regenerated.

The challenge of Li extraction from seawater lies in the background of Na ions. Li has a similar chemistry to Na but a much lower concentration. $FePO_4$ has a Li intercalation potential of ~0.36 V versus SHE while it has a Na intercalation potential of ~0.19 V versus SHE.[25] This thermodynamic preference of Li intercalation could compensate for a molar concentration difference of ~0.0012 Li/Na. In brines or salt lake water, where the Li to Na concentration ratio is ~ 0.0018 to 0.3, the intercalation chemistry is supposed to have near 100% selectivity from the calculation as shown in Figure 1C.

In the case of seawater, the concentration of Li is ~ 0.180 ppm comparing with $\sim$10,800 ppm for Na. The low concentration ratio of 5×10^{-5} of Li/Na would not compensate for the thermodynamic preference of Li intercalation, so the Na intercalation would compete with Li to be intercalated into the electrode. On the other hand, the kinetics of Li and Na intercalation offers another preference for Li. The activation barrier difference between Li and Na diffusion is $\sim$0.05–0.2 eV with Na possessing higher activation energy barrier.[19,26,27] Considering the competition between Li and Na, different strategies were taken to promote Li intercalation in this paper.

First, to increase the electrode and electrolyte (seawater) contact, we introduce a hydrophilic coating to the surface of $FePO_4$ after the electrode fabrication. Here, we chose amorphous TiO_2 as the coating material which was deposited by atomic layer deposition (ALD). It was shown that the diffusivity of Li in amorphous TiO_2 was on the same order as $FePO_4$; therefore, the thin coating would not increase the activation barrier for Li diffusion.[28] Also, the TiO_2 has a smaller Li diffusion barrier comparing with Na, which could help improve the selectivity of Li to Na.[29] Two thickness, 3 and 5 nm of TiO_2 coating were investigated compared with the bare $FePO_4$ electrode. The thin layer of TiO_2 coating did not change the electrode conductivity significantly as shown in the electrochemical impedance spectroscopy (Figure S2). The electrode resistance was 1.53, 6.08, and 4.65 Ω for 0, 3, and 5 nm of TiO_2 coated $FePO_4$. During the seawater lithiation cycle, it is obvious from the potential curve (shown in Figure 2A) that both 3 and 5 nm of TiO_2 coatings have lowered the overpotential for Li insertion. We then tested the Li and Na recovered from the electrode through a delithiation process in freshwater solution. It is shown in Figure 2B that the Li/(Li + Na) molar ratio was $30.2\% \pm 2.1\%$, $48.0\% \pm 1.9\%$, and $44.9\% \pm 7.4\%$ for $FePO_4$ electrode with 0, 3, and 5 nm of TiO_2 coating. Since the 3 nm TiO_2 coating gave the highest selectivity, we adopted this condition for all the later electrochemical method selection tests. The coating test points to the fact that the activation barrier for Na intercalation is higher than Li so that lowering the overpotential could help promote Li intercalation.

The next strategy we adopted to improve the selectivity of Li extraction is optimizing the electrochemical lithiation method. Different electrochemical intercalation method would lead to different overpotentials to drive the Li extraction process. We compared the constant current lithiation method to pulse-rest and pulse-rest-reverse pulse-rest methods. For the pulse-rest method, 10 s lithiation with 10 s rest (P_{10s}) and 1 s lithiation with 1 s rest (P_{1s}) was tested. The potential curves are shown in Figure 2C. For the same capacity of Li extraction, both pulse-rest method P_{10s} and P_{1s} showed ~ 0.05 V smaller overpotentials than the constant current method. The electrode impedance was similar in all tests (shown in Figure S3). As a result, the recovered Li/(Li + Na) molar ratio was higher in pulsed electrochemical methods P_{10s} and P_{1s} of $49.7\% \pm 0.35\%$ and $47.4\% \pm 5.1\%$ than that in the constant current method of $31.4\% \pm 1.7\%$ (Figure 2D). The pulsed lithiation method gave the electrode a rest period for Li and Na to redistribute among all the particles in the electrode and ensured a more uniform Li/Na content in all the particles, which improved the electrode homogeneity and reduced the overpotential of intercalation.[30–32] Besides the pulse-rest method, the pulse-rest-reverse pulse-rest method was also tested. In this method, in one cycle there is both forward pulse and reverse pulse. The forward pulse and its rest periods are both 10 s and the reverse pulse with the same amplitude and its rest periods are 2 and 10 s ($P_{10s}R_{2s}$), respectively. The reverse pulse is often used in the electrochemical process to create a more uniform concentration front.[33,34] The selectivity of this pulse-rest-reverse pulse-rest method was $50.2\% \pm 0.78\%$ as in Figure 2D. It is also higher than the constant current method. The introduction of pulsed electrochemical methods was successful in
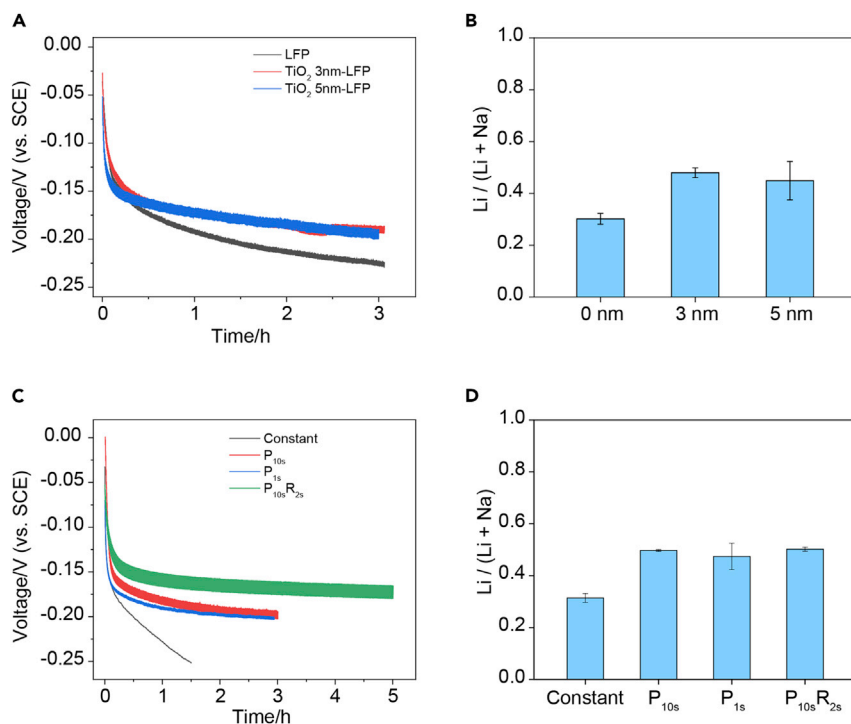
Figure 2. Li Extraction Selectivity

(A) Intercalation potential curves in seawater of $FePO_4$ electrodes with 0, 3, and 5 nm of TiO_2 coating.

(B) Li selectivity results using $FePO_4$ electrodes with different thicknesses of TiO_2 coatings.

(C) Intercalation potential curves in seawater using $FePO_4$ electrodes with 3 nm of TiO_2 coating with different electrochemical methods: constant current, P_{10s}, P_{1s}, and $P_{10s}R_{2s}$.

(D) Li selectivity results using $FePO_4$ electrodes with 3 nm of TiO_2 coating with different electrochemical methods. Error bars represent the standard deviation of at least three replicate measurements.

facilitating Li intercalation rather than Na. In the three pulsed methods, the first cycle selectivity was similar to an extraction ratio of Li/Na of ∼1:1 which is equivalent to the selectivity of Li to Na of 1.8×10^4 from seawater.

The cycle stability of the three pulse electrochemical methods (P_{10s}, P_{1s}, and $P_{10s}R_{2s}$) was also studied. Identical electrodes were cycled 10 times for each pulsed electrochemical method. Each cycle involved the Li extraction and recovery process. Both Li selectivity and faradic efficiency were measured. During the cycle tests, these three methods showed an obvious difference in stability as shown in Figure 3. In both pulse methods P_{10s} and P_{1s}, the selectivity and Coulombic efficiency showed signs of decline. The decline was faster in the case of P_{1s}. The selectivity started to decline at the 5th cycle from a Li/(Li + Na) molar ratio of ∼50% to 31.9% ± 0.40%. At the 7th cycle, the Li/(Li + Na) molar ratio was only 13.5% ± 0.68%. In P_{10s}, the selectivity started to decline at the 6th cycle and before the 10th cycle, the selectivity was between 30% and 36%. In the 10th cycle, the selectivity dropped to 10.8% ± 0.97%. However, for the case of the $P_{10s}R_{2s}$ method, there was no sign of instability of the electrode, and the selectivity was ∼50% for 10 cycles. The decline in electrode cycle stability in P_{10s} and P_{1s} methods could result from the co-intercalation behavior of Li and Na. During co-intercalation, the diffusivity of Li and Na were different, and this could lead to local jamming from the slower diffusion Na. In contrast, the reverse pulse and rest period would allow Li and Na to redistribute and decrease the local stress of the electrode. Also, we hypothesize that
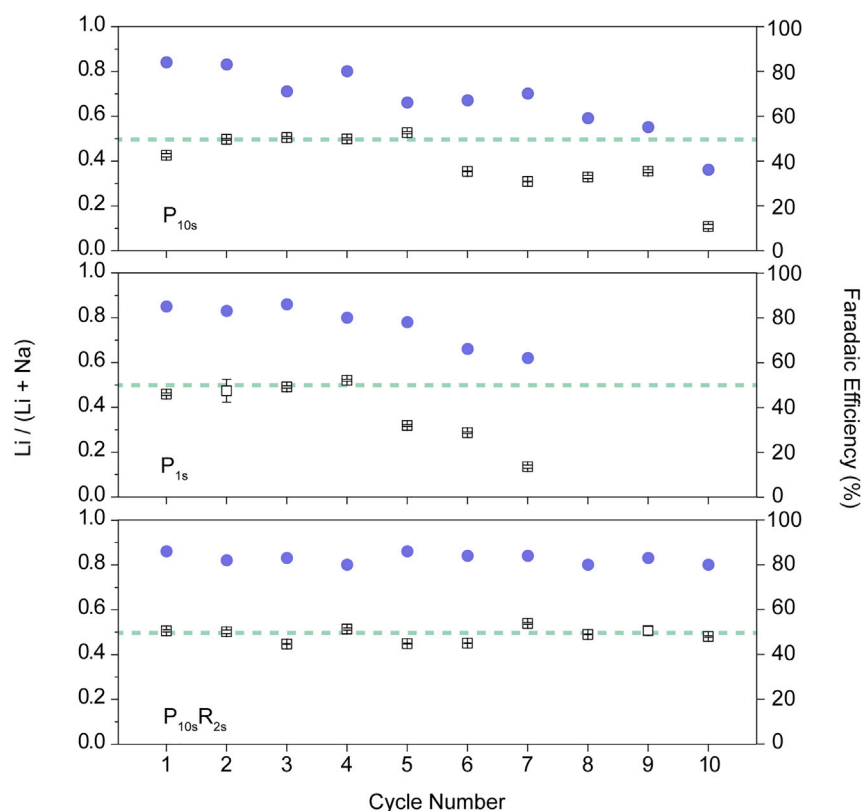
Figure 3. Li Selectivity and Faradic Efficiency Results for the Stability Test Using Different Electrochemical Methods

Error bars represent the standard deviation of three replicate measurements.

the reverse pulse can help remove Na from the electrode because Na deintercalation has a lower potential than Li deintercalation. This is beneficial to enhance the electrode's long-term stability.[30] Also, we did a stability test on the TiO_2-coated $LiFePO_4$ by directly soaking the electrode in seawater for 24 h and measured the electrode Li and Fe content by dissolution. From the Li and Fe concentration, we calculated back the mass loading of the $LiFePO_4$, which is similar to the original mass loading we measured with an error of −2% and +4%, respectively.

The $FePO_4$ particles were characterized in the $P_{10s}R_{2s}$ method using both scanning electron microscopy (SEM) (Figure S5) and transmission electron microscopy (TEM) (Figure 4). Another intercalation was done after the 10th cycle for electrode characterization. From the SEM images, there is only a slight change in the electrode morphology. After SEM imaging, the $FePO_4$ particles were sonicated off the electrode for TEM characterization. Single-particle mapping is shown in Figure 4. Three particles are shown to represent the particles on the electrode. Li element was mapped with electron energy loss spectroscopy (EELS). Na and Fe elements were mapped by energy-dispersive X-ray spectroscopy (EDX). Fe mapping was used as a reference for $LiFePO_4$.

The Li EELS signal showed that the intercalation followed the phase transformation similar to sole Li intercalation in battery cathodes with edges of higher concentration of Li.[35–37] The Na mapping did not give the same feature where edges have higher concentrations. However, it was clear from the mapping that Na existed uniformly in
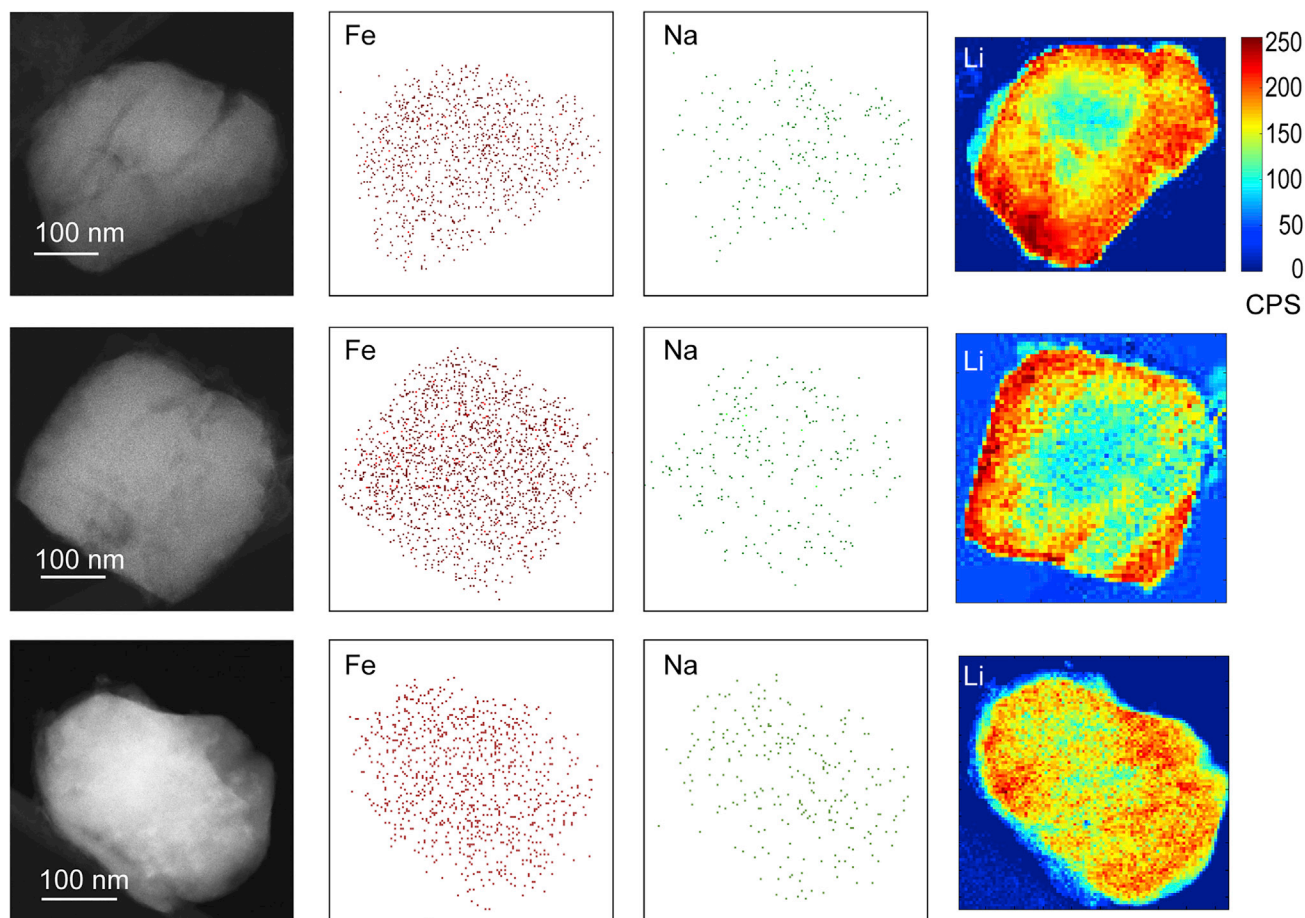
Figure 4. TEM Characterization of FePO$_4$ Particles after 10 Cycles of Li Extraction and Recovery Using P$_{10s}$R$_{2s}$ Electrochemical Method.
From left to right: TEM image of FePO$_4$ particle, Fe EDX elemental mapping, Na EDX elemental mapping, and Li EELS elemental mapping.

the particle surface, which points to the fact of Li and Na co-exist in the structure. The co-intercalation was also confirmed using X-ray diffraction (XRD) shown in Figure S6. The electrode showed both peaks from LiFePO$_4$ and NaFePO$_4$. From the morphology aspect, the particle remained its integrity after cycling, but small cracks were noticed on the particle, which could come from the electrode expansion after intercalation.

Finally, the electrochemical intercalation was demonstrated to work for artificial brines with different Li to Na molar ratio and for salt lake water obtained from Salt Lake in Utah. Artificial solutions with Li to Na ratio of 5.4×10^{-5}, 5.0×10^{-4}, and 4.0×10^{-3} were tested. Li to Na ratio of 5.4×10^{-5} is similar to the seawater case. As shown in Figure 5, using the same P$_{10s}$ electrochemical method, the selectivity was 50.2% $\pm$ 0.78%, 94.3% $\pm$ 4.0%, and ~100% (Na below detection limit), respectively. This points to the thermodynamic preference of Li to Na in intercalation to FePO$_4$ material as shown in Figure 1C. The repetitive extraction using artificial solution with Li to Na ratio of 5.4×10^{-5} is shown in Figure S4. We also collected lake water from Salt Lake in Utah. Through inductively coupled plasma mass spectrometry (ICP-MS) measurement, the lake water contains 21.4 ppm of Li and 4.26×10^4 ppm of Na. Both Li and Na concentrations were higher than that in seawater and the Li/Na ratio is 1.6×10^{-3}. At the same P$_{10s}$ electrochemical method where the current is C/5, the recovered Li/(Li + Na) molar ratio was
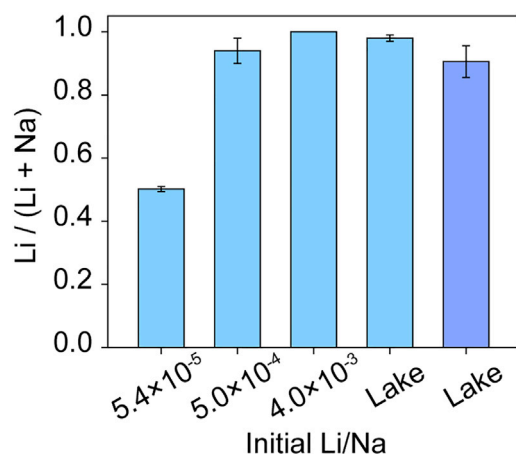
Figure 5. Li Selectivity Results Using P_{10s} Electrochemical Methods and FePO$_4$ Electrode with 3-nm TiO$_2$ Coating in Solutions with Different Initial Li to Na Molar Ratio and Authentic Lake Water

For lake water, two different current rates were tested. C/5 current rate result was shown in light blue (left), and 1C current rate result was shown in darker blue (right). Error bars represent the standard deviation of three replicate measurements.

98.1% $\pm$ 1.0%. A higher current rate of 1 C for the P_{10s} electrochemical method was also tested. The recovered Li/(Li + Na) molar ratio was 90.6% $\pm$ 4.7%. The higher current test represents the case when higher productivity was needed, and the selectivity result showed great potential for the electrochemical Li extraction to be both selective and with high yield in brine mining. In a real application, we expect an additional step similar to that in brine mining to be added after the current recovery step to precipitate Li to Li$_2$CO$_3$ for further use.

DISCUSSION

In summary, we demonstrated the successful extraction of Li from both seawater and salty lake water with the FePO$_4$ electrode using the electrochemical intercalation method. We showed that by lowering the intercalation potential through the hydrophilic coating and also pulsed electrochemical method intercalation, Li selectivity can be enhanced. By using the pulse-rest-reverse pulse-rest method, we achieved 10 cycles of stable Li extraction from seawater with 1:1 Li/Na recovery, which is equivalent to the high selectivity of 1.8 $\times$ 10^4. Although this demonstration of electrochemical Li extraction from seawater shows great potential, deployment of this method would require 100 to 1,000 s of electrochemical cycles before electrode replacement is required to maintain high faradic efficiency. Hence, even a small amount of intercalation of Na into the electrode material after repeated cycles would lead to stress cracks and a loss of electrochemical capacity. We seek to develop improved hydrophilic interface coatings that will serve as a barrier against Na intrusion into the electrode. Furthermore, the filtering of micro, nano, and molecular materials present in seawater (or alternatively salt lake water or produced water from oil recovery) would be necessary to prevent long-term fouling of the electrodes. We believe these obstacles are surmountable, and this work offers the prospect of securing an adequate supply of Li to allow the massive deployment of EVs.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the Lead Contact, Steven Chu (schu@stanford.edu).

Materials Availability

This study did not generate new unique materials.

Electrode Synthesis and Electrochemical Method

The $LiFePO_4$ electrodes were made by coating a paste containing 80% $LiFePO_4$ (MTI), 10% polyvinylidene fluoride (PVDF, MTI), and 10% of conductive carbon black (MTI) onto a 1 cm^2 carbon felt substrate (99.0%, 3.18-mm thick, Alfa Aesar). TiO_2 was coated onto the $LiFePO_4$ electrode using ALD at 200°C, 0.4 Å/cycle in O_2 plasma (Fiji 2, Cambridge Nanotech) with a tetrakis(dimethylamido)titanium (IV) precursor heated at 75°C. To obtain the TiO_2-$FePO_4$ electrode for Li extraction, the electrode was delithiated first in $MgCl_2$ solution with C/5 rate to a cutoff voltage of 0.2 V versus saturated calomel electrode (SCE). Seawater was collected at Half Moon Bay, California and filtered by a 0.2-μm filtration unit (Corning) to remove particles and microorganisms. Li extraction was carried out in a 300 mL filtered seawater in the N_2 atmosphere using either direct current or pulsed electrochemical method at a current rate of C/5 with SCE as the reference electrode and $NaFePO_4$ as the counter electrode. The $NaFePO_4$ electrode was obtained and regenerated by running the intercalation process using a $FePO_4$ electrode in 1 M NaCl solution. In the cycle stability test, for each cycle, the intercalation capacity used was 20% to ensure that Li concentration in seawater did not decrease to below 60% of its initial concentration.

Li Extraction Selectivity

After finishing the Li extraction in seawater and other mentioned conditions, the electrode was delithiated in $MgCl_2$ solution of 50 mM with constant current of C/5 rate to a cutoff voltage of 0.2 V versus SCE with a graphite rod (Sigma-Aldrich, 99.995%) as the counter electrode. The solution before and after the delithiation process was collected for ICP-MS for Li and Na concentration measurement.

Characterization

SEM (FEI Nova NanoSEM 450) with beam energies of 5 kV was used for imaging. All TEM characterizations were carried out using a FEI Titan environmental (scanning) transmission electron microscope (E(S)TEM) operated at 300 kV. The microscope was equipped with an aberration corrector in the image-forming (objective) lens, which was tuned before each sample analysis. XRD (PANalytical Material Research Diffractometer) was carried out using Cu Kα radiation.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.joule.2020.05.017.

AUTHOR CONTRIBUTIONS

C.L., S.C., and Y.C. conceived the concept; C.L. designed the experiments, synthesized the electrodes, and conducted the electrochemical tests and selectivity

measurements; Y.L. conducted the TEM characterization; D.L. helped with electrode synthesis; P.-C.H. and G.Y. helped with electrochemical measurement; B.L. helped with ALD coating; T.W. and G.Y. helped with ICP-MS test; C.L., S.C., and Y.C. analyzed the data and co-wrote the paper. All the authors discussed the whole paper.

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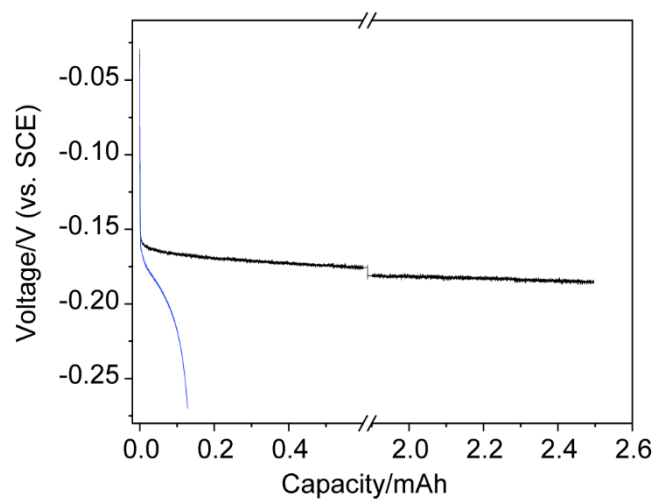
Supplemental Information

Lithium Extraction from Seawater

through Pulsed Electrochemical Intercalation

Chong Liu, Yanbin Li, Dingchang Lin, Po-Chun Hsu, Bofei Liu, Gangbin Yan, Tong Wu, Yi Cui, and Steven Chu

Supplementary Information

Supplementary Figure 1. The potential curve of two 3 nm of TiO_2 coated $FePO_4$ electrodes with similar mass loading running at constant reducing current (C/5 rate) in seawater exposed to the different atmosphere: O_2 (black) and N_2 (blue). When O_2 is present, the reduction reaction is dominated by the O_2 reduction reaction rather than Li intercalation.
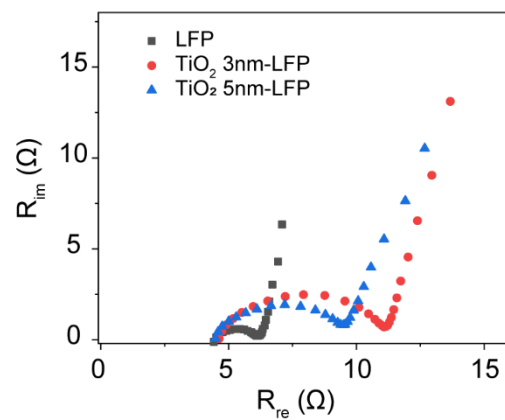
Supplementary Figure 2. Electrochemical impedance spectroscopy of LiFePO$_4$ electrode with 0 nm, 3 nm and 5 nm of TiO$_2$ coating.
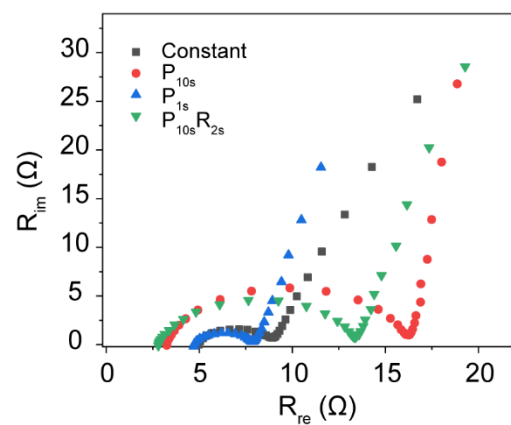
Supplementary Figure 3. Electrochemical impedance spectroscopy of the 3 nm of TiO_2 coated $FePO_4$ electrodes in the selectivity study using different electrochemical methods.
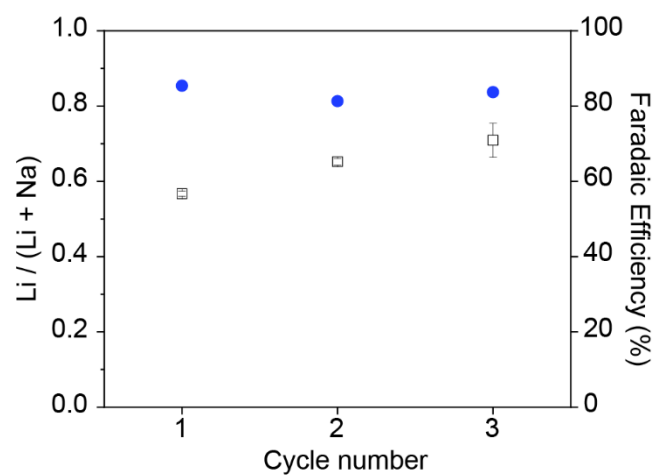
Supplementary Figure 4. Li selectivity and Faradaic efficiency results using simulated seawater of 1:20,000 LiCl to NaCl (total concentration of 0.5 M) and pulse-rest-reverse pulse-rest electrochemical method.
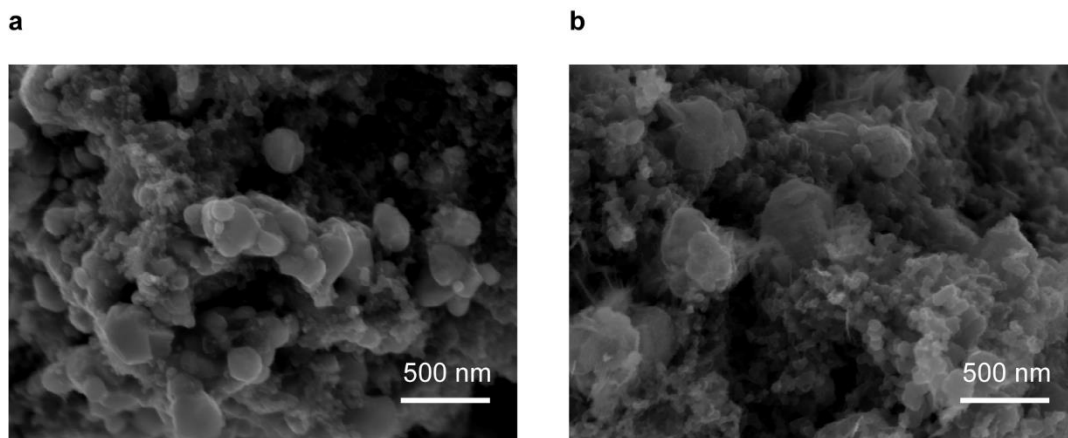
Supplementary Figure 5. SEM images showing the 3 nm TiO_2 coated $FePO_4$ electrodes before (a) and after (b) the 10 cycles stability test using the pulse-rest-reverse pulse-rest method.
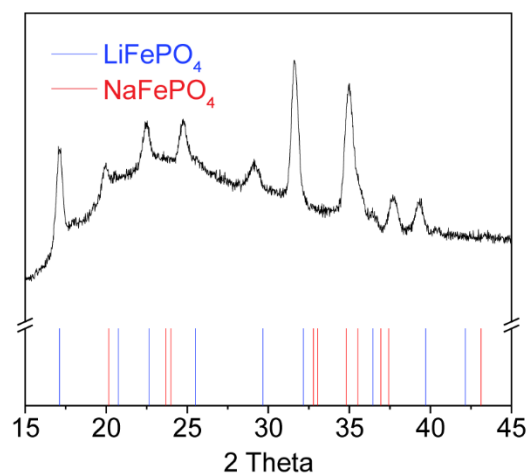
Supplementary Figure 6. XRD image showing the 3 nm TiO_2 coated $FePO_4$ electrodes after the 10 cycles stability test using the pulse-rest-reverse pulse-rest method. $LiFePO_4$ reference (JCPDS 040-1499). $NaFePO_4$ reference (JCPDS 029-1216).

Calculation of Figure 1c.

E_{Li}-E_{Na} potential was calculated from the Nernst equation shown below. E^0_{Li} is 0.36V vs standard hydrogen electrode (SHE) and E^0_{Na} is 0.19 V vs SHE.[1–3]

$$E_{Li} = E^0_{Li} - 0.059 log \frac{1}{[Li^+]}$$

$$E_{Na} = E^0_{Na} - 0.059 log \frac{1}{[Na^+]}$$

$$E_{Li} - E_{Na} = E^0_{Li} - E^0_{Na} - 0.059 log \frac{[Na^+]}{[Li^+]}$$

Electricity cost estimation.

Step 1 Lithium extraction: $FePO_4$ as the negative electrode and $NaFePO_4$ as the positive electrode

Step 2 Li recovery:

Part 2.1 Li recovery: $(Li/Na)FePO_4$ as the positive electrode and C as the negative electrode

Part 2.2 $NaFePO_4$ electrode regeneration: $FePO_4$ as the negative electrode and C as the negative electrode

The cost of Li is

$$E_1 = V_1 \cdot Q_1$$

$$E_{21} = V_{21} \cdot Q_{21}, E_{22} = V_{22} \cdot Q_{22}, Q_1 = Q_{21} = Q_{22}$$

$$Q_1 = \frac{n_{Li} \cdot F}{FE\%}$$

$$C_{Li} = \frac{(E_1 + E_{21} + E_{22}) \cdot P_e}{n_{Li}}$$

The electrochemical cell voltages (the difference between positive and negative electrode) for step 1, 2.1 and 2.2 are V_1 (0.04V), V_{21} (1.2V), and V_{22} (1.4V). The capacity in each step is Q_1, Q_{21}, and Q_{22}. Energy consumption for each step is E_1, E_{21}, and E_{22}. The molar of Li is n_{Li}. F is Faradaic constant, 96485 C/mol. FE% is the percentage of electric current used for Li extraction and we used the selectivity Li/(Li+Na). FE% = 50%. The cost for Li is C_{Li} and the unit price of electricity is P_e. P_e = $0.10/kWh.

Based on the current setup, the electricity cost of Li is estimated to be $2.0/kg. With material and setup optimization, we expect the electricity cost to be significantly lower. Intrinsically, the $V_{21} + V_{22}$ is the water-splitting voltage in our case. Since we used the C electrode, the overpotential is high and the total voltage is 2.6V. Considering a 10 mA/cm^2 current density, with better catalysts, a decrease in 1V is achievabled[4,5].

Additionally, in the real application, renewable energy will be used to power the electrochemical processes with a price of $0.04/kWh[6]. Therefore, the Li electricity cost is decreased to $0.5/kg. The market price of Li is $8-16/kg between 2017 and 2020 and is projected to increase in the coming decades. With electricity cost possibly being <5% of Li price, electrochemical Li extraction shows great potential as an alternative mining method.

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