SUPPORTING INFORMATION

Batteries for lithium recovery from brines

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1. Electrochemical Thermodynamics details

In Figure S1 is reported the schematic representation of the electrochemical system AgCl /

LiFePO₄. The two separated electrochemical reactions can be written as:

$$\operatorname{FePO}_{4(\alpha)} + \operatorname{Li}^{+} + e_{(\alpha)}^{-} \rightarrow \operatorname{LiFePO}_{4(\beta)}$$
 S1

$$AgCl_{(\beta')} + e^{-}_{(\alpha')} \rightarrow Ag_{(\alpha')} + Cl^{-}_{(\epsilon)}$$

Where α is the FePO₄ phase, β the LiFePO₄ phase, ϵ the electrolyte, β ' the AgCl phase and α ' the Ag phase.

α'	β'	з	β	α
Ag	AgCl	LiCl, NaCl and KCl in H ₂ O	LiFePO ₄	FePO ₄

Figure S1. Galvani representation of the electrochemical system

The Gibbs free energy change for the transferring of a species i from a system 1 to a system 2, ΔG_i , in isothermal conditions is equal to the sum of the Gibbs free energy changes of the two systems

$$\frac{\Delta G_i}{RT} = V_1 c_{1,F,i} \ln c_{1,F,i} - V_1 c_{1,I,i} \ln c_{1,I,i} + V_2 c_{2,F,i} \ln c_{2,F,i} - V_2 c_{2,I,i} \ln c_{2,I,i}$$
 S3

where V represents the volume, c_i the concentration of the species i, the subscript 1 and 2 refer to the system 1 and 2, respectively, and the subscript I and F refer to the initial and final state, respectively. The conservation of mass for the transferred species gives:

$$V_{1}c_{1,I,i} - V_{1}c_{1,F,i} = V_{2}c_{2,F,i} - V_{2}c_{2,I,i} = \Delta n_{i}$$
 S4

Where Δn_i represents the total transferred amount of species i. Substitution of equation S4 in S3

and straightforward mathematical manipulation gives:

$$\frac{\Delta G_i}{RT} = V_1 c_{1,I,i} \ln \frac{c_{1,F,i}}{c_{1,I,i}} + V_2 c_{2,I,i} \ln \frac{c_{2,F,i}}{c_{2,I,i}} + \Delta n_i \ln \frac{c_{2,F,i}}{c_{1,F,i}}$$
S5

If the total transferred amount of species i is small with respect to its initial amount in system 1 and big with respect to its initial amount in the system 2, then equation S5 can be simplified with the following formula:

If more species are transferred, the total change in Gibbs free energy is the sum of the individual ΔG_i 's. It is important to mention that equation S6 shows in particular that the process of transferring is thermodynamically favoured until the final concentration in the system 2 is lower than "e" times the final concentration in the system 1. In plain words, no energy is required to concentrate twofold a species, if only a small amount is transferred and $V_1 >> V_2$. These conditions are fulfilled in our experiments. The theoretical required energy was calculated using equation S6 for Li⁺, Na⁺, and Cl⁻, and the results was normalized by the amount of recovered lithium.

2. Calculation of the energy from the integral area

The real energy spent during the experiments was calculated normalizing the integral area in the ΔE vs. q graph by the amount of recovered lithium. In this graph the length of the Li+ capture and release steps have been matched, in fact the capture step lasted always for 2 hours, which correspond to a charge of -2 mAh, but the third step (ion release) had a lower length. As consequence, part of the charge transferred in the first step is lost. This lost is equivalent to circa 0.35 mAh, which corresponds to circa 17% of the total charge exchanged in the first step. The

origin of the difference between in charge between the capturing and releasing step is not yet clear and subject to further study.

3. Water analysis

At the end of the second step a sample of solution of circa 200 µl was analysed. These samples were analyzed by the Wessling Laboratorien GmbH by ICP (Inductively Coupled Plasma).

Abbreviations and methods	ISO Certification	Executive location
Metals / elements in water (ICP-	ISO 11885 / ISO 17294-2 ^A	Environmental Analysis
OES / ICP-MS)		Altenberge
Sulfate in water	EN ISO 10304 D19/D20 ^A	Environmental Analysis
		Bochum
Chloride in water	EN ISO 10304-1 ^A	Environmental Analysis
		Bochum

The solution of the recovery cell contained 50 mM KCl plus the ions, Li^+ , Na^+ and Cl^- released during the experiment. For this reason the K^+ was used as inner standard. The results were normalized by the amount of K^+ and presented as concentration in the recovery cell at the end of the experiment.

4. Electrode preparation and electrochemical characterization

The electrodes were composed by a carbon cloth (CC AvCarb 1071 HCB, Fuel Cell Earth) current collector of $5x1 \text{ cm}^2$, covered by drop casting with a slurry on a geometrical surface of $2x1 \text{ cm}^2$. CC was used to avoid any corrosion problems due to the very aggressive environment. Two mixtures were prepared: the first based on LiFePO₄ (80% w.t), Super-P (10% wt.) and PVdF (10% wt.) for the LiFePO₄ (LFP) electrodes; the second based on Ag particles (85% wt.), Super-P (7% wt.) and PVdF (8% wt.) for the Ag electrodes. N-methyl pirrolidone was added to the mixtures and the resulting slurries were stirred overnight. The drop casted slurries were dried in oven at 100 °C for 1 hour. The final mass loadings for LFP and Ag electrodes are around 20-25 mg/cm^2 and 30-40 mg/cm^2 of active material, respectively.

The electrochemical characterization was carried out in a three electrode cell with Ag|AgCl|KCl (3 M) electrode as reference electrode (RE) through galvanostatic cycling. In the case of LFP electrode, the counter electrode was another LFP electrode with higher loading, which was acting as a source/sink of lithium ions. The CE for the Ag electrode was a platinum wire. The LFP electrode was cycled in a 0.5 M Li₂SO₄ solution between 0.05 and 0.5 V at a current intensity of 1 mA. The Ag electrode was cycled also with a current intensity of 1 mA in the potential range from -0.150 to 0.150 V. Before starting the lithium recovery cycle the LFP electrode was oxidized (lithium was removed) with 1 mA current up to 0.5 V. On the other hand the Ag electrode needed to be reduced (chlorides removed) until -0.150 V and afterwards charged with 2 mA for 15 minutes. In this way the LFP electrode was completely delithiated and therefore ready to start the lithium recovery with the first step (capturing of lithium ions); on the other side on the Ag electrode the small amount of AgCl deposited was acting as a charge buffer.



Figure S2. Electrochemical characterization of the LFP electrode in 0.25 M Li₂SO₄.

The Figure S2 presents the electrochemical characterization of the LFP electrode. It is possible to observe the plateau at circa 0.2 V and its reversibility. As expected, there are no other plateaus until 0.5 V.

5. Brine cell and recovery cell

Two main cells are used in this study: the brine cell (used in the first step) and the recovery cell (used in the third). The brine cell is a 500 ml round bottom flask, which is filled with 300 ml brine. The electrodes are placed as in Figure S3. The recovery cell is made of PMMA and has a volume of circa 350 µl. Its technical schematic is reported in Figure S4.



Figure S3. Schematic representation of the brine cell.



Figure S4. Schematic of cell geometry, all the values given in mm (a). Real picture (b)

6. Consideration about the resistance of electrolyte and limiting currents

The resistance of the electrolyte was checked before every experiment through EIS. The values are 5.4 $\pm 0.2 \Omega$ for the brine cell and 10.6 $\pm 1.3 \Omega$ for the recovery cell. The latter is strongly affected by the variation of the salt concentration during the lithium recovery step. The Figure S5 shows the EIS for a 1/100 sample in the brine cell (a) and in the recovery cell (b), respectively.



Figure S5. Measured potentiostatic electrochemical impedance spectroscopy in the brine cell (a) and in the recovery cell (b)

In Figure S5a the impedance is measured in a three electrode setup between the working electrode and the reference electrode.

In order to take in account the geometry of the cell, the total resistance of the electrolyte was estimated to be circa double of the measured value. On the contrary, in the recovery cell a two electrode setup was used for measuring the impedance, and therefore the total resistance of the electrolyte coincides with the measured value. In Figure S3b it is observed an increase in the value of the impedance, due to the formation of a thick AgCl film on the Ag surface during the precedent step (first step). The energy ohmic losses were calculated in accordance to the Joule's effect with the following Eq.:

$$W = R_s I^2 t$$
 S7

where t is the time (2 h), I the current (1 mA), and R_S the resistance of solution (16 Ω).

In the brine cell, due to the very low concentrations of the lithium-ions, it is foreseen that the system may reach the limiting diffusion currents in the liquid phase. In order to evaluate such effect, the diffusion limiting current of Li^+ in the brine cell, I_1 , is calculated according to the following equation:

$$I_l = nFAD \frac{c_b}{\delta}$$
 S8

where A is the geometrical surface area, D the diffusion coefficient of Li^{+1} , c_b the concentration of Li^+ in the bulk of the solution, and δ the diffusion layer thickness (estimated around 100 µm for systems subject only to natural convection).

The Table S1 shows the energy ohmic losses normalized by the recovered lithium and the diffusion limiting currents in the brine cell for every sample. It can be observed that for the highest concentration of lithium, almost all the energy required (given in table 2 main text) is due

to the ohmic losses, while the limiting diffusion current becomes important already in the 1/1000 sample, and critical for lower concentrations.

Li/Na ratio	$W / Wh mol^{-1} Li^+$	I_l / mA
1/100	0.8	10
1/1000	1.8	1
1/10000	3.4	0.15
0/1	3.8	0.05

Table S1. Ohmic loss calculated from the Eq. S7 and diffusion limiting current calculated from the Eq. S8.

7. Materials

NaCl: BioXtra, ≥99.5% (Sigma-Aldrich) 5 ppm Li

LiCl: Granular, BAKER ANALYZED ACS Reagent ≥99%

Polyvinylidene difluoride (PVdF): Solvay Solexis SolefS 6020 or SolefS 1013

Super-P C65: Timcal

LiFe(PO)₄ (LFP): MTI Corporation EQ-Lib-LFPO

N-Methyl-2-pyrrolidone (NMP): ACS reagent, ≥99.0% (Sigma-Aldrich)

Artificial Brine solution: saturated NaCl, 50 mM PB, pH 8.0

Carbon cloth: AvCarb 1071 HCB, Fuel Cell Earth

Silver particle: Silver powder, spherical, APS 0.5-1 micron, 99.9% (metals basis), Alfa Aesar

References

1. K. Tanaka and M. Nomura, J. Chem. Soc., Faraday Trans. 1, 1987, 83, 1779–1782.