# Sustainable Selective Extraction of Lithium Chloride from Natural Brine Using a Li$_{1-x}$Mn$_2$O$_4$ Ion Pump

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The spontaneous electrochemical extraction of lithium chloride from natural brine of high altitude salt flats in Northwest Argentina and recovery in a dilute electrolyte is demonstrated in two experiments: i) a highly selective LiMn$_2$O$_4$ insertion cathode and polypyrrole anion selective anode (salt capturing) and ii) an LiMn$_2$O$_4$ anode and lithium deficient Li$_{1-x}$Mn$_2$O$_4$ cathode separated by anion selective membrane (selective ion exchange). The entropy driven transfer of LiCl from concentrated brine to a dilute recovery electrolyte has been experimentally studied by ion pumping and the LiCl activity measured in natural brine.
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The increasing demand for lithium due to the growth of the market for energy storage in lithium batteries for portable electronics, electric vehicles and remote electrification using renewable energy sources prompts for new renewable method for its extraction from continental brines and hard rock.

Among the possibilities for the extraction of lithium, electrochemical methods can play a key role. Since the pioneering work of Kanoh and co-workers[1,2] who explored the insertion of lithium ions into an electrochemical Pt/λ-MnO$_2$ cell and studied the insertion/ extraction kinetics from λ-MnO$_2$/LiMn$_2$O$_4$ in LiCl aqueous solutions[3] several efforts have been reported. La Mantia et al.[4–7] introduced entropic cells to extract lithium first with an olivine battery electrode: LiFePO$_4$ cathode and Ag/AgCl reversible chloride anode for the selective recovery process. They have more recently described a nickel hexacyanoferrate anode as alternative to the silver anode[6] and distinguished two cases of selective electrochemical ion pumping: salt capturing, i.e. LiFePO$_4$/AgCl and selective exchange, i.e. LiFePO$_4$/MKNi [Fe(CN)$_6$].[7]

Also a λ-MnO$_2$/Ag battery was reported by Lee and co-workers with artificial brine, and λ-MnO$_2$/activated carbon hybrid super capacitor.[8] A highly selective Li/Na electrochemical process based on the olivine lithium battery cathode material LiFePO$_4$ coated with polydopamine using the I$^-$/I$_3^-$ redox couple separated by a membrane as supply of electrons to reduce the Li$^+$ insertion material has been reported.[9] Hoshino disclosed an electrodialysis method using an ionic liquid based membrane technology[10,11] while a fast and efficient chemical redox insertion of lithium ions into solid FePO$_4$ has been also reported by Owen and co-workers.[12]

In our laboratory a fast, efficient, low environmental impact and low energy alternative electrochemical method for the extraction of lithium chloride from brine or sea water has been developed.[13,14] The two-step electrochemical process extracts LiCl selectively from natural brine in an undivided electrochemical cell with a lithium deficient Li$_{1-x}$ Mn$_2$O$_4$ (x→1), LMO cathode and a chloride ion reversible polypyrrole (PPy) electrode and then recovers high purity LiCl in a dilute electrolyte. We have recently reported the design, simulation and experimental validation of an electro-chemical reactor to accomplish this method.[15]

As depicted in Scheme 1 in the first step the exchange of chloride at the oxidized PPy electrode takes place simultaneously to lithium intercalation in lithium deficient Li$_{1-x}$Mn$_2$O$_4$ with high selectivity, thus extracting LiCl from natural brine. In a second step, after rinsing the electrodes thoroughly the brine electrolyte is exchanged with a dilute LiCl recovery solution and the electrode potential is reversed using electricity from solar panels, so that lithium releases at the Li$_x$Mn$_2$O$_4$ anode and the PPy cathode releases chloride ions.

A similar approach but using an anion selective membrane has been recently reported using symmetric cells comprised of LiFePO$_4$ /FePO$_4$[16–18] and LiMn$_2$O$_4$/ Li$_{1-x}$Mn$_2$O$_4$[19] by combining a totally lithiated anode and a delithiated cathode in two compartments separated by an anion exchange membrane. LiMn$_2$O$_4$ (LMO) has also been reported as a matrix for the isotopic separation of $^6$Li/$^7$Li with the lighter isotope, $^6$Li, preferentially fractionated with an isotope separation factor ranging from 0.989 to 0.971 at 25°C.[20]

In the present communication we disclose new experimental evidence of the spontaneous extraction of lithium using an entropic ion pump based on highly selective LMO electrodes and pseudo-capacitive polypyrrole electrode and also two LiMn$_2$O$_4$/λ-MnO$_2$ system with an anion selective membrane. We show for the first time a direct evidence of the spontaneous uptake of lithium chloride by a lithium deficient LMO electrode and an oxidized polypyrrole electrode in contact with natural brine from Olaroz salt flat (Jujuy Province, Argentina). Furthermore, we show how the current generated by this spontaneous process can be applied to another cell to recover LiCl in a recovery solution using the same electrodes in a diluted LiCl electrolyte under the opposite polarization and what is the maximum concentration that can be recovered when the chemical potential of LiCl equals that of the natural brine. The activity of LiCl in natural brine, has also been measured for the first time. The complex high salinity electrolyte exhibits a very high salting out effect due to the high concentration of NaCl, KCl, MgCl$_2$, etc.

## Experimental

Natural brine from Olaroz, Jujuy (Argentina) and concentrated brine by solar evaporation has been employed with a chemical composition analyzed by ICP-OC given in Table I.

LiMn$_2$O$_4$/Pt electrodes were prepared by thermal decomposition of a LiNO$_3$ and Mn(NO$_3$)$_2$ mixed solution (Sigma Aldrich, Li: Mn molar ratio of 0.5) on a Pt sheet. The Pt substrate was coated with a thin layer of the solution which was first evaporated at 70°C, further heated in air at 650°C for 12 hs and finally cooled down to room temperature, yielding a thin layer of polycrystalline single phase LiMn$_2$O$_4$ characterized by XRD and SEM.[13,14,21]

The chloride reversible polypyrrole counter electrode was obtained by electrochemical polymerization of an aqueous solution of 0.1 M pyrrole/1.2 M HCl on large surface area platinum mesh (Goodfellow PT008710) under potential control at 1V during 1 hour. Aqueous solutions of natural brine, 0.1 M LiCl (Sigma Aldrich) and 0.1 M NaCl (Sigma Aldrich) were used as electrolytes.

Electrochemical experiments were carried out in a three-electrode undivided Teflon cell with a LiMn$_2$O$_4$ working electrode, a polypyrrole/Pt counter electrode and an Ag/AgCl (in KCl 3 M) reference electrode (all potentials herein are quoted with respect to that reference), using an Autolab PGSTAT 30 potentiostat (Autolab, Ecochemie, Holland) equipped with Nova 1.10 software.

Different states of charge were achieved by partial delithiation of LiMn$_2$O$_4$ (or partial lithiation of λ-MnO$_2$) by applying a constant potential until the current was well below 1 μA. In all cases the

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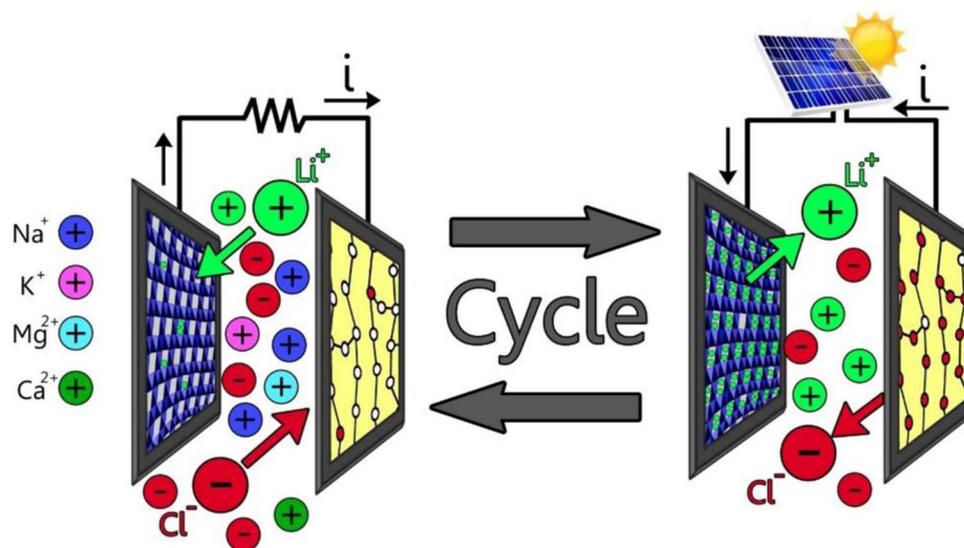
**Scheme 1.** Scheme of the two-step electrochemical extraction of LiCl from brine using a $Li_{1-x}Mn_2O_4$. $Li^+$ insertion electrode coupled to a PPy electrode selective to anions immersed in brine (1st. step) and dilute LiCl recovery electrolyte (2nd. Step).

state of charge (soc) of the $LiMn_2O_4$ electrode was studied by X-Ray diffraction analysis.[14,22]

Partial delithiation of $LiMn_2O_4$ is achieved in 0.1 M LiCl aqueous solution, but then the $Li_{1-x}Mn_2O_4$ electrode is in contact with natural brine of higher lithium chloride activity. The surface composition of the spinel will depend on the chemical potential of LiCl in the electrolyte and therefore instantaneous self-charge is observed from the evolution of the open circuit potential but is limited by the slow diffusion of lithium ions in the solid and further current application.

The cell comprised two 6 mL electrolyte reservoirs separated by a 0.5 mm thick anion exchange membrane (AMI-7001, Membranes International Inc.), with an exchange capacity of 1.3 meq/g in a Teflon cell. The membrane was pre-conditioned by immersion in 0.05 M LiCl during 48 hours. The membrane resistance was 60 $\Omega.cm^2$ as measured by impedance spectroscopy.

At the left compartment a delithiated $Li_{1-x}Mn_2O_4$ electrode, was placed in a natural brine solution. Delithiation was achieved by passing a 25 $\mu A.cm^{-2}$ constant current against a large area polypyrrole electrode in 0.1 M LiCl until a potential of 0.91 V vs. Ag/AgCl; 3M KCl (x = 0.85) was reached.

### Results and Discussion

Using a $Li^+$ insertion cathode and $Cl^-$ reversible electrode, LiCl can be extracted from brine electrolyte by control of the $Mn^{IV}/Mn^{III}$ ratio in the spinel oxide electrode. The extraction reactions are:[13,14]

$$xLi^+ (brine) + Li_{1-x}Mn_{1-X}^{III}Mn^{IV}O_2 + xe^- (cathode)$$

$$\leftrightharpoons LiMn^{IV}Mn^{III}O_4 \qquad [1]$$
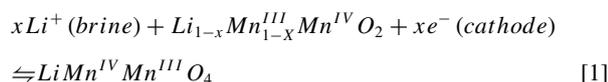
**Table I. Chemical composition of brines analyzed by ICP-OC.**

| Cation | Brine (ppm) | Concentrated Brine |
|---|---|---|
| $Na^+$ | 115.600 | 8.895 |
| $Li^+$ | 1280 | 5.208 |
| $K^+$ | 10.780 | 47.050 |
| $Mg^{2+}$ | 2.618 | 3 |
| $Ca^{2+}$ | 3.609 | 16 |
| $Cl^-$ | 84.980 | - |
| Boron | 783 | 1840 |
| $SO_4^{2-}$ | 11.330 | - |

and,

$$xCl^- (brine) + x\,PP^o (anode) \rightleftharpoons x\left[PP^+Cl^-\right] + xe^- (anode) \qquad [2]$$

and the overal process:

$$xLi^+ (brine) + xCl^- (brine) + Li_{1-x}Mn_{1-X}^{III}Mn^{IV}O_2 + x\,PP^0$$

$$\leftrightharpoons LiMn^{IV}Mn^{III}O_4 \; x\left[PP^+Cl^-\right] \qquad [3]$$
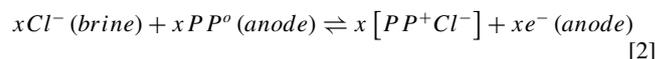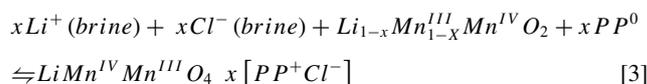
A hybrid $LiMn_2O_4$ battery electrode and carbon high capacitance electrode has been proposed for energy storage supercapacitor. The use of polypyrrole (PPy), as anion selective counter electrode in the present strategy, operates at low overpotential and the lithium extracting device has cell voltage at less than 1 V. Alternatively, an anion selective membrane can be used between $LiMn_2O_4$ electrodes of different state of charge (soc).[19]

The electrode $Li_xMn_2O_4$ (solid)/$LiCl_{aq}$(liquid) has two degrees of freedom, the occupied fraction of lithium, x in the solid and the activity of LiCl in the electrolyte. Since we deal with very different activities of LiCl in brine and recovery electrolytes we need to introduce a formal standard potential, $E_{0.5}^*$ which corresponds to 1M LiCl in the electrolyte and x = 0.5 in the lithium intercalation isotherm of the solid $Li_{1-x}Mn_2O_4$ which is $E_{0.5}^* = 0.867$ V vs. Ag/AgCl; 3M KCl.[21]

Hence,

$$E - E_{0.5}^* = F(x) \quad \text{and} \quad E_{0.5}^* = E^0 + \frac{RT}{F}\ln a_{LiCl} \qquad [4]$$

with $E^0$ and the activity of LiCl in the electrolyte we can obtain any charging curve by displacing vertically the normalized charging curve. In the absence of interactions, for an ideal solid solution, $F(x)^{ideal} = \frac{RT}{F}\ln a_{LiCl}$ given by the mixing entropy. However, in LMO there are electrostatic interactions and the expression of F(x) is more complex with two plateaux as depicted in Figure 1.[22]

### Spontaneous Extraction of LiCl from Natural Brine

We expect the spontaneous uptake of $Li^+$ from lithium containing electrolyte in a $Li_{1-x}Mn_2O_4$/PPy° cell, according to Eq. 3 if electrons are allowed to circulate in the external circuit between PPy anode and LMO cathode. The experiment is depicted in Scheme 2 with a 10 k$\Omega$ resistor load connecting a de-lithiated LMO cathode and a reduced PPy anode both in contact with LiCl containing brine.

During the discharge of the $Li_xMn_2O_4$/ PPy° cell in natural brine the spontaneous extraction of lithium ions at the LMO cathode takes
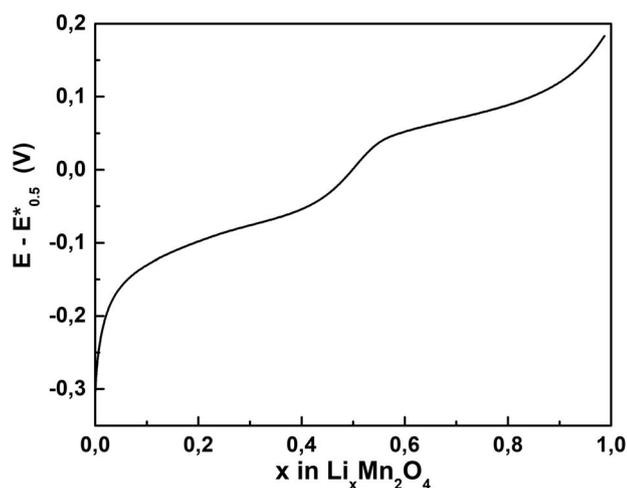
**Figure 1.** Normalized charging curve of $Li_xMn_2O_4$ in 1 M LiCl as a function of soc.
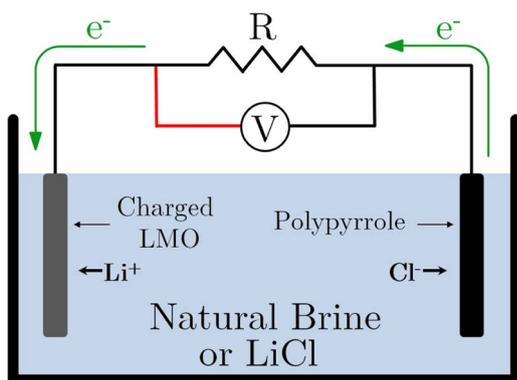


**Scheme 2.** Scheme of an undivided LMO/PPy cell in natural brine connected to an external resistos.
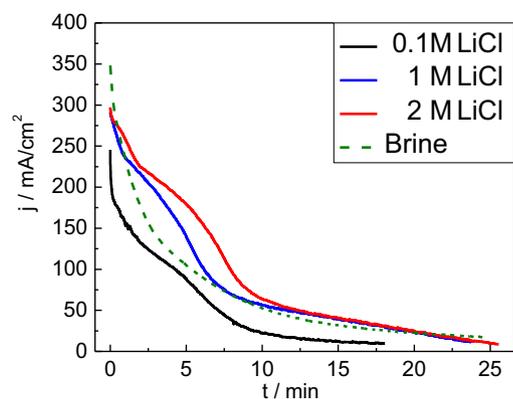


**Figure 2.** Current transients for the spontaneous extraction of LiCl from natural brine using an $Li_xMn_2O_4$ (x →0) and $PPy^+Cl^-$. Electrode area 0.2 cm² and electrolyte volume 6 mL.

place according to:

$$2\lambda - Mn^{IV}O_2 + x\ e^- + x\ Li^+ \rightarrow Li_xMn_x^{III}Mn_{(2-x)}^{IV}O_4 \quad (0 < x \leq 1) \quad [5]$$
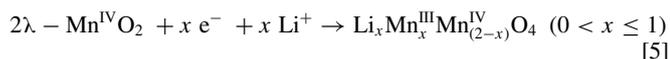
which is coupled to the charge of the polypyrrole anion selective capacitor (Eq. 2) and a current flows in the external circuit for different concentrations of LiCl and natural brine as shown in Figure 2 which demonstrates the spontaneous uptake of lithium chloride.

Figure 3 shows the $Li_xMn_2O_4$ (x →0) - $PPy^+Cl^-$ electrochemical total cell potential, $\Delta E_{cell}$, as a function of the charge integrated from
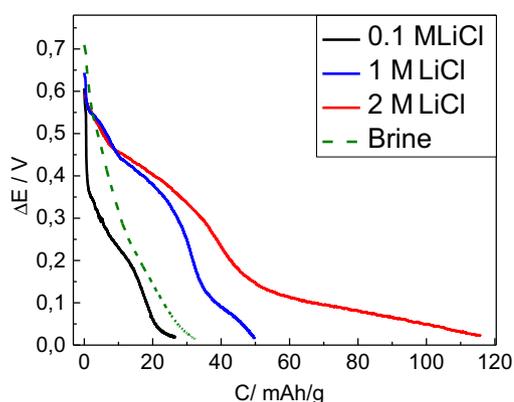


**Figure 3.** Spontaneous, $\Delta E_{cell}$, discharge curves of $Li_xMn_2O_4$ (x →0) and $PPy^+Cl^-$ cell as a function of charge circulated for different LiCl concentrations.
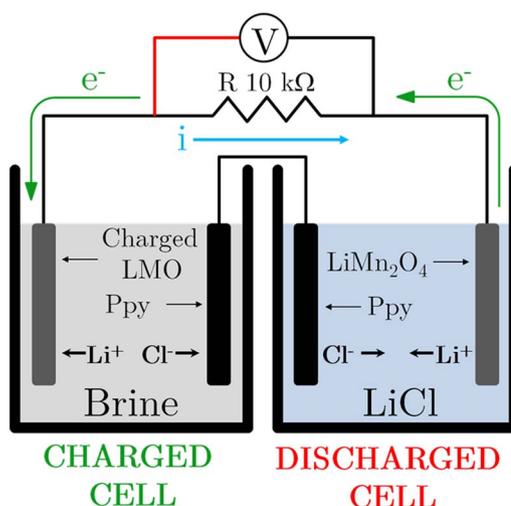


**Scheme 3.** Diagram of a LiCl spontaneous extraction cell (left) connected to a recovery cell (right) in dilute LiCl electrolyte.

the current transients in Figure 2 due to the intercalation of lithium ions in LMO and chloride ions adsorption on $PPy^+$. Notice that the transient curve for natural brine (0.18 M LiCl) lies between those of 0.1 M and 1M LiCl, respectively. The LMO electrode was initially charged with 144 mAh/g by applying a constant current, almost the theoretical 148 mAh/g reaching a potential of 0.91 V. In all the electrolytes, the spontaneous uptake of $Li^+$ ions involved much less charge than the theoretical capacity of LMO, 148 mAh/g due to internal and measuring resistances.

The spontaneous uptake of lithium chloride from lithium containing electrolyte is an energy producing process in the asymmetric hybrid lithium ion battery/supercapacitor configuration.[14] Therefore, the next question is how to use the energy produced in the spontaneous first step of LiCl extraction from brine to drive the LiCl recovery in dilute solution in the second step. As shown in Scheme 3 we have therefore coupled the spontaneous extraction of lithium chloride (left cell) to recovery of LiCl (recharged, right cell) by measuring the current flow across an external 10 kΩ load resistor.

Formally this experiment with two anion selective PPy electrodes is equivalent to the extraction with $Li_{1-x}Mn_2O_4$/anion membrane/ $LiMn_2O_4$ as recently reported,[19] except for the Donnan potential across the membrane and the mass transport overpotential at the membrane. When natural brine is in contact with the electrode in the cell on the left cell compartment and is connected to the electrode in the right compartment by a 10 kΩ resistor there is a spontaneous flow of
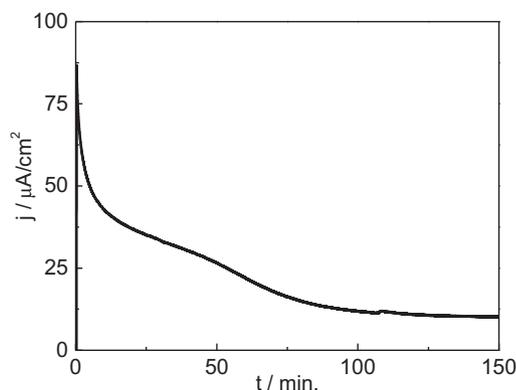
**Figure 4.** Current transient at the cell described in Scheme 3, with natural brine in the left compartment and 0.1 M LiCl electrolyte at the right compartment. LMO electrode area 0.2 cm$^2$, polypyrrole on 4 cm$^2$ carbon felts.



**Scheme 4.** Schematic representation of a double LMO experiment with anion exchange membrane between natural brine and dilute LiCl electrolyte.

current through the external circuit and the current transient is depicted in Figure 4.

The current transient across the external $10\,k\Omega$ resistor is a demonstration of the spontaneous transfer of LiCl from a more concentrated LiCl in the brine electrolyte to a more dilute recovery electrolyte. The driving force for this spontaneous process is the difference in the chemical potential of LiCl in both electrolytes. This experiment is based on the concept of mixing entropy battery as discussed by La Mantia and co-workers.[23] The process will remain spontaneous until the recovery LiCl electrolyte activity equals the activity in the natural brine. Therefore, the next question is what would be the maximum LiCl concentration in the recovery electrolyte to sustain a spontaneous transfer of LiCl from natural brine and at what LiCl concentration in the right hand cell the activity equals the LiCl activity in the complex brine electrolyte. Beyond that concentration external energy for instance from solar panels needs to be supplied to continue the extraction of lithium chloride from brine.

Examination of Scheme 3 shows the movement of ions in the electrolytes and electrons in both polypyrrole electrodes and the external circuit. As Li$^+$ ions are released from the electrode in the left cell, Cl$^-$ ions are adsorbed by the polypyrrole electrode on the same compartment. Since electrons can flow between both polypyrrole electrodes, release of Cl$^-$ ions takes place in the right compartment while Li$^+$ ions are intercalated into the LMO electrode. Thus LiCl is transferred from left to right cell compartments. If we replace the double polypyrrole electrode by an anion exchange membrane selective to chloride ions which can migrate between both compartments, we have the double lithium insertion electrode cell.[19]

### Double LMO Cell with Anion Selective Membrane

The double Li$_{1-x}$Mn$_2$O$_4$ electrode cell as depicted in the Scheme 4 with fully lithiated and delithiated spinel oxide electrodes respectively, has been assembled in two 6 mL electrolyte reservoirs separated by a 0.5 mm thick anion exchange membrane (AMI-7001, Membranes International Inc) in a Teflon cell. At the left compartment a delithiated Li$_{1-x}$Mn$_2$O$_4$ (x = 0.85) electrode, was placed in contact with a natural brine solution. At the right hand side compartment, a fully lithiated freshly prepared LiMn$_2$O$_4$ electrode was immersed in a 0.1 M LiCl recovery electrolyte. Two matched Ag/AgCl; 3 M KCl reference electrodes were placed on both sides of the membrane to monitor any potential drop while operating at open circuit potential or under an applied current.

When both terminals of the cell were connected to a $10\,k\Omega$ resistor a spontaneous current flowed through the external circuit and its evolution together with the potential at each electrode vs. Ag/AgCl were monitored. At start, the electrode potential of the lithiated electrode (right) was 0.56 V while the delithiated LMO electrode (left) was 0.80 V. The spontaneous current flow across $10\,k\Omega$ was followed and
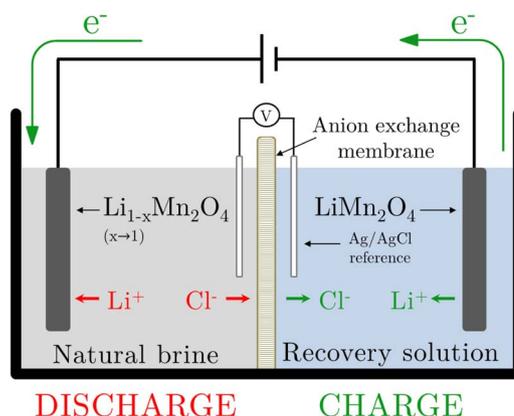
the time dependence is depicted in Figure 5. After 4900 seconds, the end potentials were respectively 0.76 V and 0.72 V with a residual current of 0.7 μA and the total charge circulated was 67 mC.cm$^2$.

Examination of the LMO titration curve in Figure 1 (i.e. electrode potential vs. soc) and the evolution of each electrode potential demonsttrates that the insertion of lithium ocurred at the de-lithiated electrode in contact with the brine while release of lithium took place at the fully lithiated electrode in contact with 0.1 M LiCl. This was further confirmed by lithium ion concentration measurement in dilute solutions by ion chromatography. Therefore, the spontaneous transfer of LiCl from the concentrated brine to the dilute LiCl electrolite takes place.

In another experiment both LMO electrodes of the cell were connected to a potentiostat/ galvanostat and a constant current was applied to the cell while monitoring the cell potential $\Delta E_{cell}$ time evolution. Figure 6 compares the time dependence of $\Delta E_{cell}$ for three applied current densities: 25, 50 and 100 μA.cm$^{-2}$. A positive $\Delta E_{cell} > 0$ implies a spontaneous lithiation process at the Li$_{1-x}$Mn$_2$O$_4$ (x = 0.87) electrode (left) and delithiation of LiMn$_2$O$_4$ (right). Notice that the cell potential becomes zero, $\Delta E_{cell} = 0$, after circulating a charge of 29, 34 and 36 mC.cm$^{-2}$ for 100, 50 and 25 mA.cm$^{-2}$ respectively. The faster the process the less efficient is the transference of LiCl from brine to the recovery solution. From that point on energy must
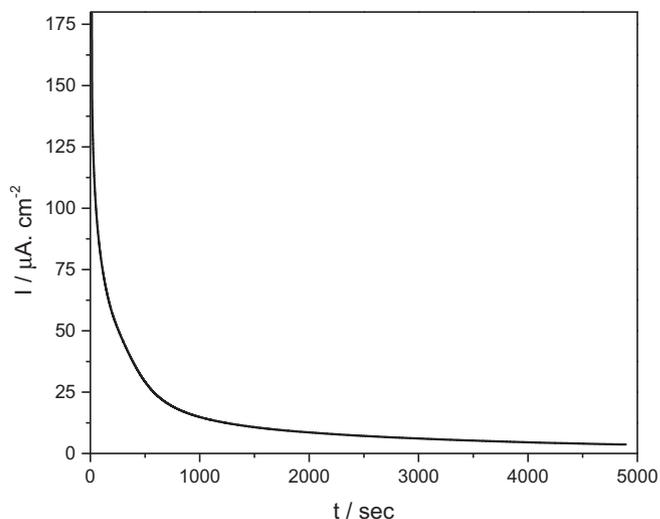


**Figure 5.** Current transient across a $10\,k\Omega$ resistor load for the cell depicted in Scheme 3 comprised of Li$_{1-x}$Mn$_2$O$_4$ (x = 0.87) electrode in brine and LiMn$_2$O$_4$ electrode in dilute 0.1 M LiCl recovery solution separated by anion exchange membrane. A = 0. 2 cm$^2$.
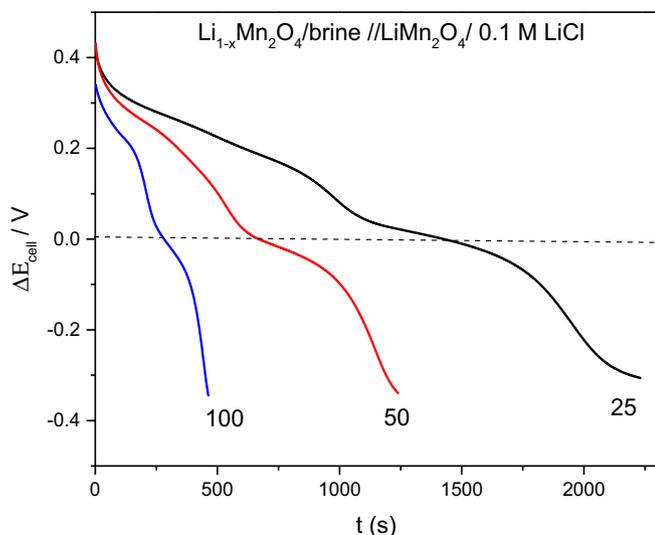
**Figure 6.** Total cell voltage, $\Delta E_{cell}$, time evolution for $Li_{1-x}Mn_2O_4$ (x = 0.87) in brine and $LiMn_2O_4$ in dilute 0.1 M LiCl recovery solution separated by anion exchange membrane for different applied current densities, 25, 50 and 100 $\mu A.cm^{-2}$. A = 0.2 $cm^{-2}$.



**Figure 8.** Cell potential vs. time for $Li_{1-x}Mn_2O_4$ in contact with natural and concentrate brine from Olaroz salt lake respectively and $LiMn_2O_4$ in contact with 0.1 M KCl recovery solution at 50 $\mu A$.

be applied in order to continue extraccion of LiCl from brine and concentration of the recovery electrolyte. The final potential is always $-0.4$ V.

In both experiments, the cathode uptakes lithium ions from natural brine by intercalation producing an excess of chloride ions that migrate to the cathode throught the anion selective membrane.

$$LiMn_{1-x}^{III}Mn_{1+x}^{IV}O_4 + yLi^+ + ye \rightarrow Li_{1-x+y}Mn_{1-x+y}^{III}Mn_{1+x-y}^{IV}O_4 \quad [6]$$
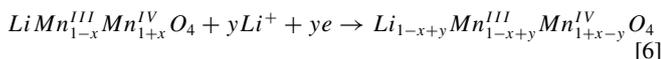
while the anode releases lithium ions into the recovery electrolyte and chloride ions from the cathode compensate charge,

$$LiMn^{III}Mn^{iv}O_4 \rightarrow Li_{1-x}Mn_{1-x}^{III}Mn_{1+x}^{IV}O_4 + xLi^+ + xe \quad [7]$$
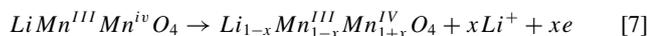
Thus, while electron current flows throught the external circuit the ion current in the electrolyte is depicted in Scheme 4.

The evolution of the respective electrode potentials for each LMO electrode respect to a Ag/AgCl; 3M KCl is shown in Figure 7 as a function of the fraction x of $Li^+$ ions intercalated in the crystal structure of each eletrode (soc). The cell potential $\Delta E_{cell}$, reflects the difference between both electrode potentials, while the anode potential
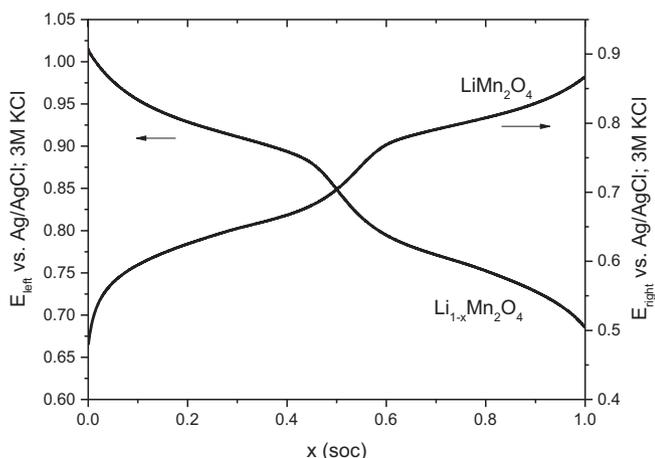


**Figure 7.** Dependence of the electrode potential of both LMO electrodes on the respective state of charge, x.

decreases, the cathode potential increases. When both electrodes reach the same composition, i.e. x = 0.5, then $\Delta E_{cell} = 0$.

We have further investigated the effect of the brine composition on the efficiency of this extraction process. Two different brines were studied: The natural brine from Olaroz salt lake in Jujuy, Argentina and a concentrated sample of that brine under solar irradiation with compositions described in Table I. The electrodes in this case were two platinum plates covered with a slurry containing 80% $LiMn_2O_4$, 10% conducting Vulcan XC-72 carbon black (Cabot Corporation) and 10% PVDF binder in methyl pyrrolidone, and dried with a final mass of 5 mg containing 0.2 mg of lithium in each electrode. One of the $LiMn_2O_4$ electrodes was delithiated electrochemically using a polypyrrole counter electrode, and used as cathode.

In this experiment the lithium defficient cathode was in contact with the respective brines while the fully lithiated $LiMn_2O_4$ was in contact with a recovery 0.1 M KCl electrolyte. Potassium chloride was chosen as background conducting electrolyte to measure the LiCl build up during the process. The electrode surface was 0.2 $cm^2$ in both cases and a 50 $\mu A$ (250 $\mu A.cm^{-2}$) constant current was applied to the cell while monitoring the cell potential, $\Delta E_{cell}$ time evolution and the results are shown in Figure 7.

As expected the brine with larger lithium concentration showed a larger $\Delta E_{cell}$ at the start of the galvanostatic experiment as shown in Figure 8. Similar discharge curves for both lithium battery cathode electrodes were observed but the charge to reach $\Delta E_{cell} = 0$ for the concentrate brine was twice as much that for the natural brine, i.e. 16 mAh/g LMO and 29 mAh/g LMO which nevertheless is less that the theoretical 148 mAh/g for $LiMn_2O_4$.

Within the stability limits of LMO, at constant current the yield of LiCl released at the anode in the recovery solution which should equal the amount intercalated from brine in the cathode is less for the natural brine which contains less lithium and more sodium. This can be rationalized from our previous results, the electrochemical exchange current for the interfacial exchange of lithium ions between the aqueous electrolyte and the $LiMn_2O_4$ solid crystalline structure follows a square root dependence with the lithium ion concentration.[21] Therefore, the larger lithium concentration in the brine the faster the exchange at the solid/electrolyte interface and thus the rate of intercalation/release.[21] Furthermore, we have shown with faradaic impedance spectroscopy that sodium ions in the electrolyte inhibit the exchange of lithium ions at the $LiMn_2O_4$/electrolyte interface due to $Na^+$ adsorption and blocking of lithium adsorption sites at the $LiMn_2O_4$ crystal surface as revealed by XPS.[14]
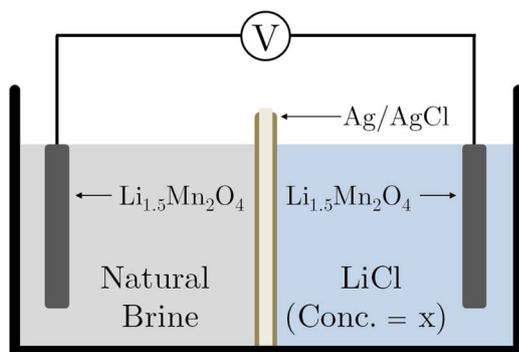
**Scheme 5.** Electrochemical Hemlmholtz cell without transport comprised of two matched $Li_{1.5}Mn_2O_4$ electrodes separated by a double Ag/AgCl electrode.

## Mesurement of LiCl Activity in Natural Brine

As has been shown, the transfer of LiCl from the more concentrated to the dilute solution takes place driven by the chemical potential gradient until both electrodes reach the same potential and hence $\Delta E_{cell} = 0$. Then, the next question would be what is the maximum LiCl concentration in the recovery solution that allows spontaneous ion transfer. In order to determine the lithium chloride concentration in the recovery electrolyte that offsets the ion transfer from the natural brine, the electrochemical Hemlmholtz cell without transport depicted in Scheme 5 has been employed.

Two matched $LiMn_2O_4/Li_2Mn_2O_4$ ($Li_{1.5}Mn_2O_4$) lithium reversible electrodes were placed in natural brine and LiCl recovery solutions of different concentration respectively. Both compartments of the cell were separated by a silver plate coated with AgCl on both faces, which acted as double chloride ion reversible electrode and electronic conductor. The respective half-cell reactions are:

$$LiMn_2O_4\,(s) + Li^+\,(ac) + e^- \rightleftarrows Li_2Mn_2O_4\,(s) \qquad [8]$$

and,

$$Ag\,(s) + Cl^-\,(ac) \rightleftarrows AgCl\,(s) + e^- \qquad [9]$$
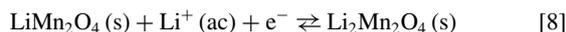
and, the cell potential difference is given by the activities of lithium in brine and LiCl electrolyte respectively:

$$\Delta E = \frac{RT}{F}\ln\left(\frac{a_{LiCl,brine}}{a_{LiCl,recovery}}\right) \qquad [10]$$

Figure 9 depicts the dependence of $\Delta E_{cell}$ with the concentration of LiCl in the electrolyte from which the maximum concentrations of
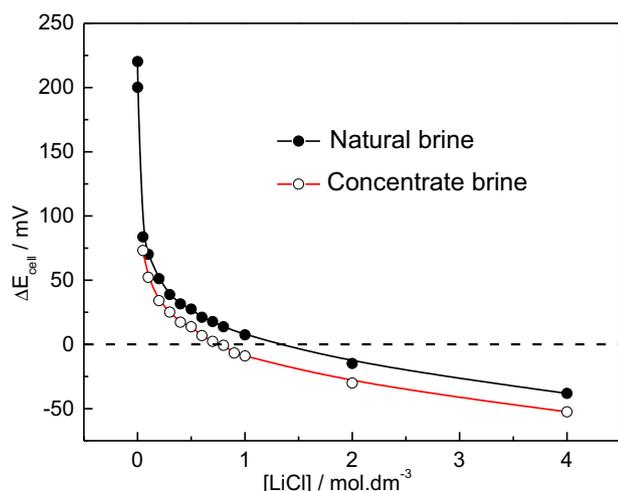


**Figure 9.** Dependence of $\Delta E_{cell}$ vs. concentration of LiCl in the recovery electrolyte.
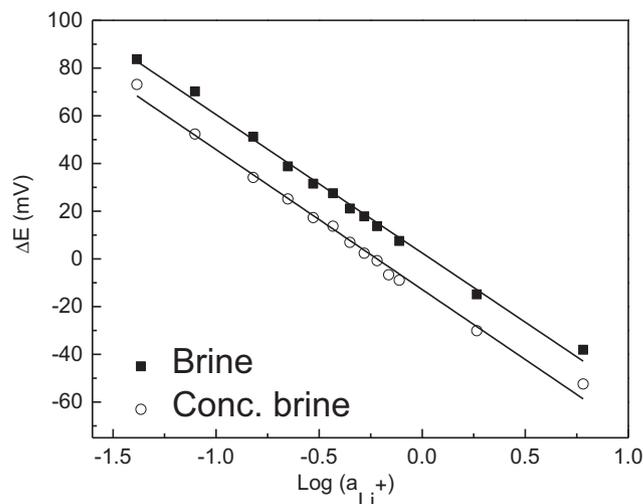


**Figure 10.** Nernstian dependence of $\Delta E_{cell}$ vs. log $(a_{Li}^+)$.

LiCl in the recovery electrolyte for the spontaneous transfer of LiCl from brine, ($\Delta E_{cell} = 0$) are 1.34 M and 0.77 M respectively for natural brine and the concentrate brine.

Figure 10 depicts the Nernstian dependence of $\Delta E_{cell}$ with the LiCl activity in the recovery electrolyte for natural brine and concentrate brine respectively, with good linearity and a slope close to 60 mV. The activity of LiCl at $\Delta E_{cell} = 0$ are 1.13 M and 0.61 M for the analytical concentrations of 0.18 and 0.74 M respectively. A strong salting out effect is thus observed due to the high content of salts, i.e. 5 M NaCl in natural brine.

The ionic strength of natural brine is higher than the concentrated brine in spite of the lower LiCl analytical concentration in the former. This is due to the precipitation of NaCl in the first steps of the evaporation lime-soda process. The dependence of the activity coefficient of LiCl with ionic strength shows a similar trend to the observed activities in the present study.

## Conclusions

Using a $LiMn_2O_4$ cathode and a polypyrrole anode, we have shown the spontaneous extraction and transfer of LiCl from natural brine and concentrate LiCl solutions to dilute recovery solutions by allowing electron flow through an external resistor.

This spontaenous process enables the second step of LiCl recovery, which requires energy supply, by injecting current from the spontaneous LiCl extraction to the non spontaneous recovery process at the $LiMn_2O_4$ anode.

The spontaneous transfer of LiCl in a double $Li_{1-x}Mn_2O_4/LiMn_2O_4$ cell with an anion selective membrane, from natural brine to dilute recovery electrolyte was demonstrated likewise the $LiMn_2O_4/PPy$ cell.

The maximum LiCl concentration in the recovery electrolyte for the spontaneous transfer fom natural brine has been determined together with the activity of LiCl in natural brines, which shows a strong "salting out" effect due to the complex high salinity of the brines.

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