



A LiMn_2O_4 -Polypyrrole System for the Extraction of LiCl from Natural Brine

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A highly selective LiMn_2O_4 -Polypyrrole electrochemical cell for the extraction of LiCl from natural brine is described. Reproducible intercalation of Li^+ in $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) and Cl^- in oxidized polypyrrole (PPy^+) is achieved with an overall cell voltage of less 1 V over more than 200 cycles with 50% charge efficiency and 5–10 $\text{Wh}\cdot\text{mol}^{-1}$ energy consumption. No insertion of Na^+ has been observed.

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Lithium has attracted interest in recent years due to its use in batteries, pharmaceuticals, coolants, aluminum smelting, ceramics, enamels and glasses, nuclear fuels, etc. Electric vehicle development relies on high energy density batteries and lithium batteries demand lithium and lithium compounds for cathode materials and electrolyte salts. Lithium manganese oxide, lithium iron phosphate, or mixed metal oxides such as lithium cobalt nickel manganese oxide can be used as active materials for lithium ion battery cathodes.

Lithium chloride and lithium carbonate, are obtained from Li-containing spodumene (lithium aluminum silicate) or from Li-rich brines from high altitude salt lakes such as the Salar de Atacama in Chile, Salar de Uyuni in Bolivia, and Salar del Hombre Muerto in Argentina. The current soda lime method for the extraction and purification of lithium from high altitude salt lakes relies on brine evaporation and fractional crystallization of Li, Na, K, Mg chlorides. Evaporation in open shallow ponds to concentrate the salts is followed by addition of Solvay to precipitate Li_2CO_3 and the lithium-depleted brine is discarded. This simple chemical process takes place at 4,000 meters above sea level where water is scarce and thus it has a high environmental impact. The extraction process alters the water balance, introduces chemicals into the environment, and generates large volumes of NaCl and MgSO_4 waste. For that reason there has been a search for environmentally benign methods to extract lithium from brines efficiently and at low cost. Different electrochemical strategies have been reported: Kanoh^{1,2} reported the insertion of lithium ions into an electrochemical Pt/ λ - MnO_2 cell and studied the kinetics of lithium insertion/extraction from λ - MnO_2 / LiMn_2O_4 in LiCl aqueous solutions.^{3,4} La Mantia and co-workers^{5–7} used an entropic cell to extract lithium with battery electrodes: LiFePO_4 cathode and Ag/AgCl reversible chloride anode for the selective recovery process, and also have recently described a nickel hexacyano ferrate anode as alternative to the silver anode.⁸ A similar λ - MnO_2 /Ag battery was reported by Lee and co-workers for artificial brine, or λ - MnO_2 /activated carbon hybrid super capacitor.⁹ A recent report describes a highly selective Li/Na electrochemical process based on olivine LiFePO_4 coated with polydopamine with the I^-/I_3^- redox couple separated by a membrane.¹⁰

Hoshino proposed an electro dialysis method using an ionic liquid-based membrane technology.^{11,12} Fast and efficient chemical redox insertion of lithium ions into solid FePO_4 has been reported by Owen and co-workers¹³ while $\text{LiFePO}_4/\text{FePO}_4$ electrochemical cell with anion exchange membrane was reported for the extraction of Li from brine.¹⁴

An alternative electrochemical method for the extraction of lithium chloride from brine or sea water has been developed recently in our research laboratory.¹⁵ In this electrochemical method, which is fast, efficient, has low environmental impact and low energy consumption, lithium rich brine is the electrolyte of an undivided electrochemical cell comprised of a lithium deficient $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode and a chloride reversible polypyrrole (PPy) anode. Under a potential difference of less than 1 V, intercalation of lithium ions in the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode

and exchange of chloride at the oxidized PPy electrode takes place simultaneously with high selectivity. In a second step, after rinsing the electrodes thoroughly the electrolyte is exchanged with a lithium recovery solution and the electrode potential is reversed, so that lithium releases at the $\text{Li}_x\text{Mn}_2\text{O}_4$ anode and the PPy cathode releases chloride ions. During the lithium chloride uptake, only Li^+ ions are selectively intercalated at the cathode and Cl^- ions are exchanged at the anode while the release of LiCl into the recovery electrolyte takes place in the second step.

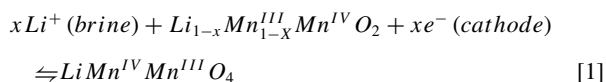
LiMn_2O_4 is a stable phase with half lithium content in the discharge curve from λ - MnO_2 to $\text{Li}_2\text{Mn}_2\text{O}_4$.^{16,17} The mixed oxide, LiMn_2O_4 has a spinel structure (space-group Fd3m) and the unit cell contains 56 atoms: A cubic close-packed array of oxygen ions occupying the 32e sites; 16 Mn ions are located in the octahedral 16d sites (MnO_6) and 8 Li ions in the tetrahedral 8a sites.¹⁸

Lithium ions can be inserted in λ - MnO_2 cubic phase and extracted from LiMn_2O_4 in aqueous solutions by a topotactic Li^+ insertion reaction within the cubic symmetry with isotropic expansion of the cell.^{1,19}

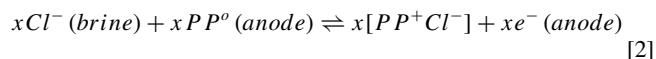
Using an electrode reversible to chloride ions it is possible to extract Li^+ and Cl^- ions from brine solutions by adjusting the redox state of manganese ions in the oxide lattice. We describe the use of polypyrrole electrochemically deposited on carbon felt as the reversible chloride electrode.

In analogy to the LiMn_2O_4 positive lithium ion battery electrode in non aqueous electrolyte, the available positions for lithium insertion into λ - MnO_2 are tetrahedral 8a sites in the spinel structure.¹⁸ There are two sets of non equivalent 8a sites which can be occupied in $\text{Li}_x\text{Mn}_2\text{O}_4$ (with $x \ll 1$) respectively by four lithium ions each leading to two peaks in the cyclic voltammetry. The transition occurs at $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ composition.

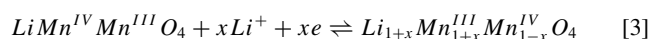
The electrode reactions at the $\text{Li}_x\text{Mn}_2\text{O}_4$ /brine interface during the extraction and release of LiCl from brine within the cubic $\text{Li}_x\text{Mn}_2\text{O}_4$ structure are:



while at PPy chloride reversible electrode, oxidation of polypyrrole occurs with simultaneous uptake of chloride anions to compensate the excess positive charge in the polycation.^{20,21}

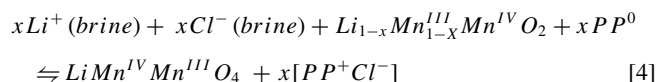


LiMn_2O_4 is half way between cubic λ - MnO_2 (Mn^{IV}) and tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ ($\text{Mn}^{\text{III/IV}}$) oxides. Further lithium-ion insertion in the LiMn_2O_4 phase is known to cause Jahn-Teller distortion as a consequence of unstable Mn^{3+} (d4) formation in an octahedral environment, which leads to a first order transition with a change from cubic to tetragonal symmetry to form $\text{Li}_2\text{Mn}_2\text{O}_4$ which takes place close to 3 V vs. Li/Li^+ :



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At this point, since 16c octahedra share faces with the 8a tetrahedra, the Li ions in the 8a tetrahedral sites are displaced into the vacant 16c sites, causing the phase transition. Complete filling the 16c positions yields a composition corresponding to $\text{Li}_2\text{Mn}_2\text{O}_4$. Therefore, the overall electrochemical reactions at the $\text{Li}_x\text{Mn}_2\text{O}_4/\text{PPy}$ battery cell are:



Initially the fully lithiated LiMn_2O_4 is subject to anodic treatment in an electrolyte with low or nil Li^+ concentration before the uptake of LiCl from brine solution under cathodic polarization. In chloride containing solutions the PPy counter electrode is reversible to chloride ions and avoids chlorine evolution which otherwise occurs on a Pt counter electrode.

Experimental

LiMn_2O_4 (LMO) was obtained from Sigma-Aldrich, and also prepared by a ceramic process (firing and grinding) from MnCO_3 and Li_2CO_3 and the resulting mixed oxide was characterized by XRD. $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes were prepared by casting a slurry of LiMn_2O_4 (80% w/w), 10% PVDF and 10% Vulcan carbon X-72 (Cabot Corp.) dispersed in N-methyl pyrrolidone onto flat carbon plates Poco and dried at 105°C .

The electrolyte was natural brine from Salar de Olaroz in the province of Jujuy, Argentina. The chemical composition of the natural brine was analyzed by ICP resulting Na^+ 115.600 ppm (5 M NaCl), K^+ 10.780 ppm (0.28 M KCl), Mg^{2+} 2.618 ppm, Li^+ 975–1280 ppm (0.18 M LiCl), B 1.440 ppm, with a dynamic viscosity of 2.077 Cp, density 1.2710 $\text{g}\cdot\text{cm}^{-3}$ and conductivity 0.1735 $\text{S}\cdot\text{cm}^{-1}$.

The chloride reversible polypyrrole counter electrode was obtained by electrochemical polymerization of an aqueous solution of 0.1 M pyrrole on large surface area platinum mesh (Goodfellow PT008710) in 1.2 M HCl in water under potential control at 0.8–1 V vs. Ag/AgCl, 3 M KCl, during 1 hour (SI). Alternatively large surface area 0.2 cm thick and 0.09 $\text{g}\cdot\text{cm}^{-3}$ carbon felts from Morgan AM&T were employed to electro polymerize pyrrole.

XRD measurements were performed over a 1.3 cm^2 stainless steel cast with $\text{Li}_x\text{Mn}_2\text{O}_4$ ink (LiMn_2O_4 , Carbon Vulcan and PVDF; 80:10:10% w/w ratio) after being polarized for 2 hours either at 0.4 V or 1.1 V vs Ag/AgCl.

The reference electrode was an Ag/AgCl; 3 M KCl (0.21 V vs. NHE) and all potentials herein are quoted with respect to that reference electrode. Electrochemical potential or current were controlled with an Autolab PGSTAT 30 potentiostat (Autolab, Ecochemie, Holland) with Nova 1.10 software. Electrochemical measurements were carried out in PTFE three electrode undivided cells, which consists of PPy deposited on large surface area carbon felt as counter electrode, $\text{Li}_x\text{Mn}_2\text{O}_4$ ink deposited on carbon plates and Ag/AgCl (in KCl 3 M) reference electrode.

In preparative scale experiments a reticulated vitreous carbon (RVC) monolith ($3 \times 2 \times 0.4$ cm) was employed with 56 cm^2 total area (calculated from 112 $\mu\text{F}\cdot\text{cm}^{-2}$ capacitance and 2 $\mu\text{F}\cdot\text{cm}^{-2}$ for basal plane HOPG). The RVC three dimension electrodes were further impregnated with LiMn_2O_4 mixed with Vulcan carbon and PVDF. A similar RVC counter electrode was covered by polypyrrole by electro-polymerization from 0.1 M pyrrole in HCl solution. Electrolysis of brine was carried out in a 20 mL cell with the two RVC electrodes capturing Li^+ and Cl^- respectively by applying 1 mA under stirring for extended periods. Then, the brine was replaced by 0.1 M KCl recovery solution after extensive rinsing with small aliquots of MilliQ water. The recovery solutions were analyzed for lithium, sodium and potassium with ion chromatography using a CS16 cationic column in a Dionex DX100 ion chromatographer (SI 6–7). This column has a high Li:Na separation ratio when using 30 mM methane sulfonic acid as eluent.

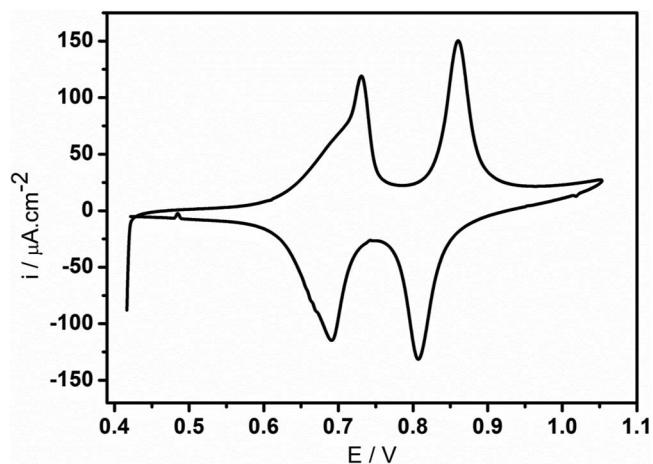


Figure 1. Cyclic voltammetry of 0.2 cm^2 LiMn_2O_4 in brine with PPy counter electrode at $2 \text{ mV}\cdot\text{s}^{-1}$.

Results and Discussion

Figures 1 and 2 depict typical cyclic voltammetry at low scan rate of LiMn_2O_4 (LMO) electrode and polypyrrole deposited on carbon electrode (PPy) respectively in contact with natural brine solution. In both cases a polypyrrole counter electrode of area well in excess to the working electrode was used.

Two redox processes characterize the cyclic voltammetry of LiMn_2O_4 in the potential range between 0.5 and 1.1 V, which are comparable to those reported for $\text{Li}_x\text{Mn}_2\text{O}_4$ in non aqueous EC/DMC 1M LiPF_6 electrolyte^{18,22,23} and in LiNO_3 aqueous solutions.²⁴ The two redox processes have been ascribed to a two-step lithium extraction/intercalation between LiMn_2O_4 and $\lambda\text{-MnO}_2$.^{16,23,25}

In the present work, the LiMn_2O_4 electrode potential was restricted to a potential window 0.4 and 1.1 V in order to keep the lithium stoichiometry within the $0 \leq x \leq 1$. At lower potential the $\text{LiMn}_2\text{O}_4 / \text{Li}_2\text{Mn}_2\text{O}_4$ two phase system determines the potential close to 0 V.

The unit cell of the spinel LiMn_2O_4 contains 56 atoms: A cubic close-packed array of oxygen ions occupying the 32e sites; 16 Mn ions are located in the octahedral 16d sites (MnO_6) and 8 Li ions in the tetrahedral 8a sites.¹⁷ Lithium ions can be inserted in $\lambda\text{-MnO}_2$ cubic phase and extracted from LiMn_2O_4 in aqueous solutions by a topotactic Li^+ insertion reaction within the cubic symmetry with isotropic expansion of the cell.^{1,23}

The typical capacitive cyclic voltammetry (CV) of PPy electrode in natural brine is shown in Fig. 2 for the polymer in the oxidized

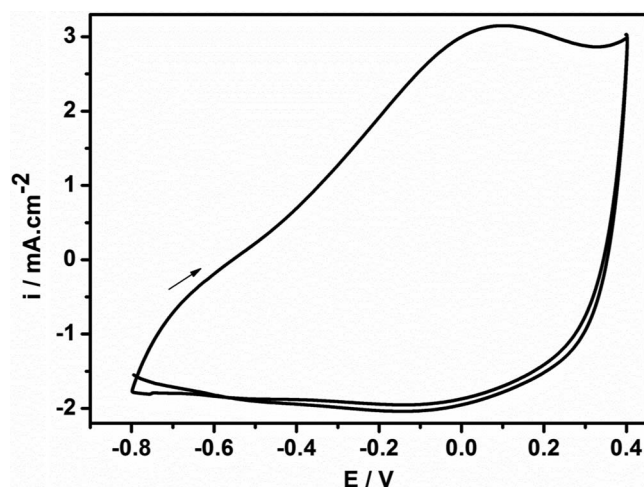


Figure 2. Cyclic voltammetry of 0.2 cm^2 PPy electrode in brine with PPy counter electrode at $2 \text{ mV}\cdot\text{s}^{-1}$.

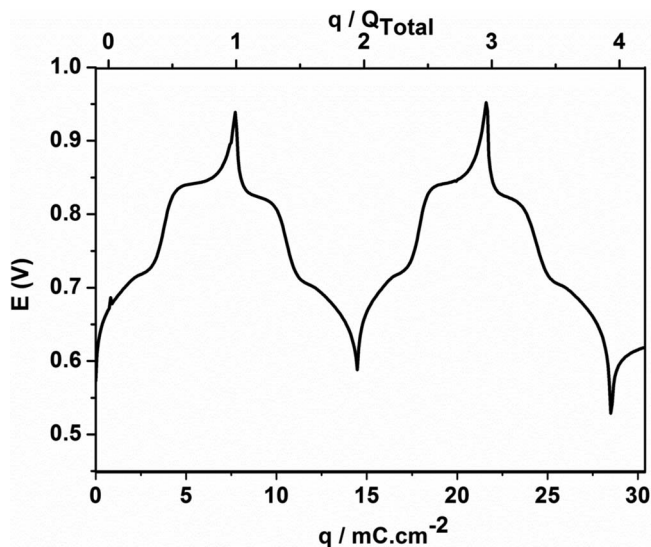


Figure 3. E vs. q plot for a galvanostatic charge and discharge of 0.2 cm² LiMn₂O₄ electrode of 40 μg.cm⁻² in 0.1 M LiCl, for current pulses of 50 μA.cm⁻².

conductive state. A similar current-potential curve has been recorded with PPy with chloride counter ion in LiCl solution as shown in SI2 and SI3.

EQCM ion exchange properties of PPy have been reported and the nature of the ion exchange to satisfy charge compensation has been shown to depend on the nature and charge of the ions in solution.^{26,27} The CV in Figure 2 and the simultaneous EQCM mass increase in the oxidation cycle and mass decrease upon reduction confirm that PPy in brine (SI2) and in pure LiCl (SI3) solutions behaves as anion exchange system.

A typical galvanostatic charge/discharge of Li_xMn₂O₄ (40 μg.cm⁻²) on carbon at 2.5 mA.cm⁻² in 0.1 M LiCl is shown in Figure 3. We have normalized the charge to the total charge of 7.5 μC.cm⁻². Since the capacity of LiMn₂O₄ is 533 C/g, total extraction of lithium corresponds to 21 μC.cm⁻²; therefore in this experiment only 36% of the lithium contained in the mixed oxide has been extracted. We are investigating at present the origin of this capacity drop.

The two plateaux in the discharge-charge curves at constant current correspond to the occupancy by four lithium ions two sets of non equivalent 8a sites. A gradual isotropic process from LiMn₂O₄ with lattice parameter 8.245 Å to [Mn₂O₄] (λ-MnO₂) with 8.028 Å takes place in the stoichiometry range 1 ≤ x ≤ 0 within the cubic lattice.²³

Figure 4 depicts the evolution of Li_xMn₂O₄ and PPy electrode potentials vs. Ag/AgCl respectively in brine at constant current during one discharge-charge cycle. For Li_xMn₂O₄ the two step Li⁺ intercalation-release is observed while the oxidation-reduction of polypyrrole electrode takes place in a narrow potential interval in the oxidized conducting state of polypyrrole (see Figure 2). The overall cell potential is less than 1 volt

The extraction process of lithium chloride from natural brine requires that both electrodes be stable in large number of LiCl extraction/recovery cycles. We have therefore applied 200 repetitive 2.5 mA.cm⁻² anodic and cathodic current pulses, following the potential of both electrodes vs. Ag/AgCl as shown in Figure 5.

It is of mention the reproducibility and stability of both electrode processes in repetitive extraction-recovery cycles within the stoichiometry 0 ≤ x ≤ 1 of λ-MnO₂/LiMn₂O₄ in the potential range of polypyrrole electrode stability. The detailed behavior of PPy chloride electrode is being investigated at present.

The potential with respect to Ag/AgCl vs. charge curves for the 1st, 100th and the 200th cycle are shown in Figure 6. A 22% and 36% capacity drops were observed in 100 and 200 cycles respectively, which can be due to the loss or inactivation of some LiMn₂O₄ active material during repetitive LiCl extraction/recovery cycles.

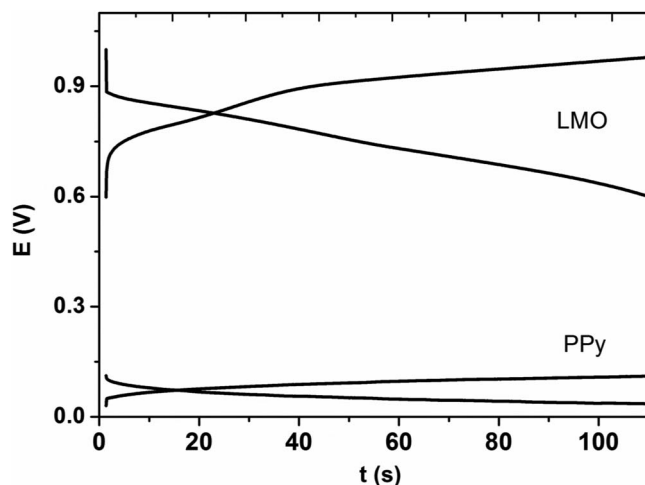


Figure 4. Electrode potential (E) with respect to Ag/AgCl vs. time plots for LiMn₂O₄ (520 μg.cm⁻²) and PPy electrodes in brine during 2.5 mA.cm⁻² current pulses.

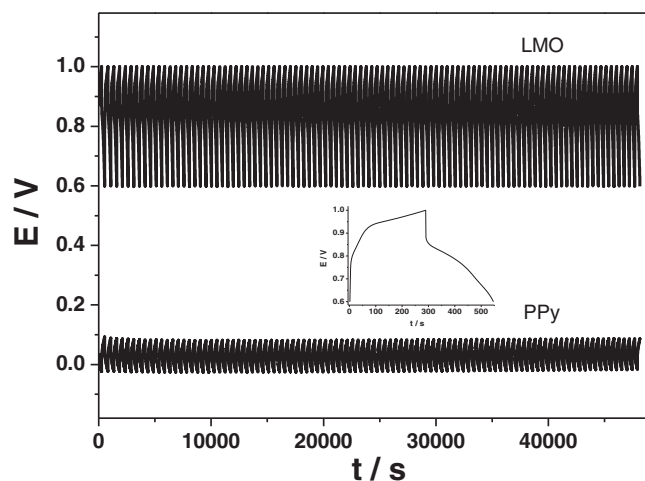


Figure 5. Electrode potential, E, against Ag/AgCl vs. time plots for 200 consecutive LiCl extraction /insertion cycles with a LiMn₂O₄ (520 μg.cm⁻²) / PPy battery cell in brine solution for 2.5 mA.cm⁻² current pulses. The inset shows a detail of two cycles.

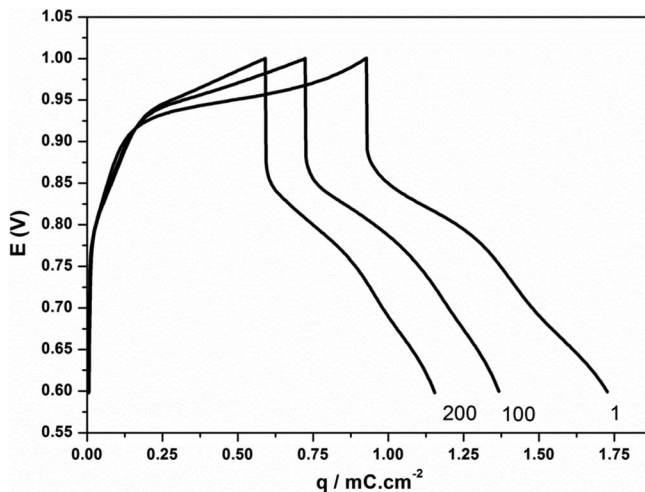


Figure 6. Electrode potential (E) against Ag/AgCl vs. time plots for LiMn₂O₄ on carbon (520 μg.cm⁻²) and PPy electrodes in brine during 2.5 mA.cm⁻² current pulses for cycles 1, 102 and 200.

Table I. Charge, mass and recovery efficiency.

Q / C	m _{Li+} (calc.) / mg	m _{Li+} (exp.) / mg	% recovery
42.8	3.10	1.73	56
57.5	4.17	2.23	53
61.2	4.43	2.01	45

Direct evidence of effective lithium extraction from brine has been obtained by following the lithium ion concentration change in 0.1 M KCl recovery solution using ion chromatography. As internal reference KCl has been used. Table I compares the mass of Li⁺ recovered to the mass calculated from the total anodic charge in several extraction/recovery experiments.

In these experiments on the same sample the recovery efficiency is about 50% and this is thought to be related to some carbon oxidation accounting for excess anodic charge. See Fig. S110.

The energy involved in the closed cycle with spontaneous battery electrode in the extraction step and the energy consuming recovery step can be calculated with the circular integral of ΔE -q curve in Figure 7.^{5,29}

$$W = \oint_C \Delta E \cdot dq \quad [5]$$

Where W is the energy in J, ΔE is the cell voltage in V, and q is the charge, in coulomb, involved in the LiCl extraction-recovery cycle. Figure 7 depicts the total cell voltage (ΔE) vs. charge (q) during the insertion and extraction of LiCl using RVC impregnated with LiMn₂O₄/carbon ink. The energy required to extract Li⁺ in that experiment is 1.57 J which corresponds to 5 Wh.mol⁻¹ of Li⁺ based on 8.5 coulombs, or 10 Wh.mol⁻¹ taking into account a 50% recovery efficiency as discussed above. The energy values obtained in the present work are comparable to previous reports.^{5,29}

Notice that in the experiment described in Fig. 7 LiCl is extracted from 0.2 M brine and released in 25 mM LiCl solution.

The use of polypyrrole as chloride selective electrode has a number of advantages over other alternatives such as Ag/AgCl,^{5,29} Pt,^{1,2} or carbon⁹ counter electrodes. The cell potential vs. time curves for 2.5 mA.cm⁻² current pulses using carbon felt and platinum as counter electrodes are shown in Figures 8 and 9.

Using Pt as counter electrode the hydrogen electrode potential is attained in the cathodic cycle but in the anodic excursion Cl₂ and O₂ evolution take place with large cell voltage.

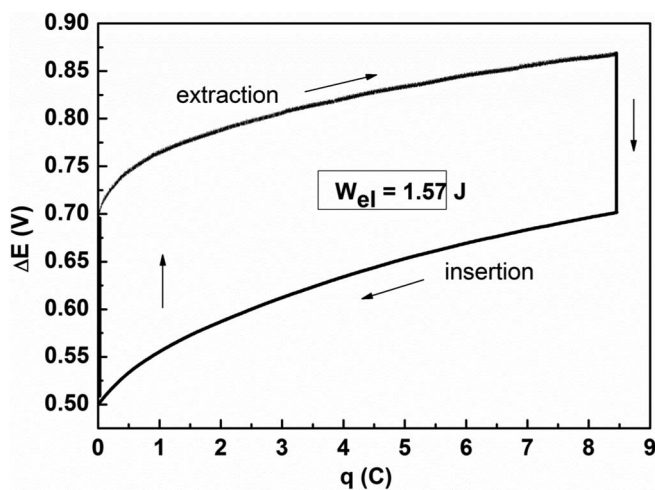


Figure 7. Total cell voltage (ΔE) vs. charge (q) for 147 mg of LiMn₂O₄-Vulcan carbon ink deposited onto RVC during at 1 mA constant current cathodic and anodic pulses with brine and 25 mM LiCl as recovery solution.

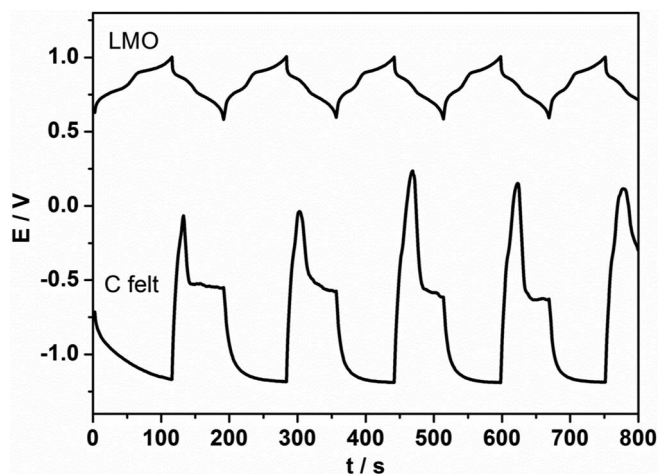


Figure 8. E vs. time plots for consecutive LiCl extraction/insertion cycles with a LiMn₂O₄ (1.12 mg.cm⁻²)/carbon felt battery cell in brine solution for 500 μ A.cm⁻² current pulses, limited to 0.6 and 1.1 V.

The curves of cell voltage (ΔE) vs. charge (q) for extraction and insertion of Li⁺ and Cl⁻ ions in brine using different counter electrodes are shown in SI. From the experimental energy consumption calculated with Eq. 1 and the theoretical contribution from the mixing entropy gain calculated using the method described by La Mantia (see SI),⁵ the energy consumed in the overall process for the different counter electrodes are compiled in Table II.

The cell Li_xMn₂O₄/PPY consumes the lowest energy per mol of Li⁺ extracted from brine of all the different configurations explored in the present work and recovered either in brine or 25 mM LiCl electrolyte.

Therefore, none of these counter electrode alternatives can be compared to polypyrrole in brine solutions. The Li_xMn₂O₄/PPY cell is the most energy efficient extraction system.

In a previous communication¹⁵ we have shown that Na⁺ ions cannot be intercalated in LiMn₂O₄ spinel structure under cathodic polarization in 0.1 M LiNO₃ aqueous solution from the evidence of X-ray diffraction pattern which does not shift the reflections to higher 2 θ values as the electrode is de-lithiated as has been shown elsewhere during Li_xMn₂O₄ oxidation.³⁰

Figure 10 depicts the XRD patterns of the Li_xMn₂O₄ electrode polarized sequentially at 0.6 V and 1.1 V in brine and then the brine was replaced by 1 M NaCl solution and the electrode polarized at 0.6 V.

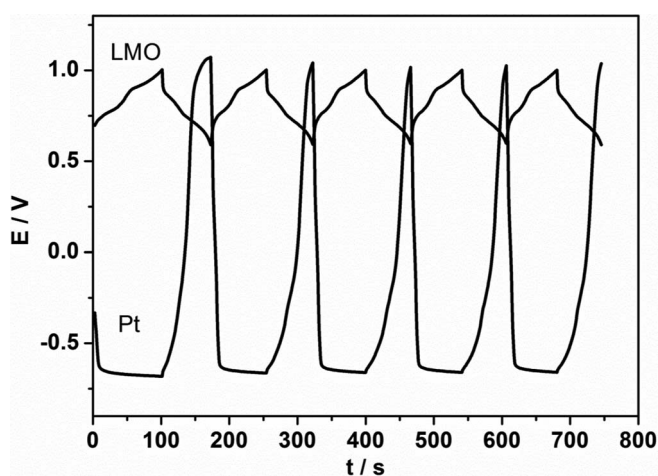


Figure 9. E vs. t plots for consecutive LiCl extraction/insertion cycles with a LiMn₂O₄ (1.2 mg.cm⁻²)/Pt battery cell in brine solution for 2.5 mA.cm⁻² current pulses, limited to 0.6 and 1.1 V.

Table II. Energy consumption for different experiments.

Electrode	Extract./Recov. Electrolyte	Theory W.h.mol ⁻¹	Experiment W.h.mol ⁻¹
Li _x Mn ₂ O ₄ / PPy	Brine/Brine	0	9.4
Li _x Mn ₂ O ₄ / C	Brine/Brine	0	24.6
Li _x Mn ₂ O ₄ / Pt	Brine/Brine	0	20.7
Li _x Mn ₂ O ₄ / PPy	Brine/25 mM LiCl	-5.18	5

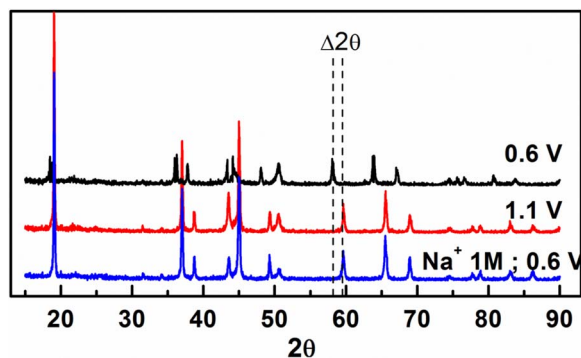


Figure 10. XRD pattern of an electrode prepared by deposition of Li_xMn₂O₄ (80% w/w), Vulcan carbon (10%), and PVDF (10%) in N-methylpyrrolidone on Pt polarized at 0.6 V and 1.1 V in brine solution respectively, and at 0.6 V in 1 M NaCl.

After reduction of Mn^{IV} at 0.6 V the oxidation of Li_xMn₂O₄ at 1.1 V results in the shift of the XRD reflections to smaller 2θ values due to the isotropical lattice expansion upon insertion of Li⁺.³⁰

The polarization of Li_xMn₂O₄ in Li⁺ free 1 M NaCl solution at 0.6 V did not change the XRD pattern which demonstrates that sodium is not inserted into the spinel oxide. The cyclic voltammetry of Li_xMn₂O₄ in 1 M NaCl shows no cathodic current unlike in brine or LiCl solutions (see SI9). Therefore, unlike LiFePO₄ which has a negative influence of Na⁺ as reported by Liu and co-workers¹⁴ and more recently Kim et. al,¹⁰ Li_xMn₂O₄ in 1 M NaCl can selectively extract lithium ions.

Adsorption of sodium ions on the Li_xMn₂O₄ crystal surface, on the other hand, has been detected by XPS experiments.¹⁵ Also brine can be occluded in three dimensional carbon electrodes loaded with Li_xMn₂O₄ and therefore washing the electrode surfaces between the extraction and recovery steps is essential. Analysis of the recovery solutions with ion chromatography has shown the presence of traces of sodium ions which could be minimized by careful rinsing the electrodes between extraction and release cycles. Rinsing solutions show a decrease of sodium content with repetitive washing the electrodes with small water aliquots (see SI8).

Conclusions

The effective intercalation/release of Li⁺ ions at the Li_xMn₂O₄/ natural brine electrolyte interface and exchange of chloride ions at the polypyrrole modified electrode occurs with high selectivity in the 0.6–1.1 V interval within the 0 < x < 1 lithium composition range of Li_xMn₂O₄/λ-MnO₂, and exhibits reproducibility for more than 200 cycles of LiCl capture and release. Direct evidence of LiCl extraction and release from natural brine has been obtained by ion chromatography of recovery solutions. The LiCl recovery efficiency of 50% observed with respect to the anodic charge is probably due to electrochemical oxidation of Vulcan carbon which has been experimentally confirmed. Integration of ΔE vs. charge curves for the capture and release cycle results in 5 W.h.mol⁻¹ energy based on the anodic charge and 10 W.h.mol⁻¹ based on the concentration of lithium recovered.

XRD patterns demonstrate that Na⁺ is not inserted in the Li_xMn₂O₄ crystal structure, but adsorbed sodium and occluded brine solutions require a major effort in the rinsing steps to avoid sodium contamination of the LiCl extracted with the present method.

A comparison of polypyrrole with carbon felt and platinum counter electrodes to capture Cl⁻ has shown that polypyrrole is more energy efficient, while platinum evolves chlorine in the anodic cycle and hydrogen under cathodic polarization.

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