

Leaching Optimization of Battery Black Mass for Lithium Recovery by Electrochemical Junction Transfer (ETJ) Technology

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■The work described herein constitutes one last research projects with Jean-Marie's active involvement. We are honored to be able to share authorship with him one more time.

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A process of cation recovery based on intercalation properties into host matrix has been previously developed in the laboratory. It consists in a selective extraction from a waste electrolyte (battery leachates, industrial effluents...) to a recovery electrolyte, separated by an Electrochemical Junction Transfer (ETJ). The ETJ is constituted of a porous material coated by an active matrix (LiMn₂O₄). The transfer from synthetic electrolytes like Li₂SO₄ was successfully carried out whereas the transfer from real waste (spent Li-ion batteries leachate) was problematic. First studies by cyclic voltammetry confirmed a limited behaviour and showed that the blockage could be attributed to 2 phenomena: the presence of organic compounds coming from Li-ion battery components and the acidity of leachates during transfer. The goals of our work were to eliminate these organic compounds and to define the optimized pH range for an efficient transfer. Different methods (chemical treatment on leachates or thermal treatment directly on crushed battery Black Mass) for removing organic compounds were performed. After a thermal treatment on Black Mass (T = 500 °C, t = 72 h) and a pH adjustment (pH = 5), the selective transfer of Lithium was carried out with a faradic yield close to 100%.

1. Introduction

At present time, our modern life extensively uses portable, thin, light equipment (cellular phones, laptop, remote controllers, digital cameras...) with batteries as power sources. In most cases, lithium-ion secondary battery (LiB) technology has been applied because it delivers high power capacity. Tomorrow, it could also become crucial for electric vehicles. Consequently the numbers of LiBs are set to grow in the future as are the volumes of used equipment and batteries that need recycling. This recycling is essential to avoid harmful substances in the environment and to recover some valuable elements having scarce natural resources. Two classes of processes, including physical processes (mechanical, thermal, mechanochemical) and chemical ones (acid/base leaching, bioleaching, solvent extraction, precipitation, electrochemical process) have been applied for the recovery of cobalt and lithium, one of the primary objectives in the recycling of spent LiBs as presented in the review of Xu et al. (2008). These processes aim to apply a funnel principle where every non-wished element is extracted one by one, using the classical chemical reactions until the desired element remains.

We proposed another approach using an electrochemical transfer junction (ETJ), allowing a selective extraction of the desired metallic cation between two electrolytes (Seghir et al., 2008, Seghir et al. 2010a, Seghir et al., 2010b; Guyot et al. 2013). The process is based on insertion/de-insertion reactions in a host-Lattice (HL) (Potel et al., 1984; Schöllhorn, 1980). The ETJ is constituted of a porous ceramic material coated by an active matrix. The global phenomenon of intercalation, diffusion, de-intercalation represented by $[HL]_{\downarrow} + xne^{-} + xM^{n+} \leftrightarrow [MxHL]_{\downarrow}$ allows the transfer of mobile cationic species from a medium to the other one through the ETJ. The advantages of this electrochemical process are the use of non-polluting reagents and a limited number of steps while their drawback is a reactivity limited at the electrode

interface, and not in the bulk of solution. This process was extended to the study of the lithium recovery through LiMn_2O_4 junctions by electrolysis in aqueous solution (Guyot et al., 2012). If the previous work experimentally demonstrated the validity of a lithium withdrawal from synthetic solutions containing the Co^{2+} cation, this paper reports the influence of the medium acidity and of the organic carbonates present in the Li-ion battery on the LiMn_2O_4 intercalation properties and describe the investigations of lithium transfer from a real industrial liquid waste (sulphuric leachate of a Black Mass).

2. Experimental

LiMn_2O_4 material, chosen for its intercalation capacity of Lithium via electron/ion transfer was synthesized by reaction of stoichiometric mixtures of Li_2CO_3 and MnCO_3 (Sigma Aldrich). The mixture of analytical grade precursors (>99.9 %) was calcined for 8 h at 800°C for LiMn_2O_4 to yield the desired oxide powders. Porous ceramic substrates (diameter: 24 mm, thickness: 1 mm, surface: 4.5 cm^2) were synthesized from a mixture of kaolin, alumina and potato starch developing a porosity according to the protocol already described (Seghir et al., 2010a). The covering of ceramic substrate was based on a slurry of host matrix (80 wt %), polyvinylidene fluoride binder (10 wt %, Aldrich, 99 %) and graphite (10 wt %, Sigma Aldrich, 99 %), all in N-methyl pyrrolidone (Acros Organics, 99 %) (Levi et al., 1999). The suspension was stirred for two hours, spin coated (2000 tr/min Ika-Werke) onto porous substrates and dried at 110°C for 1 h leading to a $\sim 70\text{-}150\ \mu\text{m}$ thick layer. An electrical contact by graphite paste was done around the ETJ in order to monitor the potential. The electrochemical $\text{Li}^+ \text{Mn}_2\text{O}_4 / \text{Li}_x\text{Mn}_2\text{O}_4$ system was verified in Li_2SO_4 (0.5 M). The potentiodynamic study at 0.33 mVs^{-1} in a conventional cell of three electrodes was performed using crystallite bed electrodes procedure with glassy carbon (Boulanger and Lecuire, 1988). All potentials are expressed versus Silver Chloride/Silver electrode (AgCl/Ag). According to the literature (Robert and Alzieu, 2005) and producers estimates (EPBA, 2007), indicative chemical compositions of Li-ion batteries show the presence of organic electrolytes and/or polymers. These species can thus be found in wastes and leachates. We chose arbitrarily to check the influence of carbonate propylene (CP), diethyl carbonate (CDE) and dimethyl carbonate (CDM). Solutions of lithium sulphate (0.5 M) added by CP, CDE and CDM (Acros Organics), 10 % v/v for each, were prepared.

The Black Mass samples from spent LiBs used in our study were kindly donated to us by the company Eurodieuze (Moselle France). The Black Mass was produced by a first grinding under water, a magnetic separation for isolating the metallic elements and a separation by density to eliminate the plastic elements. The cathode materials were then dried and ground a second time leading to a black residue (Black Mass) which contains lithium, cobalt and other metallic elements coming from the electrodes. 50 mL of sulphuric acid H_2SO_4 (2 Mol.L^{-1}) was added to the Black Mass (5 g). The suspension was agitated for 2 h at 80°C . The solid residue was separated by filtration. The final pH of eluate is equal to 2. The eventual modification of pH was performed by adding a solution of NaOH (6 Mol.L^{-1}). In order to eliminate the organic carbonates, a thermal treatment of Black Mass was performed for 72 h at 500°C in an oven (Nabetherm). The annealed Black Mass was then leached in the same conditions as described former.

The transfer from the intercalation compartment 1 ($\text{Li}_2\text{SO}_4\ 0.5\text{ Mol.L}^{-1}$) to the de-intercalation compartment 2 ($\text{Na}_2\text{SO}_4\ 0.1\text{ Mol.L}^{-1}$) was performed in a galvanostatic mode between platinated titanium electrodes (22 cm^2) connected to a PRT20-2 potentiostat (Tacussel). The transfer Li^+ amount was achieved by atomic absorption spectroscopy (Varian AA240FS) on 1 mL of stirred compartment 2 sampled every hour.

3. Study of the synthetic electrolytes

3.1 Voltammetric curves

Cyclic voltammograms (CV) for LiMn_2O_4 in an aqueous $\text{Li}_2\text{SO}_4\ 0.5\text{ Mol.L}^{-1}$ solution reveal two pairs of redox peaks (Fig.1a) corresponding to the lithium ion intercalation or de-intercalation into or from the spinel $0 \leq x \leq 0.5$ and $0.5 < x \leq 1$ in accordance with literature (Bach et al. 1998; Wang et al., 2007; Manjunatha et al. 2011). The signals show reversible intercalation processes, the anodic peaks are centred at 1.01 and 1.15 V, while corresponding cathodic peaks are centred at 0.83 and 0.99 V. The cyclability (evidenced by the shape and intensity of peaks) for deintercalation/intercalation of Li^+ ion is relatively high.

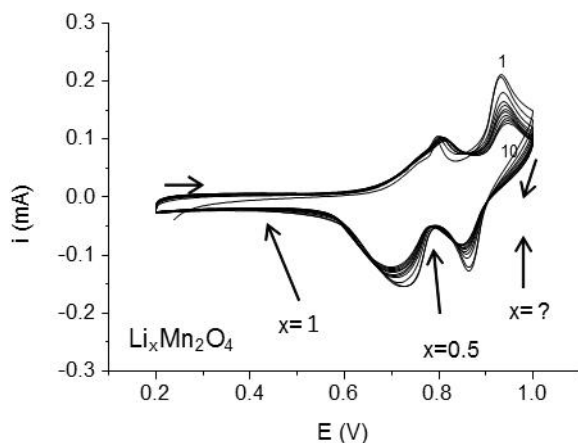


Figure 1: Cyclic voltammograms (10 cycles) at $0.33 \text{ mV}\cdot\text{s}^{-1}$ with glassy carbon as current collector of LiMn_2O_4 electrodes in aqueous electrolyte Li_2SO_4 $0.5 \text{ Mol}\cdot\text{L}^{-1}$ at room temperature.

It was important to verify the influence of the organic carbonates, found in the lithium-ion battery, on the insertion of the lithium ion into LiMn_2O_4 . The voltammograms obtained in a mixture 5 % in volume of each of organic carbonate (CP, CDE, CDM) have the same feature (Figure 2a) as that obtained in pure lithium sulphate. The signals of intercalation and deintercalation are stable in intensity and in potential. The cyclability is maintained. The mixture in 5 % organic products has thus no effect on the contrary to the mixture in 10 % of each of these three species (Figure 2b). From the first cycle, no signal is either observed in oxidation or in reduction. The organic products may adsorb on the surface of the electrode and blocked the charge transfer. A strong concentration of organic carbonates has a fatal effect on the intercalation process. The organic species must be eliminated because they can disturb the insertion and consequently the transfer of lithium or at least their content must be reduced because a low content do not seem to be a drawback.

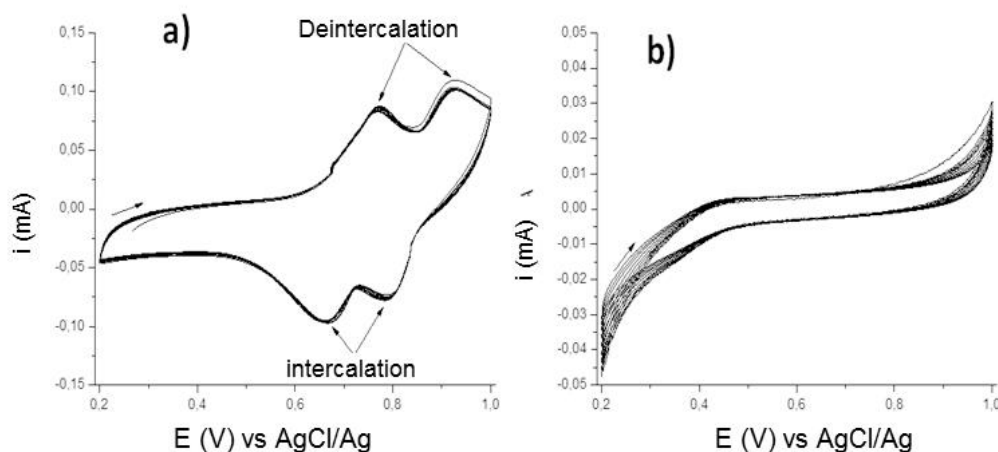


Figure 2: Cyclic voltammograms (10 cycles) at $0.33 \text{ mV}\cdot\text{s}^{-1}$ with glassy carbon as current collector of LiMn_2O_4 electrodes in aqueous electrolyte Li_2SO_4 $0.5 \text{ Mol}\cdot\text{L}^{-1}$ at room temperature in presence of dimethyl carbonate, diethyl carbonate and propylene carbonate a) each at 5 % v/v b) each at 10 % v/v

3.2 Electrochemical transfer of lithium

The transfer of lithium was tested with a LiMn_2O_4 ETJ for current densities ranging from 4 to $12 \text{ mA}\cdot\text{cm}^{-2}$. An hourly control evidenced that the quantity of Li^+ transferred according to current density is proportional to the time excepted for $12 \text{ mA}\cdot\text{cm}^{-2}$ from 4 hours of processing (Figure 3). The faradic yield of transfer was calculated with Faraday's law by comparing the experimental charge to the theoretical one corresponding to an exchange of 1 electron by lithium. A value of $\sim 100\%$ after 7 hours was achieved for

current densities ranging between 4 and 9 mA.cm⁻². For a higher current density (12 mA.cm⁻²), a decreased cation transfer yield is observed certainly due to a mechanical degradation of ETJ and to water oxidation. This reaction causes gas bubbles that could peel the matrix coating. Consequently a maximal value at 11 mA.cm⁻² was chosen for the real industrial leachate.

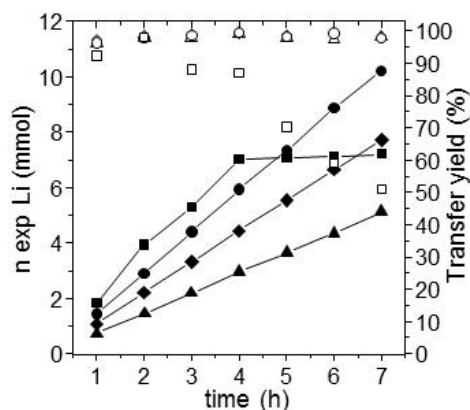


Figure 3: Lithium amount transferred (filled dots) and transfer yield (empty dots) for different current densities: 4 (▲, △), 7 (◆, ◇), 9 (●, ○), 12 (■, □) mA.cm⁻² in function of time with a LiMn₂O₄ ETJ

4. Study of Black Mass leachates

4.1 Voltammetric curves

Figure 4 shows the electrochemical behaviour of LiMn₂O₄ in real industrial solutions (Black Mass leachates from Li-ions battery having undergone various treatments). The feature of the voltammogram for a solution obtained from the direct leaching of the Black Mass (Figure 4a) does not correspond to that of a voltammogram obtained on a pure lithium sulphate solution. Only hydrogen evolution appears since the acidity is very high (pH = 1) without evidencing the intercalation process. The pH of the leachate was thus raised to 5 by addition of NaOH 6 Mol.L⁻¹ (Figure 4c). The curve shows well defined intercalation signals for the first cycles. But their intensity rapidly decreases and the signals disappear evidencing once again a progressive blocking of the matrix intercalation capacity by the organic species adsorption. Another protocol was tested. Before leaching by sulphuric acid, the Black Mass was annealed at 500 °C for 72 h. The curve (Figure 4b) looks like that obtained in Figure 1 although only one single deintercalation peak is observed, proving an elimination of the organic species by annealing treatment. But by increasing cycles the voltammogram presents a lack of stability due to the high acidity, most probably causing the dissolution of LiMn₂O₄. Finally we combine both treatments: annealing at 500 °C for 72 h of the Black mass, followed by a sulphuric leaching and a final adjustment of pH at a value of 5 by adding NaOH. The voltammogram recorded in these conditions (Figure 4d) evidences a feature totally homogeneous to the synthetic solution with stability in the potential range and in the signal intensity even after 7 cycles. The intercalation was not disrupted or blocked by organic carbonates and the dissolution of the host lattice was not occurring.

4.2 Electrochemical transfer of lithium

The transfer of lithium was tested with a LiMn₂O₄ ETJ for a current density equal to 2.5 mA/cm² for 6 h with 3 leachates having a lithium concentration of 0.2 Mol.L⁻¹ coming from a direct leaching by sulphuric acid, a leaching by sulphuric acid followed by a pH adjustment (pH = 5) or a sulphuric leaching of an annealed Black Mass for t = 72 h at T = 500 °C followed by a pH adjustment (pH = 5). For the sulphuric leachate (Figure 5a), the lithium is regularly transferred, the yield is stable but is only around to 10 %, implying a partial functionality of the ETJ surface. For the transfer tested after the annealing of the Black Mass, the figure 5b shows a transferred lithium quantity not proportional to the time. The transfer yield which is initially at 60 % falls down to 20 % after 2 h since the organic carbonates blocking the surface of ETJ preventing the insertion of lithium. Confirming the voltammetric study, the efficiency for the last leachate is highlighted by a regular evolution of the lithium transferred quantity to the time and a clear improvement of the transfer yield at 90 %.

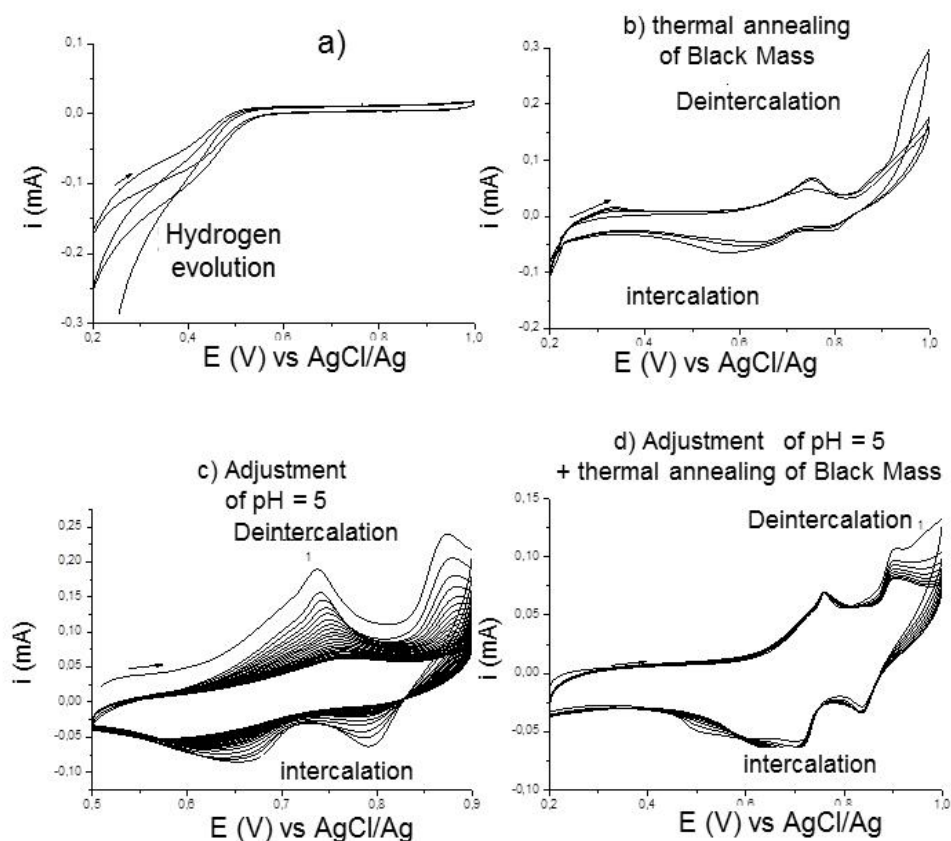


Figure 4: Cyclic voltammograms (3 or 10 cycles) at $0.33 \text{ mV}\cdot\text{s}^{-1}$ with glassy carbon as current collector of LiMn_2O_4 electrodes at room temperature in sulphuric leachates: a) on a raw Black Mass and $\text{pH} = 2$, b) on a annealed black mass and $\text{pH} = 2$, c) on a raw Black Mass followed by an adjustment at $\text{pH} = 5$., d) annealed Black Mass for $t = 72 \text{ h}$ at $T = 500 \text{ }^\circ\text{C}$ followed by an adjustment at $\text{pH} = 5$

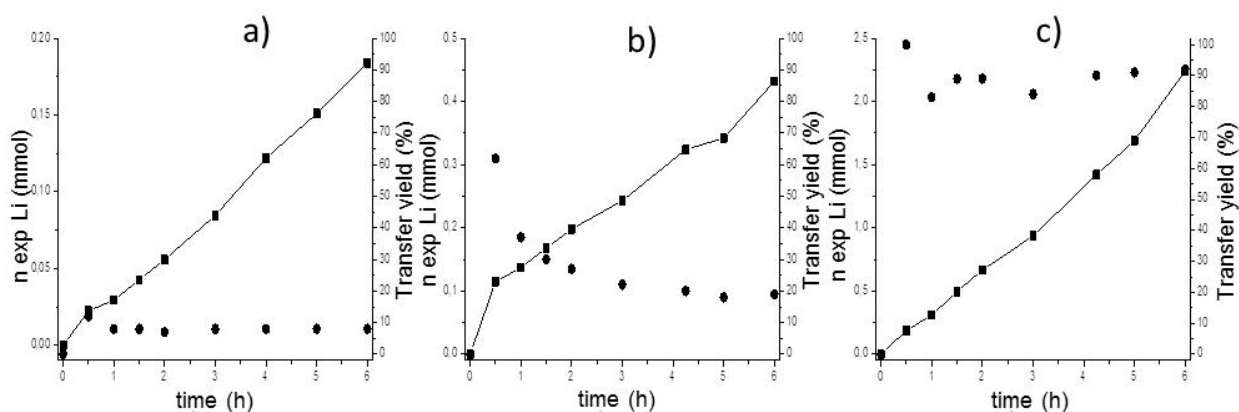


Figure 5: Lithium amount transferred (\blacksquare) and transfer yield (\bullet) for $I = 2.5 \text{ mA}/\text{cm}^2$ in function of time for different sulphuric leachate: a) on a raw Black Mass and $\text{pH} = 2$, b) on a raw Black Mass followed by an adjustment at $\text{pH} = 5$, c) on a annealed Black Mass for $t = 72 \text{ h}$ at $T = 500 \text{ }^\circ\text{C}$ followed by an adjustment at $\text{pH} = 5$ with a LiMn_2O_4 ETJ

5. Conclusions

Electrochemical transfer junctions based on oxide layer onto porous ceramics were synthesized. The reality of the principle of a lithium recovery with LiMn_2O_4 was proved in pure Li_2SO_4 aqueous electrolytes, medium of most batteries leachates. The maximal applied current density to avoid ETJ (LiMn_2O_4) degradation was determined; the value is limited at $11 \text{ mA}\cdot\text{cm}^{-2}$. The main advantage of this process (even if the fluxes are low) lies in the decrease of the number of steps required to separate these cations found in leachates and the use of an aqueous medium. For Black Mass Li-ion Battery leachates, the analytical study by voltammetric curves showed that the real leachates were not directly operational for transferring lithium since a blocking of ETJ by organic carbonates contained in the battery electrolytes was observed. Moreover the acidity of the industrial leachates led to the dissolution of the LiMn_2O_4 matrix. These drawbacks were by-passed by a preliminary heat treatment (at $500 \text{ }^\circ\text{C}$ causing the degradation of the organic products) of Black Mass before leaching and by an adjustment of the final solution ($\text{pH} = 5$) to avoid the degradation of the active ETJ material. These preparations make ETJ very promising for a new recycling process of metal values from spent lithium-ion (LIBs) or lithium metal batteries. It would offer a competitive alternative to current technology.

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