

Rafael Trocoli, Fabio La Mantia

# ELECTROCHEMICAL ION PUMPING: A VERSATILE PROCESS FOR ELECTRO- CHEMICAL ENERGY CONVERSION

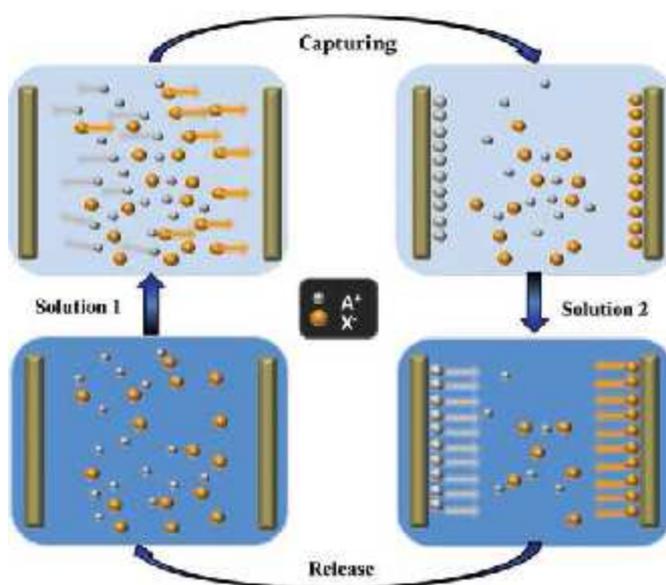
## ABSTRACT

Renewable energy generation based on water salinity differences between two streams, the production of fresh water by desalination of seawater, and highly selective lithium recovery process from brines, are three important issues that need to be improved for a sustainable future according with the current demands. Electrochemical ion pumping methodology has recently become an interesting alternative to the present processes, owing to its energy efficiency, stability, selectivity, and simple construction. A review of the newly achievements reached in this field and the future needs are described in this work.

## 1. INTRODUCTION

The possibility to capture or release ions from or to an aqueous solution with high efficiency is becoming nowadays a very attractive technology. Indeed, such a technology could have multiple applications, such as recovery of energy from salinity gradients, desalination of seawater, and recovery of precious or valuable salts from aqueous or organic solutions. Several electrochemical and chemical methods, based on ion selective (anionic and cationic) or water selective membranes, have been developed in the years [1]. They all suffer of similar drawbacks, which are relative to the use of membranes: rapid fouling due to the presence of organic matter in the water; clogging of the pores with the salt; lower efficiency at higher salinity gradient; poor selectivity towards single ions [2]. To overcome these drawbacks, capacitive de-ionization and mixing was developed by Brogioli [3]. This electrochemical method is based on the use of materials for supercapacitors and ultracapacitors to capture and release ions from the solution. This methodology can be described by a cycle composed by 4 steps: at first the ions in solution 1 are attracted to the surface of the electrodes (typically activated carbons) by increasing the voltage of the electrochemical cell; in the second step solution 1 is replaced by solution 2; further, by decreasing the voltage applied to the cell, the ions captured at the interface are released in solution 2 (step 3); at last, the cycle is closed by replacing solution 2 with solution 1 (step 4) (see figure 1). As seen in figure 1, for maintaining the electro-neutrality principle, for each cation captured on one electrode, an anion has to be captured on the

other electrode. In particular, when solution 1 has a higher salinity of solution 2, the method produces energy from the salinity differences (capacitive mixing); if solution 1 had the same salinity of solution 2, the method uses energy to generate a salinity difference (capacitive deionization). The method can also be used to capture a specific cation or anion from solution 1 and release in solution 2 for further treatment. This last point was less explored in the case of the capacitive and membrane methods. In general, this class of processes could be referred as electrochemical ion pumping, because during the cycle the ions are pumped from one solution to another solution. In particular, the capacitive mixing was used for extracting energy from the mixing of freshwater from rivers and seawater, a natural source of salinity difference [3a]; capacitive deionization was used to treat seawater and brackish water in order to obtain freshwater [3b]. Although the working principle is very intriguing, this method has shown several disadvantages, in particular low selectivity towards specific ions, and low amount of captured salt per cycle, low charge efficiency due to self-discharge processes. These disadvantages are due to the nature of the ion capturing process: using the interface to capture the ions has the disadvantage that the volume where the ions can be confined is relatively small (low amount of salt),



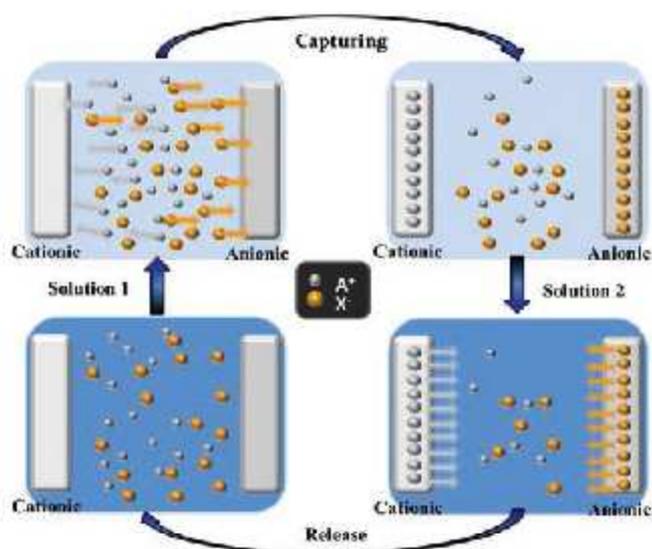
**Fig. 1: Capacitive mixing and desalination cycle. During the capturing phase, the ions in solution 1 are attracted to the surface of the electrodes. During the release phase, the ions are repelled from the surface of the electrodes and are released in solution 2. Solution 1 and 2 can have different compositions.**

Rafael Trocoli, Dr. Fabio La Mantia (Corresponding author)  
Ruhr-Universität Bochum, Center for Electrochemical Sciences (CES)  
Semiconductor & Energy Conversion  
Universitätsstr. 150 NC 4/67, 447 80 Bochum, Germany  
Phone: +49 (0)234-32 29 433  
E-Mail: fabio.lamantia@rub.de (Fabio La Mantia)

it is easily subject to disturbance from external species (high rate of self-discharge), and the interaction with the ions are mostly electrostatic and therefore unspecific (low ion selectivity).

## 2. MIXING ENTROPY BATTERY

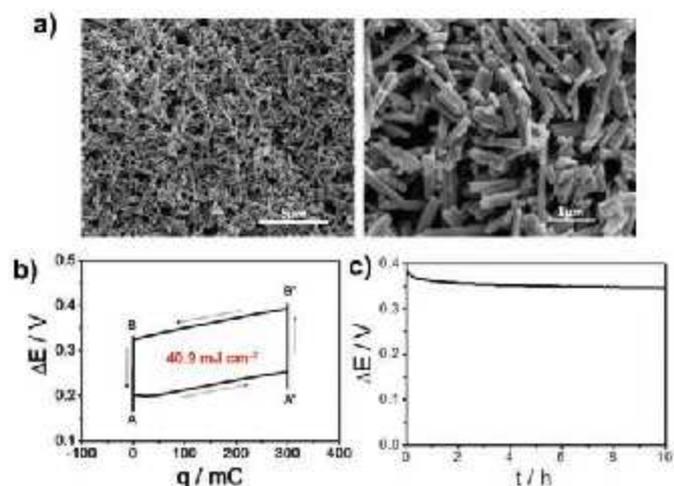
At variance with supercapacitors and ultracapacitors, intercalation batteries have the advantage to store ions in the bulk of the material, thus enabling a higher amount of ions to be captured from the solution 1 during the first step. Moreover, such intercalation mechanism can be also highly versatile and selective, thus favouring the intercalation of ions of a single kind from a mixture of different salts. Finally, battery materials are designed and optimized in order to minimize the amount of interactions with other chemical compounds, so that the self-discharge rate is typically low. Although it appears as an ideal choice, batteries are also typically slow systems: for completing one cycle it could be necessary several hours, thus lowering the power output of the system. Other mechanisms can be used in battery materials, such as conversion and dissolution / precipitation mechanisms, but they have similar features with the intercalation mechanism. Nonetheless, it is possible to improve the specific power of the battery device by nanostructuring the active materials. In this way, the larger surface area exposed to the solution, and the shorter distances that the ions have to travel inside the solid phase allow for a faster capturing and release of the ions in solution. For working properly and maintain the electro-neutrality principle, the materials have to be chosen so that one electrode is capturing / releasing cations (cationic electrode) while the other is capturing / releasing anions (anionic electrode). If both electrodes are capturing / releasing cations, the battery will not be able to extract energy from salinity differences, or generate salinity difference by using electric energy (see figure 2). Based on this concept, La Mantia et. al [4] proposed a novel electrochemical ion pumping named *mixing entropy battery*, which is able to capture and release ions from the solution by storing them inside the bulk crystal structure of the active materials.



**Fig. 2:** Electrochemical ion pumping cycle. The solution 1 and solution 2 can have different concentration of ions, or contain a mixture of ions. The cationic material and the anionic material capture cations and anions during the capturing phase, respectively. During the release phase, the ions are released in solution 2. Due to the electro-neutrality principle (same number of cations and anions in solution), it is not possible to capture only cations or only anions.

The mixing entropy battery has shown to be able to overcome the disadvantages of the capacitive methods: by a proper selection of the active materials it has been possible to selectively capture single ions from a mixture, to remove large amounts of salt, and to work with salt at high concentration.

In 2011 [4], La Mantia et al. demonstrated that the mixing entropy battery, based on  $\text{Na}_{0.44}\text{Mn}_2\text{O}_4$ , as cationic electrode, and Ag, as anionic electrode, could be used to extract energy from the difference in salinity between two streams containing different concentrations of NaCl, in particular synthetic seawater (0.6 M NaCl solution) and synthetic fresh water (0.024 M NaCl solution).  $\text{Na}_{0.44}\text{Mn}_2\text{O}_4$  was synthesized by a polymer method [5] under the shape of nanorods, with length of 1  $\mu\text{m}$  and diameter of 200 nm (see figure 3a). The particular shape of the nanoparticles allowed for a rapid insertion / release of the sodium ions in / from the solid phase. This enabled reaching energy density of about  $29 \text{ mJ cm}^{-2}$ , power density =  $10.5 \mu\text{W cm}^{-2}$ , and stable for at least 100 cycles. Moreover, in real seawater and lake water (see figure 3b-c) an energy density of about  $41 \text{ mJ cm}^{-2}$ , and the self-discharge was equal to 10 % in one hour. This technology appeared to be very promising and to have practical application in the field of renewable energy production, reaching energy efficiencies of 75 %, to be confronted with an efficiency of 30 % for the capacitive deionization. The energy extracted from the mixing of seawater and fresh water from rivers is a natural process of solar energy conversion. Indeed, the water of the oceans evaporates thanks to the solar radiation. The evaporated water condensates and falls as rain, snow, and hail, a part of which ends in the rivers. It is clear that the same process can be done artificially in a more efficient way. Solar energy can be converted to heat and used to distillate a solution, thus producing the two streams at different salinity. In this case there is the advantage to choose the combination of materials, salt, and operating conditions, which are more convenient for the improvement of the efficiency of the process. In particular, LiCl was selected as salt, due to the



**Fig. 3:** (a) SEM image of  $\text{Na}_{0.44}\text{Mn}_2\text{O}_4$ , synthesized by the polymer precursor route. (b) Mixing entropy battery cycle; A is the immersion of the electrodes full of salt in the fresh water, A is after the release of the salt from the electrodes into the fresh water, B is the immersion of the electrodes in the seawater, B is after the capturing of the salt in the seawater. Real seawater and real fresh water are used. (c) Open circuit voltage stability of the mixing entropy battery upon immersion in seawater.  $\Delta E$  is the total potential difference of the cell;  $q$  is the charge flowing through the cell;  $t$  is the time.

high solubility of this salt (up to  $832 \text{ g dm}^{-3}$ ), with concentration  $1.5 \text{ M}$  for solution 1, and  $0.03 \text{ M}$  for solution 2.  $\text{LiFePO}_4$  was selected as material for the capturing / release of  $\text{Li}^+$ , while  $\text{AgCl}$  was taken for the capturing / release of  $\text{Cl}^-$ .  $\text{LiFePO}_4$  has the great advantage to have a rather constant potential of intercalation, and therefore the power and voltage output can be maintained constant for long time. This system was able to reach an energy density of about  $38 \text{ mJ cm}^{-2}$  (power density =  $14 \text{ } \mu\text{W cm}^{-2}$ ), with good stability for 100 cycles [4].

### 3. DESALINATION BATTERY

In 2012 [6], the same group of researchers developed the desalination battery. The desalination battery is based on the concept of the mixing entropy battery, but uses solution 1 and 2 with the same concentration, to generate two streams, one at high salinity and the second with low salinity. As solution 1 and 2, seawater was used, thus the desalination battery removes salt from seawater, producing fresh water, and releases the captured salt in other seawater, which is then released in the oceans, or could be used as by-product, if necessary. The production of fresh water from seawater is a very important process: the consumption of fresh water is becoming a world-wide problem, due to the fact that, at the current growth rate, it is estimated that humans will consume 90 % of available fresh water by 2025, by which time the population living in water-stressed areas is expected to increase to 3.9 billion. The desalination battery was built using as cationic and anionic materials nanorods of  $\text{Na}_{0.44}\text{Mn}_2\text{O}_4$ , and microparticles of silver (circa  $1 \text{ } \mu\text{m}$  in diameter), respectively. With respect to the mixing entropy battery,

the desalination battery appears as the reverse process, and thus the potential profile of the device is similar to the one of the mixing entropy battery (see figure 4a). Due to technical limitations, it was possible to desalinate up to 50 % of the seawater; for a practical application it would be necessary to reach 98 % of desalination. Although the technical limitations, dictated by the design of the cell, the energy consumption to remove 25 % of salt was equal to  $0.29 \text{ Wh dm}^{-3}$ , to be compared with the value of  $0.2 \text{ Wh dm}^{-3}$  of reverse osmosis, a well-developed technique in the field of seawater desalination. Aside the promising energy efficiency, the system had a simple construction, used readily available materials, and operated at room temperature with fewer corrosion problems than existing desalination technologies. However, from a more detailed analysis of the single electrode materials, it resulted that the silver anionic electrode is the most limiting part of the system, in terms of energy dissipation. During the desalination of the seawater, a layer of  $\text{AgCl}$  is formed on top of the silver particles. This layer is insulating: it prevents the further capturing of  $\text{Cl}^-$  and it increases the electric inner resistance of the desalination battery, thus increasing the energy losses (see figure 4b). In this respect further improvements on the performances of the desalination battery are expected by nanostructuring the anionic electrode. The desalination battery could be used also as a pre-treatment system for the reverse osmosis plant, which uses water-selective membranes. In this way, the amount of salt that the water-selective membranes have to block would be lower, thus increasing their lifespan.

### 4. RECOVERY OF LITHIUM BY ELECTROCHEMICAL ION PUMPING

The possibility to extract selectively some ions from a solution containing a mixture of salts is very attractive in the field of metal recovery. In particular, it can be used in hydrometallurgy and recycling of precious materials. Nowadays, lithium carbonate is becoming a very strategic material. It is used in the synthesis of metallic lithium, and lithium-containing compounds, which are used in several field, such as heat-resistant ceramics, greases, high strength-to-weight alloys, pharmaceuticals, lithium-ion batteries. It is also predicted that the last one will rapidly increase due to the possibility to use this power source for electromobility [7]. So, the extraction of lithium from different sources is a crucial process, which efficiency and environmental impact has to be taken into consideration. In general lithium salts, and in particular lithium carbonate, can be obtained from several sources, such as hard minerals, brine lakes, and seawater. However the production of lithium carbonate from hard minerals or seawater is not as economically competitive as the one from brine lakes. Also, the extraction of lithium from brines is traditionally based on the lime-soda evaporation process: the water of the salt lakes is pumped in different ponds in which precipitation of different salts occurs by simple evaporation of the water, thereafter boron is removed by solvent extraction with long-chain alcohols or multi-carbon diols, finally the brine is treated with lime to precipitate most of the magnesium and sulfates, followed by a reaction with a small amount of soda ash to precipitate the remaining magnesium and calcium. The precipitates are removed by settling and filtration, and the lithium carbonate formed by the reaction with soda ash is recovered [8]. This is intrinsically a very simple and inexpensive process, but it is time consuming (12–18 months) and uncontrollable (relies on natural evapora-

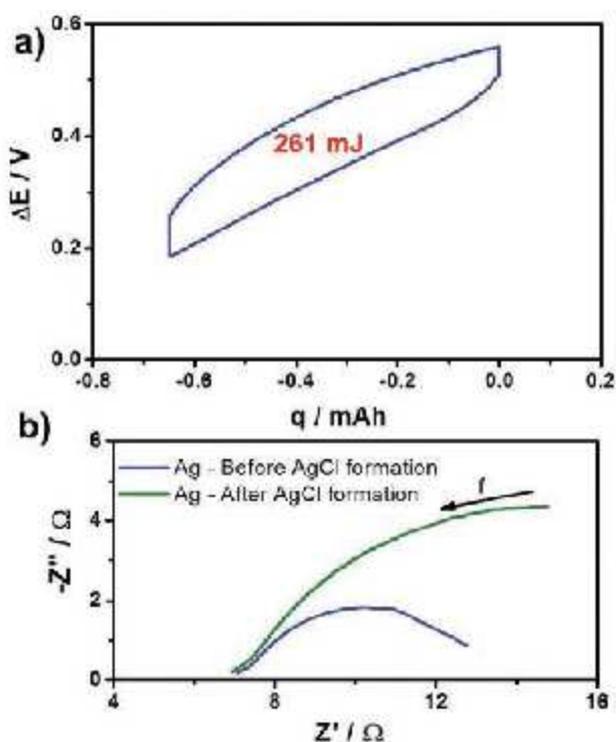
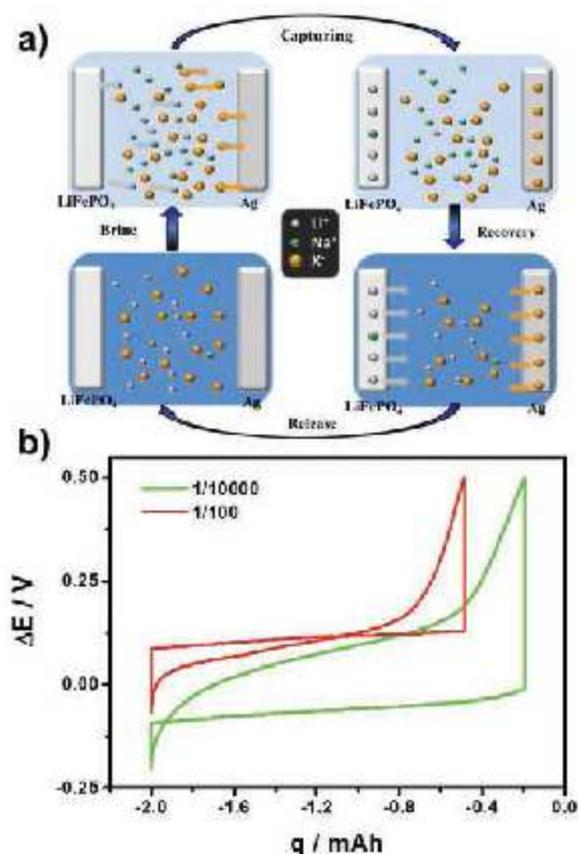


Fig. 4: (a) desalination cycle obtained by using  $\text{Na}_{0.44}\text{Mn}_2\text{O}_4$  as cationic electrode and silver particles as anionic electrode. 25 % desalination achieved. (b) Electrochemical impedance spectra of the silver electrode before and after formation of  $\text{AgCl}$ . The higher impedance values indicate higher energy losses and lower efficiency.  $\Delta E$  is the total potential difference of the cell;  $q$  is the charge flowing through the cell;  $Z'$  and  $Z''$  are the real and imaginary part of the impedance, respectively.

tion by solar energy), and moreover it shows additional drawbacks, such as the need of extensive surfaces, the substantial water consumption, the large quantities of chemical waste production, and the strong environmental impact. An improved lithium recovery technology is required to supply the actual lithium demand in a more efficient and environmental friendly way.

Two electrochemical methods have been proposed for the recovery of lithium from aqueous solutions, in particular from salt lakes or seawater. In the first method [9] a material for the selective intercalation of lithium, in particular  $\lambda$ - $\text{Mn}_2\text{O}_4$ , is used to capture  $\text{Li}^+$  from a solution in which it is in a mixture with other salts, and it is released in a second solution at higher purity. As second electrode, platinum is used. So, during the capturing of lithium, oxygen is evolved on the platinum electrode, while during the release of lithium, hydrogen is evolved, thus leaving in the second solution  $\text{LiOH}$ . Although  $\text{LiOH}$  is an attractive compound, because it can be used directly for the production of metallic lithium, this method is not simply taking a salt from one solution and putting it in another one, but it is splitting water, thus involving a reaction, which has intrinsic kinetic limitations, and requires high energy to run at a proper speed [10]. Also electrochemical ion pumping was proposed for the recovery of lithium from both salt lakes and seawater [6]. In this case, a selective cationic material is used for capturing / releasing lithium ions, while a general anionic material is chosen to capture / release chlorides or sulfates (see figure 5a). The advantage with respect to the previous method is that the energy consumption in the electrochemical ion pumping is only relative to the transference of the salt from one solution to the other, and does not involve the energy necessary for the water splitting. To understand the difference between the two methods, the thermodynamic energy necessary in the case of water splitting is equal to  $0.9 \text{ kWh kg}^{-1}$  of lithium carbonate, while in the case of the electrochemical ion pumping the thermodynamic energy consumption is below  $0.01 \text{ kWh kg}^{-1}$  of lithium carbonate.

The electrochemical ion pumping for the recovery of lithium has been extensively studied in our group [6, 11]. Instead of the classic  $\lambda$ - $\text{Mn}_2\text{O}_4$  cationic electrode, which has the disadvantage to dissolve during the release of lithium ions, and to have a very high potential (de-)intercalation potential ( $1.1 \text{ V}$  vs. NHE), located near the oxygen evolution reaction, we decided to use  $\text{LiFePO}_4$ , which (de-)intercalation potential is circa  $0.43 \text{ V}$  vs. NHE, and thus is located inside the stability window of water, and side reactions can be avoided. Moreover,  $\text{LiFePO}_4$  seems to be rather stable if a proper care is taken in cycling the electrode within the right potential window. As anionic material, silver was selected at first, to demonstrate the working principle of the lithium recovery. In this case, only chloride is captured / released, while sulfate remains in the solution 1. First observations confirmed that lithium recovery from diluted solutions is far more energy consuming than from concentrated solution. In presence of  $50 \text{ mM LiCl}$  and  $5 \text{ M NaCl}$ , selectively recovering lithium (purity higher than  $80 \%$ ) consumes  $0.028 \text{ kWh kg}^{-1}$  of lithium carbonate. If the lithium is recovered from a solution with  $500 \mu\text{M LiCl}$  and  $5 \text{ M NaCl}$  (purity higher than  $20 \%$ ), the energy consumption is equal to  $0.54 \text{ kWh kg}^{-1}$  of lithium carbonate (see figure 5b). It has been observed that the energy consumption is exclusively related to the energy dissipations, and not to the



**Fig. 5:** (a) Schematic of the lithium recovery cycle. Part of the sodium can intercalate in the  $\text{LiFePO}_4$  and be transported to the recovery solution together with lithium. (b) Experimental results of the lithium recovery cycle obtained by using brine with a ratio between lithium and sodium of 1:100 and of 1:10000.  $\Delta E$  is the total potential difference of the cell;  $q$  is the charge flowing through the cell.

thermodynamic energy cost. In particular, most of the energy is lost due to the diffusion of the lithium ions from the bulk of the solution to the surface of the electrode, where they are captured. Therefore, when the concentration is decreased, and the diffusion process becomes more critical, the energy consumption increases, too. At high concentration of lithium ions, the inner resistance of the device plays the most critical role. From the analysis above, it became clear that a proper engineering of the electrochemical device is necessary in order to improve the practical energy efficiency of the electrochemical ion pumping. In all cases it was observed that the selectivity of  $\text{LiFePO}_4$  was always above 500 (500  $\text{Li}^+$  ions are captured for each  $\text{Na}^+$  ion captured), and, strangely, increased by decreasing the concentration of  $\text{LiCl}$  in solution 1. We have postulated that the cationic material is able to intercalate sodium only in a relatively small portion of the crystal, thus most of the structure remains available to the intercalation of lithium ion at a later stage.

In a later study, the effect of the diffusion limiting current, and the applied current on the purity of the recovered lithium, as well as on the energy consumption, was investigated. Also, the presence of  $\text{K}^+$  and  $\text{Mg}^{2+}$  on the efficiency of lithium recovery was investigated. These cations, together with  $\text{Na}^+$  and  $\text{Li}^+$ , are typically present in seawater, salt lakes, and hydrothermal waters. As solution 1, synthetic brine was used, containing  $42 \text{ mM LiCl}$ ,  $108 \text{ mM KCl}$ ,  $74 \text{ mM MgCl}_2$ ,  $793 \text{ mM NaCl}$ . The experiments

confirmed that  $\text{LiFePO}_4$  has a very high selectivity towards capturing of lithium ions, and both  $\text{Na}^+$  and  $\text{K}^+$  are mostly remaining in the solution 1.  $\text{Mg}^{2+}$  appears to be the only ion which can intercalate inside the structure of the cationic material in a relatively high amount; the selectivity coefficient of  $\text{Li}^+$  with respect  $\text{Mg}^{2+}$  is equal to 34:1. Depending on the current density, the purity of the recovered lithium and the energy consumption of the recovery process are changing. In particular, the lower is the current density of the recovery process, which means the slower it is the recovery process, the higher is the purity of the lithium salt in solution 2, and it reaches 99.98% when the recovery is performed in 10 hours. However, under such slow conditions, most of the electric charge flowing through the system is due to other processes, in particular oxygen reduction, and the efficiency of lithium recovery results low. The lithium recovery efficiency reaches its maximum, equal to 93 %, when the recovery process is performed in 1 hour. In this case the purity of the lithium salt in solution 2 is equal to 97.8 %. Related to the efficiency, also the energy consumption has a minimum value when the process is performed in 1 hour. With this procedure, if a plant with the same dimensions of the salt pounds used in South America would be employed for the recovery of lithium, the same amount of lithium carbonate traditionally refined in one year by the lime-soda evaporation process would be extracted in 8 days by using the electrochemical ion pumping process.

## 5. CONCLUSIONS AND OUTLOOK

The different applications based on the electrochemical ion pumping concept (energy production, desalination, and lithium recovery) show the high flexibility of this technology and its possible impact in the present social problems, as the need of new energy conversion systems, the low cost clean water production, and a more efficient method for lithium production. Moreover the same principle could be applied to other issues, such as the pollution from heavy metals, the selective recovery of precious materials, and recycling. However, further developments are re-

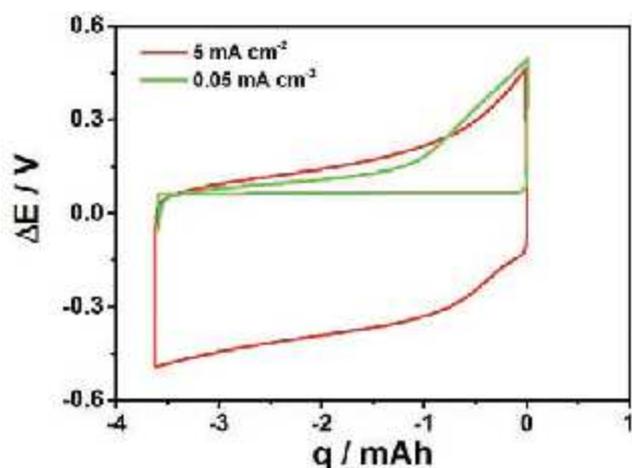


Fig. 6: Lithium recovery cycle obtained by using  $\text{LiFePO}_4$  as lithium selective electrode, and silver particles as anionic electrode at different current densities. The higher is the area inside the curve, the higher is the energy consumption.  $\Delta E$  is the total potential difference of the cell;  $q$  is the charge flowing through the cell.

	Current / $\text{mA cm}^{-2}$			Original
	0.05	0.5	5	
Li (mM)	$74 \pm 5$	$99 \pm 23$	$52 \pm 4$	42
K (mM)	$0.002 \pm 0.002$	$0.002 \pm 0.002$	$0.002 \pm 0.002$	108
Mg (mM)	$0.002 \pm 0.002$	$0.85 \pm 0.004$	$0.1 \pm 0.1$	74
Na (mM)	$0.008 \pm 0.004$	$0.93 \pm 0.004$	$17 \pm 1$	793
Purity <sub>i</sub> (%)	99.98	97.86	74.27	4.13
Efficiency (%)	69.4	92.9	48.8	--
Energy ( $\text{Wh mol}^{-1}$ )	4.0	2.8	29.5	--

Table 1: Concentration of different cations, lithium purity, and energy consumption after the process of lithium recovery at different current densities.

quired to render the methodology more economically feasible: replacement of silver as the anionic electrode, which has an high price and suffer of poor electronic conductivity upon formation of  $\text{AgCl}$ ; optimization of the cell geometry to work in a continuous mode and reduce the energy losses; utilization of electrodes with higher capacity, to improve the amount of transferred salt per unit of volume and weight. These are required steps for the final implantation of this methodology at industrial scale.

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