



## Neutralization of used Li batteries: Anodic dissolution of the iron–nickel alloy positive pins of Li–SOCl<sub>2</sub> batteries in seawater

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### Abstract

This paper reports a study of the neutralization of Li–SOCl<sub>2</sub> batteries. Immersion of these batteries in acidic seawater solutions leads to their complete discharge by short circuit, followed by corrosion of the positive pin (made of an Fe/Ni alloy). This corrosion process is desirable because it allows penetration of water into the battery, and hence, neutralization of the active mass of the batteries through their reaction with water. The most efficient corrosion of Fe/Ni electrodes is obtained in seawater containing both HCl and H<sub>2</sub>SO<sub>4</sub> in a situation of no separation between the electrode compartments, due to the reaction of the H<sub>2</sub> liberated at the cathode with the surface films on the anode (Fe/Ni pin electrodes). This reaction prevents passivation of the positive pin. Indeed, used Li–SOCl<sub>2</sub> batteries whose insulating covers were removed, corroded much quicker than regular batteries because of the impact of H<sub>2</sub> evolved at the case (the negative pole of the battery) on the dissolution of the positive pin.

### 1. Introduction

The recycling of used batteries containing a Li metal such as Li–SOCl<sub>2</sub> is an important environmental and industrial issue. Neutralization of a Li metal anode is necessary before mechanical or chemical recycling of a battery case occur. One of the least expensive methods for Li metal anode neutralization in used Li batteries is battery immersion into water containing electrolytes such as seawater [1].

Two consecutive steps take place when the battery is immersed in water. Water shorts the battery. The first step leads to a discharge of the battery through the aqueous solution containing electrolytes. In parallel to this internal discharge process, there is an external process in which the positive pin of the battery dissolves. These two processes occur simultaneously as the internal process in the battery enables the external corrosion process in which the positive pin (usually made of an Fe–Ni alloy) is naturally the anodic pole. The battery case is the cathodic pole, in which oxygen reduction process takes place. The Li anode inside the battery is connected to the battery case. Therefore, during the first step, the battery case is under negative potential, and reduction processes occur on its surface. In the case of a used Li battery, the residual capacity is usually sufficient for full anodic dissolution of the positive pin. A hole is created in the battery case as a result of the positive pin

dissolution. The water penetrating into the battery reacts with both residual lithium and SOCl<sub>2</sub>, and neutralizes them. In such a case, battery neutralization is achieved quickly under condition that passivation processes do not occur on the pins' surface.

In the second step, after a complete discharge of the battery, when the surface of the battery case loses its negative potential, corrosion processes of the battery case occur.

A complete anodic dissolution of the positive pin and, as a result, an opening in the cap of the battery, allows neutralization of the residual lithium metal by water penetration in the first step. In this work, we studied the first step of recycling of lithium-thionyl chloride batteries. Anodic dissolution of the positive pin (made of an Fe/Ni based alloy) was investigated in acid solutions. Metals such as Fe and Ni [2–7, 12], and their alloys [8–11] have the ability to form passive oxide films that reduce the anodic dissolution rate and increase the time of battery discharge and neutralization. Therefore, we looked for conditions that facilitate dissolution of the battery pins.

### 2. Experimental details

All the tests were performed in three-electrode glass cells at room temperature. The working and counter

electrodes were separated by a glass filter. A saturated calomel electrode (SCE) was used as reference electrode and platinum wire was the counter electrode. All the electrode potentials in the text and figures therefore refer to SCE  $\text{Hg}/\text{Hg}_2\text{Cl}_2$ . The working electrodes were standard Fe/Ni (50.5% Ni, 0.1% Al, 0.05% C, 0.5% Co, 0.25% Cr, 0.6% Mn, 0.025% P, 0.025% S, 0.3% Si, Fe remainder) current collectors of AA lithium-thionyl chloride batteries. Potentiostatic, potentiodynamic, and galvanostatic measurements were conducted. In the potentiodynamic mode, the working electrode was polarized from a steady-state potential that was established after 15 min, up to 3.6 V vs SCE, with a scan rate of  $10 \text{ mV s}^{-1}$ . The solutions used included 2% v/v HCl, 6% v/v HCl, and 4% v/v HCl + 1% v/v  $\text{H}_2\text{SO}_4$  in Mediterranean seawater. The specific conductivity of this seawater was  $41 \text{ mS cm}^{-1}$ , and the pH was 7.5, which usually included 0.5 M NaCl as the major electrolytic component. The instrumentation included a PAR 173 potentiostat, model 276 interface, and a multichannel battery tester from Maccor Inc. (series 2000). The morphology of the samples after anodic dissolution in different solutions was studied by scanning electron microscopy SEM (Jeol JSM 840). The passive film components were analysed by X-ray photoelectron spectroscopy (XPS, Kratos analytical AXIS His 165 and ULTRA).

### 3. Results and discussion

#### 3.1. Tests with separated working and counter electrodes compartments

Figure 1 shows dynamic polarization curves for a positive pin electrode (Fe/Ni alloy) in Mediterranean seawater. The steady state potential of the working electrode was  $-0.1 \text{ V}$  after 15 min of storage in water without acid addition. The dependence of the anodic current density on the potential has a maximum of almost  $0.16 \text{ A cm}^{-2}$  at a potential near  $0.6 \text{ V}$ . The reduction of the current density at higher potentials is

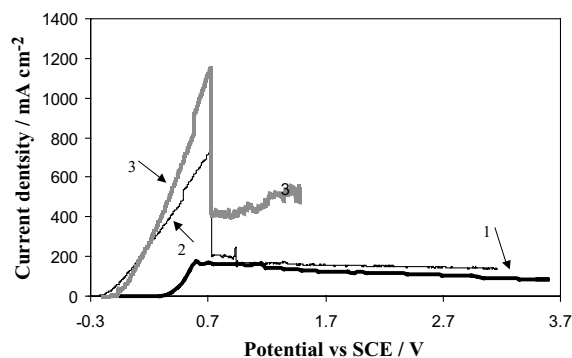


Fig. 1. Anodic polarization curves of positive pin electrodes (Fe/Ni alloy) in Mediterranean seawater (1); and with the presence of acids: 2% v/v HCl (2) and (3) 4% v/v HCl + 1% v/v  $\text{H}_2\text{SO}_4$  in an electrode cell with separated electrode compartments.

explained by passive film formation whose thickness gradually increases. A visible, yellow layer is usually formed on the surface of the Fe/Ni electrode. Intensive gas evolution was observed on both working and counter electrodes, and a yellow–green precipitation appeared on the glass membrane and on the cell bottom after anodic polarization of the electrodes. The solution became turbid due to the yellow–green suspension. This fact is explained by the formation of Fe and Ni hydroxides which are poorly soluble in water at pH 7.5. The water near the Pt wire was turbid by a white suspension. Hydrogen evolution on the Pt electrode causes local alkalization of the water near the electrode, and hence some insoluble hydroxides can be formed (e.g.,  $\text{Mg}(\text{OH})_2$ ).

Adding HCl to the seawater solution (2% v/v, pH 1) increases the critical passivating current density to  $0.7 \text{ A cm}^{-2}$ , but does not change the anodic current density in the passive region (Figure 1, curve 2). The surface of the working electrode after anodic dissolution in this solution has a metallic color; no yellow, passive film appears. The solution remains transparent and the water has a greenish tinge. The steady state potential of the working electrode shifts to negative values from about  $-0.245 \text{ V}$  for the pristine electrode to  $0.326 \text{ V}$  after anodic dissolution. The passivation potential shifts to positive values and appears at  $0.72 \text{ V}$ . This behavior correlates with the behavior of Ni electrodes in acidic and neutral chloride-containing solutions [5]. In these solutions  $\text{Cl}^-$  delays the growth of a passivating film on Ni electrodes. The passivation potential is more positive (about for 300 mV) than for Fe/Ni alloys in  $\text{H}_3\text{PO}_4$  solutions containing  $\text{Cl}^-$  [7].

Curve 3 in Figure 1 relates to anodic dissolution of Fe/Ni alloy in Mediterranean Seawater with 4% v/v HCl and 1% v/v  $\text{H}_2\text{SO}_4$ . The passivation potential does not change after sulfuric acid addition but the critical passivating current density is higher,  $1.2 \text{ A cm}^{-2}$ .

Figure 2 shows potentiodynamic response, when the initial potential applied was  $3.6 \text{ V}$  and it was scanned cathodically with a scan rate of  $10 \text{ mV s}^{-1}$ . The current density increased to high values at the beginning of the test and rapidly fell because of the formation of passivating film. The decrease in current density is explained by the increase in the passive layer thickness. The current density measured in the passive region is close to that obtained in the tests with anodic potential scan. Therefore, we suggest that the nature of the passivating film does not depend on the direction of the potential scanning.

#### 3.2. Tests with non-separated working and counter electrodes spaces

Fe/Ni alloy electrodes do not passivate if their anodic polarization in the experiments described above is conducted in seawater/4% HCl, 1%  $\text{H}_2\text{SO}_4$  solution without separation them from the counter electrodes (Figure 3). Passivation was not observed, either in

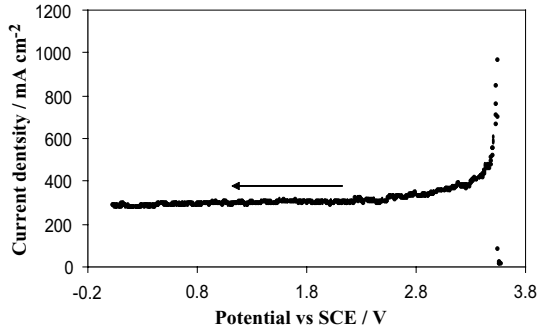


Fig. 2. Dependence of the anodic current density of a Fe/Ni alloy electrode on potential in Mediterranean seawater containing 4% v/v HCl and 1% v/v H<sub>2</sub>SO<sub>4</sub> in an electrode cell with separated electrode compartments. The arrow shows the direction of the polarization (from 3.6 V to lower potentials).

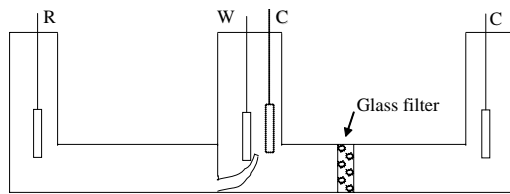


Fig. 3. A three-electrode cell with separated compartments, working (W) and counter (C) electrodes; (R) reference electrode.

potentiodynamic or in potentiostatic and galvanostatic conditions. Figures 4–6 show the results of these tests. Figure 4 shows typical chronoamperograms of the Fe/Ni alloy electrodes measured at different potentials with no separation between the working and the counter electrode compartments. Figure 5 shows a plot of  $I/E$  based on the chronoamperometric results. Figure 6 shows a potentiodynamics response of this system when the initial potential applied was high and it was scanned cathodically. A gradual decrease in the current is measured as the potential decreases. The behaviour demonstrated in Figure 4 contrasts the results in Figures 1 and 2. Specifically, when the Fe/Ni pin electrodes are polarized anodically in seawater solution containing HCl and H<sub>2</sub>SO<sub>4</sub> these electrodes are not passivated

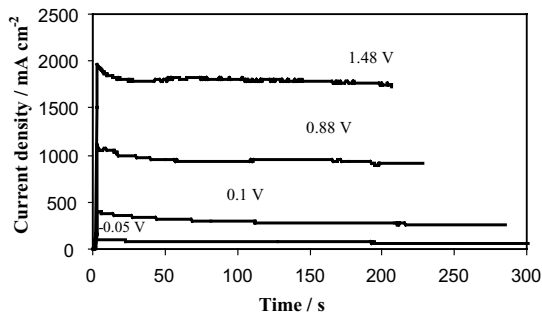


Fig. 4. Chronoamperograms obtained with Fe/Ni pin electrodes in Mediterranean seawater containing 4% v/v HCl and 1% v/v H<sub>2</sub>SO<sub>4</sub> in a cell with non-separated electrode compartments.

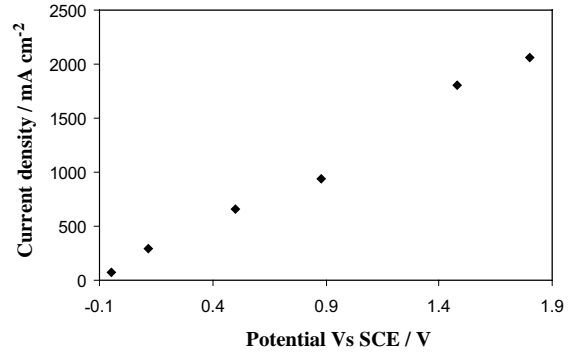


Fig. 5. Dependence of the anodic current density on the potential for Fe/Ni electrodes in solutions containing 4% HCl and 1% H<sub>2</sub>SO<sub>4</sub> in a cell with non-separated electrode compartments evaluated from Figure 4.

(while there is no separation from the cathode compartment).

Previous studies on the influence of hydrogen on the passivation of nickel electrodes [12] showed that when the solutions contain the H<sub>2</sub> gas, the self-corrosion potentials of Ni electrodes shift cathodically, the passive region becomes narrow, and the currents measured in the passive region are relatively high. The hydrogen apparently reacts with the oxide film and thus prevents, or at least delays, passivation phenomena. Indeed, in all the measurements reported above, intensive hydrogen gas evolution was observed on the cathodes. We therefore suggest that when there is no separation between the Fe/Ni electrodes and the cathodes, the hydrogen formed on the cathode reacts with the oxide films on the Fe/Ni pin electrodes and prevents passivation. In parallel experiments, Li-SOCl<sub>2</sub> batteries were able to corrode in seawater solutions under two conditions: (i) when the battery cases were covered by standard insulating tape, and (ii) when the insulating tape was removed and the entire negative case was exposed to the solution.

A much more rapid corrosion of the positive pin was observed with batteries whose insulating covers were removed and whose battery cases were fully exposed to the solution. These results correlate very well and are

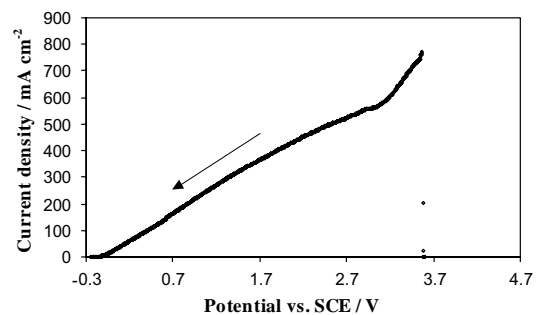


Fig. 6. Dependence of the anodic current density of a Fe/Ni alloy on potential in the seawater/4% HCl, 1% H<sub>2</sub>SO<sub>4</sub> in a cell with non-separated electrode compartments. The initial potential was 3.6 V and the potential was scanned cathodically.

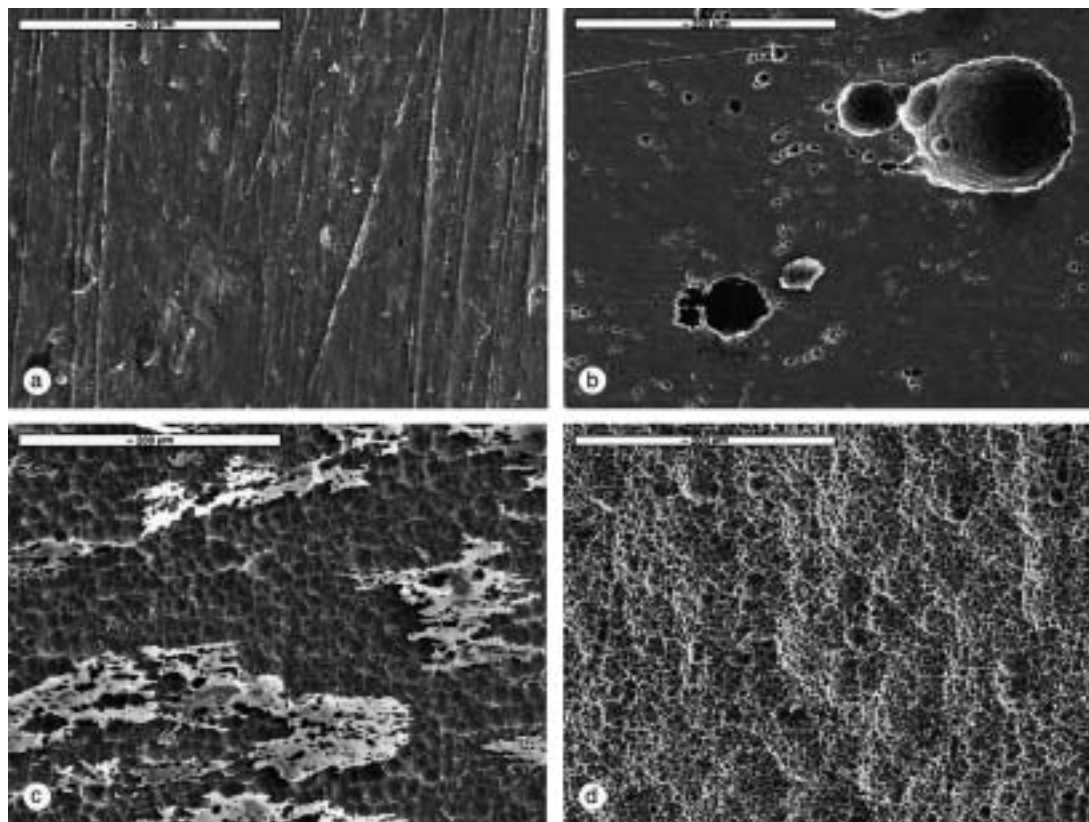


Fig. 7. SEM micrographs of pristine Fe/Ni electrodes. (a) Pristine electrode; (b) an electrode after anodic dissolution in Mediterranean seawater; (c) an electrode after anodic dissolution in Mediterranean seawater containing 4% v/v HCl and 1% v/v H<sub>2</sub>SO<sub>4</sub> with separated electrode compartments; (d) an electrode after anodic dissolution in Mediterranean seawater containing 4% v/v HCl and 1% v/v H<sub>2</sub>SO<sub>4</sub> without separation between the electrodes compartments.

explained by the experiments with the Fe/Ni pin electrodes (Figures 4–6). Removing the insulating tape from these batteries while corroding in the seawater solutions enabled a close contact between the positive pin (the anode in these tests) and the negatively charged case (the cathode). Therefore, H<sub>2</sub>, which evolves from the battery case, interferes with the passivation of the Fe/Ni battery pins. The depassivation of the Fe/Ni alloy due to the presence of hydrogen close to its surface leads to their relatively rapid corrosion.

### 3.3. Morphology and chemical composition of the passive films on the Fe/Ni alloys after anodic dissolution by SEM and XPS

Chemical analysis of the samples by XPS clearly showed that in regions of anodic dissolution (Figures 1 and 2) a Cr-rich surface layer was formed. The XPS analysis showed no Cr on the surface of samples that were not passivated (Figures 4 and 5). These XPS results correlate well with the formation of highly protective double oxide layers in [13–16]. Spinel type oxides of the Me'Me''O<sub>4</sub> type are formed on many Fe alloys. Such oxides provide higher protection than single metal oxides [11]. Alloy elements such as Cr, Ni promote the formation of double oxides FeCr<sub>2</sub>O<sub>4</sub>, NiCr<sub>2</sub>O<sub>4</sub> with small unit cell parameters and decrease the formation of

the non-passivating FeO phase. In such cases the alloy surface layer is rich in Cr, as was indeed proved by the XPS analysis described above.

Figure 7(a) shows the morphology of the pristine Fe/Ni electrode and the same after anodic dissolution in different solutions (SEM micrographs). A pitting type dissolution of the Fe/Ni alloy was observed in Mediterranean seawater (Figure 7(b)). More uniform etched surface was obtained in seawater with the presence of acids in the case of separation between the counter and the working electrode compartments (Figure 7(c)). No differences between the samples dissolved in seawater/2% HCl and seawater/4% HCl, 1% H<sub>2</sub>SO<sub>4</sub> solutions was observed. From the micrographs it is clear that the dissolution is not uniform. The grain boundaries are the preferred locations for anodic dissolution. In the case of no separation between the counter and the working electrode compartments (Figure 7(d)), there is much less difference between the dissolution rates of the grain boundaries and the grains, and hence the morphology resulting from the anodic dissolution is more uniform than in the previous cases.

The SEM micrographs in Figure 7 correlate well with the picture obtained with the electrochemical measurements. In the case of neutral solutions, passivation occurs only at certain locations (pitting). In the case of the acidic solutions the anodic dissolution is more

intense but still partially limited by passivation (see remaining passivated surface in Figure 7(c)).

It is clear that in the case of no separation between the electrode compartments the anodic dissolution takes place uniformly with no passivation (Figure 7(d)).

#### 4. Conclusion

Immersion of used Li-SOCl<sub>2</sub> batteries in seawater may lead to several processes that neutralize the residual active mass efficiently and inexpensively. The significance for technological processes is the rapid dissolution of the battery positive pin made from a Fe/Ni alloy. This dissolution enables water penetration into the battery, which reacts and neutralizes the entire active mass. In this work, we found optimal conditions for rapid dissolution of the Fe/Ni pins of Li-SOCl<sub>2</sub> batteries. The use of solutions containing both HCl and H<sub>2</sub>SO<sub>4</sub> enables passivation of these pins to worsen, and high corrosion currents are obtained. Spectral studies by XPS clearly connect passivation of these alloys with the presence of Cr compounds (probably FeCr<sub>2</sub>O<sub>4</sub>, Ni-Cr<sub>2</sub>O<sub>4</sub>) on the surface. Removal of the battery insulating covers leads to an even quicker dissolution of the pin. This is because, in the absence of insulation, the cathodic reaction of the case liberates hydrogen close to the pin. The hydrogen therefore reacts with the oxides, which partially passivate the pin, and thus allows

rapid corrosion. A good correlation between the electrochemical and morphological studies was found.

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