Water-in-salt electrolyte: performances of Cu, Ti and steel current collectors

Walter Giurlani[a,*], Eugenio Crestini[a], Maurizio Passaponti[a], Francesca Soavi[b], Massimo Innocenti[a]

UNIVERSITÀ DEGLI STUDI FIRENZE

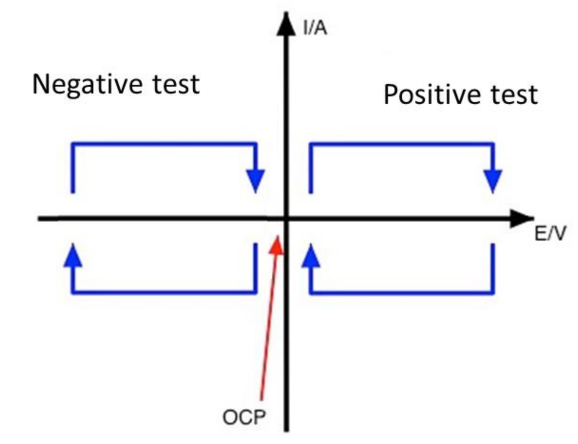
[a]Dipartimento di Chimica Ugo Schiff, Università degli Studi di Firenze, Sesto Fiorentino (FI), Italy
[b]Dipartimento di Chimica Giacomo Ciamician, Alma Mater Studiorum Bologna University, Bologna, Italy
e-mail: walter.giurlani@unifi.it

Workshop Supercapacitors Energy Storage

Water-in-salt electrolytes

The widespread use of lithium-ion batteries has raised some doubts about their environmental compatibility, mainly due to the use of the organic solvents that these devices contain. The possibility of using aqueous solvents has long been taken into consideration but the limited electrochemical water window (1.23 V) has strongly limited their development. Only in recent years, new super-concentrated electrolytes, called "water-in-salt", have been investigated [1]. In this environment the aqueous molecules are trapped in an ionic net, considerably changing their activity. This solution allows both to expand the window of usable potentials up to about 3 volts and to obtain better performance in terms of stability and energy [2-3]. Full lithium-ion cells with a potential of 2.3 V proved to be stable up to 1000 cycles. The current collectors used in these cells are generally made of aluminium; in this work different materials have been taken into consideration to improve the performance, the duration or to lower the costs. The studied collectors consist of commercial metal meshes, already used for applications in the energy sector but not yet tested in a super-concentrated aqueous environment.

Metals and solutions

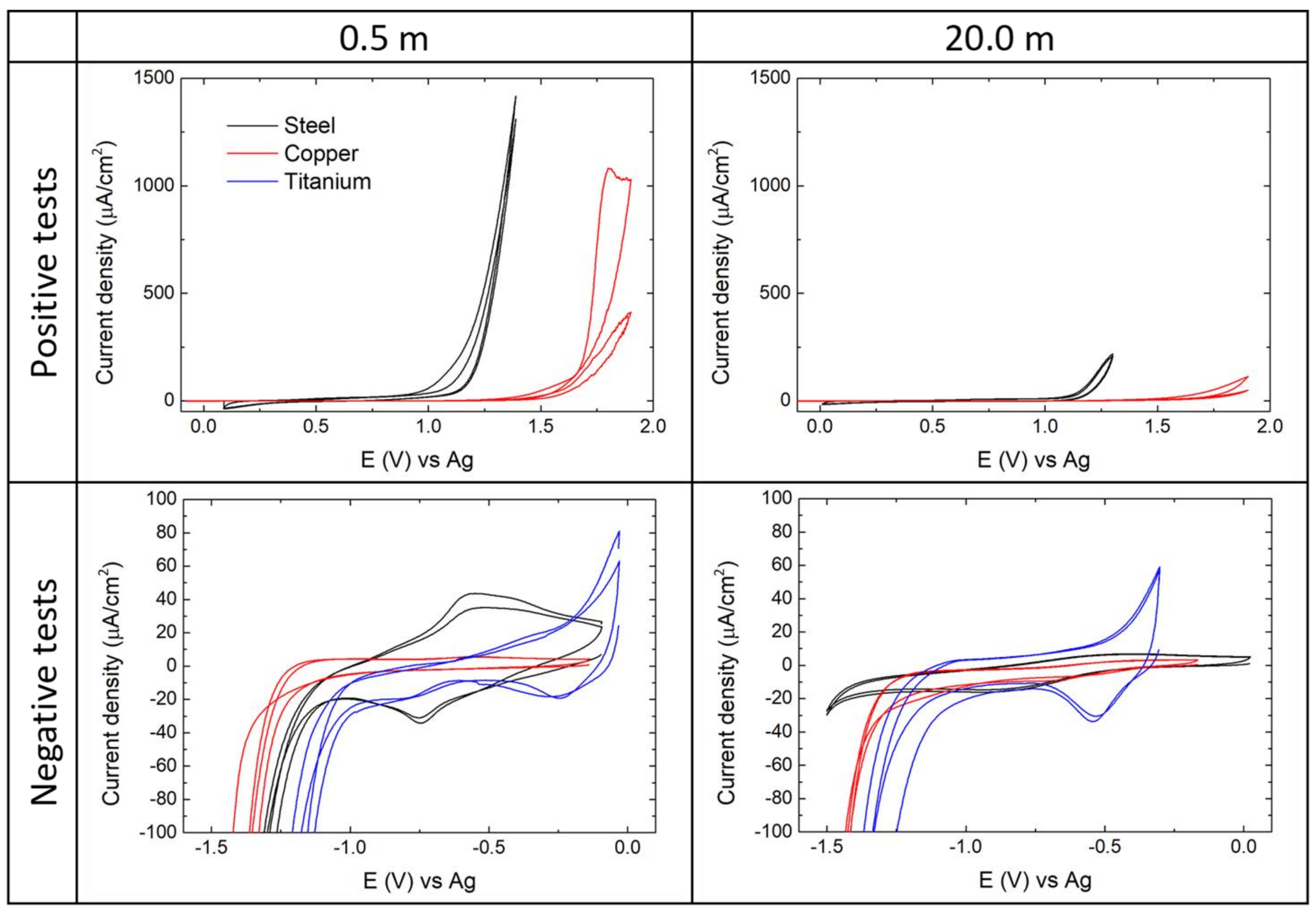


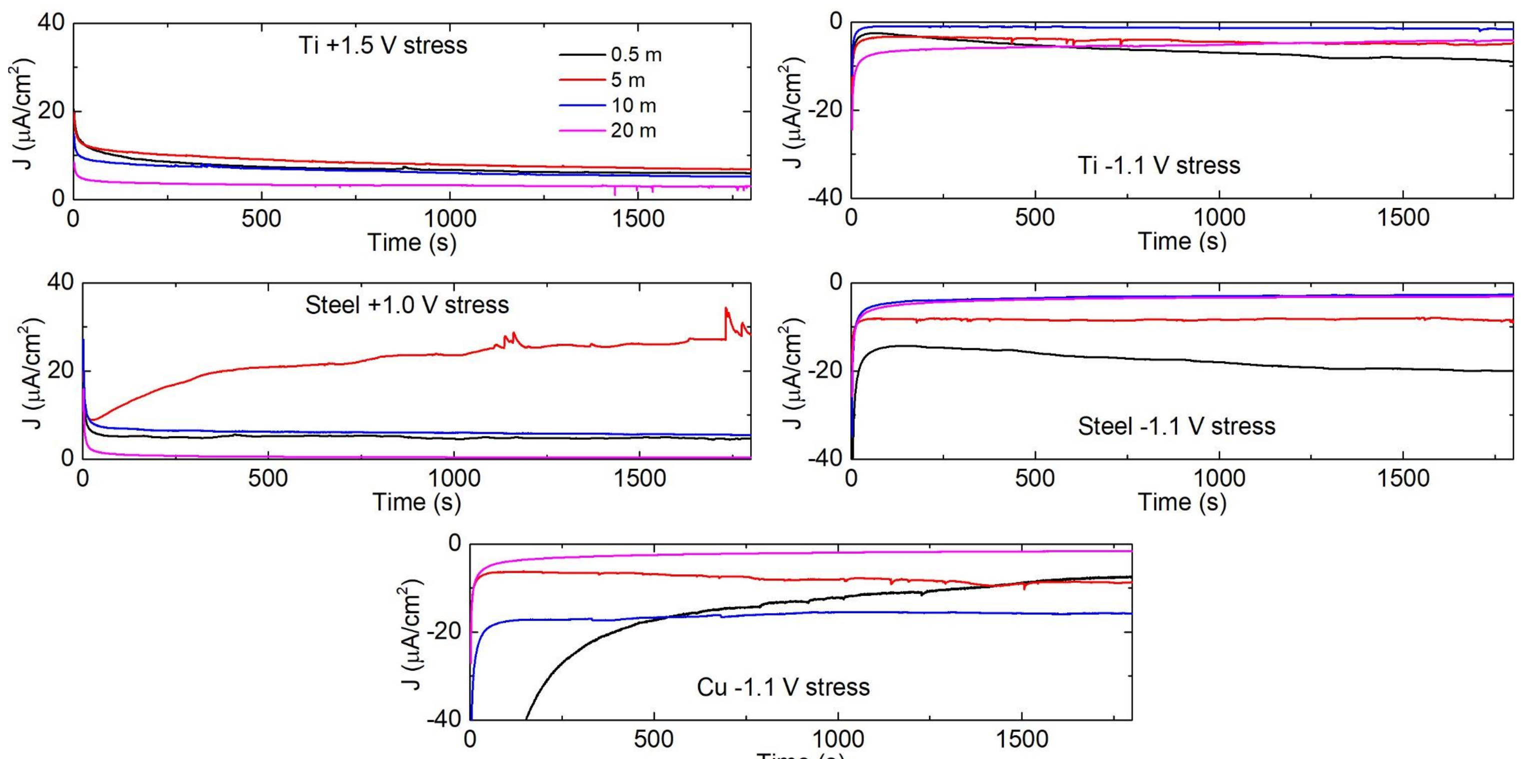
The investigated metals were steel, titanium and copper and the salt used was the LITFSI (lithiumbis(trifluoromethanesulfonyl)imide) [4] at various concentrations: 0.5, 5.0, 10.0 and 20.0 molal (concentration close to saturation). The electrodes were tested by cyclic voltammetry (CV) to evaluate the usable window and by chronoamperometry to study their stability. The study was carried out with a three-electrode system using carbon paper with drop-cast carbon black as a counter-electrode and a silver wire as a pseudo reference electrode. The CVs were performed from the OCP towards positive or negative potentials to simulate the reaction that could happen in a real cell. The chronoamperometries were performed immediately before the massive discharge for 30 minutes: +1.0 V and -1.1 V for steel; +1.5 V and -1.1 V for Ti; -1.1 V for Cu. Copper was not tested at positive potential values because it quickly undergoes to corrosion. Subsequently, SEM and XPS measurements were performed to evaluate the surface morphological end compositional modification of the current collectors.

Electrochemical behaviour

Cyclic voltammetry and potential window

The CVs performed with the minimum and the maximum concentration of LiTFSI are reported (right). During the positive polarization, Ti exhibits better performances in terms of potential window with a discharge over +1.5 V, while for steel the discharge is of about +1.0 V. Unfortunately, in consecutive CVs of Ti the max current decreases, showing a deactivation of the surface, while steel profile is reproducible. The improvement in performance (current decreasing) becomes evident by increasing the concentration of LiTFSI. During the negative scans, Cu is not satisfactory (discharge at c.a. -1.1 V); Ti doesn't change much increasing the salt concentration and the discharge begins at c.a. -1.3 V; steel performed badly at low concentrations but gets better at high concentrations, with a discharge before -1.5 V, even more negative than Ti. In summary, the couple Ti(+)/steel(-) can reach a window of 3 V, well above the 1.23 V of water.



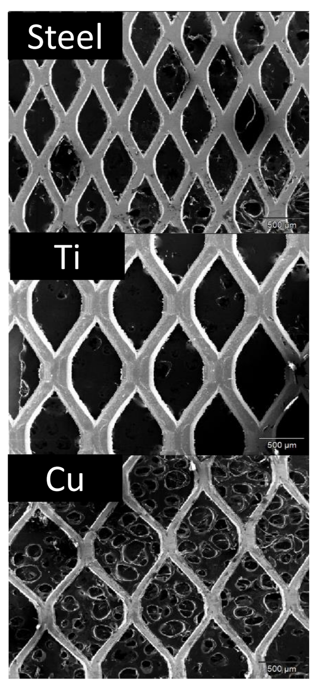


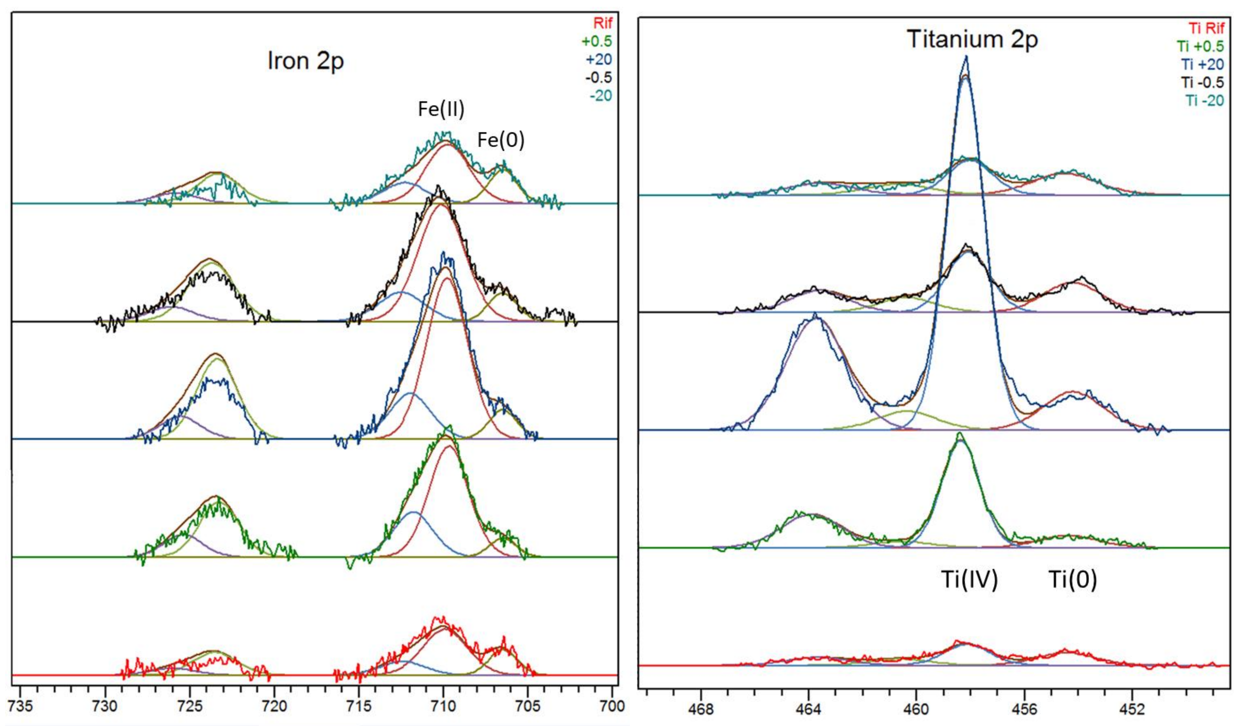
Chronoamperometry

The performed chronoamperometries (left) confirm the better stability at high salt concentrations with respect to the lower ones. Low current and fluctuations were interpreted as a better stability. Anyway, the trend is not always linear and middle concentrations sometimes behave even worse than the lower ones (e.g. steel 5 m). Only in the case of Ti under negative polarization, the 10 m solution performed better than the 20 m solution.

SEM and XPS

SEM images were used for both extracting the area of the electrodes as well as to evaluate damages on the surface after the stress performed for 30 minutes. We did not find evident changes in the morphology but longer stress will be repeated in future. On the other hand, XPS analysis on 5 meshes of steel and Ti highlights some dramatic changes in composition on the surface. The measurements were performed on an untouched sample (reference) and on samples subjected to positive and negative biases with the minimum and the maximum concentrations. Only the samples under positive polarization in the 20 m solution are similar to the reference, while all the others showed a superficial oxidation.





References

[1] Liumin Suo, Oleg Borodin, Tao et al. Science, 2015, 350, 938-943

[2] Liumin Suo, Oleg Borodin, Yuesheng Wang, et al. Advanced Energy Materials, 2017, 7, 1701189

[3]Xudong Bu, Lijun Su, Qingyun Dou, et al. J. Mater. Chem. A, 2019, 7, 7541

[4] Qi Dong, Xiahui Yao, Yanyan Zhao, Chem, 2018, 4, 1345–1358