LiFePO₄/Mesoporous Carbon Hybrid Supercapacitor Based on LiTFSI/Imidazolium Ionic Liquid Electrolyte

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ABSTRACT

A hybrid SC prepared with mesoporous carbon as the negative electrode, LiFePO_4 as the positive electrode and a $\text{LiTFSI/imidazolium}$ ionic liquid solution as electrolyte is presented. The cell was conceived on the basis that it offers all the safety features of ionic liquids (IL) and LiFePO_4 , in addition to the advantages of a high energy density device. Most of the high performance hybrids so far reported in the literature employ aqueous or organic electrolytes, whereas studies of hybrid cells based on IL still rare. Here, a fundamental study was conducted to understand how the different interfaces and mechanisms operate in a hybrid system based on IL electrolyte, and how this affects cell performance. This device was mainly characterized using cyclic chronopotentiometry that allows cell voltage and electrode potentials to be simultaneously recorded. By means of this technique, it was possible to evaluate the overall behavior of the hybrid cell and the faradaic and capacitive electrodes simultaneously, and to compare it with the performance of selected standard cells. The results show that the cell is able to attain an energy density of 43.3 W h kg^{-1} at 0.010 A g^{-1} (C/5 in relation to LiFePO_4), while maintaining a good cycling performance.

INTRODUCTION

Significant efforts have been devoted to finding new electrochemical energy storage devices capable of satisfying the high energy demand and power needs of electric and hybrid cars.¹⁻² To date batteries are the devices that have best satisfied these needs due to their high energy density.²⁻³ However, even the best battery technologies have a low power density and a poor cyclability.⁴ Supercapacitors (SCs) or electric double layer capacitors (EDLC) are electrochemical devices whose performance is complementary to that of batteries: they achieve high power densities and have a good cyclability but they are poor in energy density.⁵⁻⁶ The differences between the properties of these two devices arise from their nature of the charge accumulation processes. While in batteries the electrodes undergo redox chemical reactions in their bulk, in SCs charge accumulation takes place through the formation of an electric double layer (a purely electrostatic mechanism) on the electrode surface.³ A great deal of research is therefore being directed at finding a single electrochemical device capable of combining the advantageous properties of batteries and SCs in so-called hybrid supercapacitors or supercapatteries.⁷⁻¹¹

Hybrid SCs are defined as devices that accumulate charge by means of different mechanisms: faradaic reactions in one electrode and electric double layer in the other electrode. It is also possible to construct hybrid systems by modifying the electrolyte via the insertion of redox species capable of undergoing chemical reactions at the interface of the carbon materials.¹²⁻¹³ In terms of energy density, current hybrid supercapacitors outperform conventional SCs by almost 10 times, while achieving power density equal to, or greater than that of batteries.¹³ However, these systems retain many of the disadvantages of batteries. Their cyclability is often reduced due to the degradation of the faradaic electrode and a high resistance is created at the interface of this electrode when it is subjected to increased power demands.^{9, 14} Moreover, sometimes the use of metals such

as Ru, Ti, and Ni increases the cost of the cells.^{7, 9, 15} The final drawback worth mentioning is that, despite the high energy densities achieved by hybrid SCs, especially based on the lithium intercalation mechanism, the potentials of the electrodes operate at the limit of electrolyte stability and therefore they require electronic safety systems similar to those of ion-lithium batteries to prevent explosions from occurring in overpotential situations.¹⁵

The performance of hybrid devices greatly depends on the type of electrolyte used. The aqueous cells with the highest energy densities that use RuO_2 , Ni(OH)_2 , MnO_2 and LiMn_2O_4 as positive faradaic electrodes and activated carbon as the negative double layer electrode reach 30 W h kg^{-1} .¹⁵⁻¹⁷ On the other hand, cells with organic electrolytes can operate at high voltages and reach values of 90 W h kg^{-1} with graphite as the negative electrode (through a mechanism of intercalation/deintercalation of lithium ions) and again activated carbon as the capacitive electrode.^{15, 18} Interestingly, very little research has been carried out on hybrid SCs using ionic liquids (ILs),¹¹ a family of compounds, that because of their properties, it is thought would make very promising electrolytes.¹⁹⁻²¹ These materials achieve conductivities of the order of 10^{-2} and $10^{-1} \text{ S cm}^{-1}$, are not prone to flammability and have a large electrochemical stability window that can exceed 4 V under certain conditions.²²⁻²³ Devices constructed with ILs offer greater security in situations of overpotential, of high temperatures, and their high electrochemical stability window allows the cell to operate at high voltages, thereby maximizing their energy and power density.^{19, 21, 23}

The choice of LiFePO_4 as positive electrode for the hybrid device under study is a strategic one made on the basis of the low cost of the precursor materials, their low toxicity and high thermal and chemical stability.²⁴⁻²⁵ This cathodic material also ensures safer operation due to its intermediate potential ($\sim 3.4 \text{ V vs. Li/Li}^+$) which is lower than

the anodic stability limit of the commonly used ionic liquid-based electrolytes (~ 5 V vs. Li/Li^+).²⁴⁻²⁵ Finally, the theoretical capacity of LiFePO_4 is relatively high (170 mA h g^{-1}) and the profiles of its charge/discharge curves are suitable for external electronic control due to the fact that there is only one galvanostatic plateau caused by the insertion/desinsertion of Li^+ ions, accompanied by the charge transfer from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.²⁴⁻²⁵

Despite the advantages of ILs and LiFePO_4 mentioned above, combining these materials in a hybrid SC presents major challenges since the insertion/deinsertion of Li^+ ions in the olivine structure depends on the nature of the electrolyte. ILs are usually more viscous and chemically very different from the organic carbonates commonly used with LiFePO_4 in batteries.^{4, 26} Therefore, the compatibility of a $\text{LiFePO}_4/\text{IL}$ interface and the applicability of these materials to a hybrid cell are open to question and one of the objectives of this study. In order to clarify the situation the present work investigates a novel hybrid cell based on a LiTFSI/ionic liquid as electrolyte and LiFePO_4 as faradaic electrode. The IL chosen for this study is 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide (EMITFSI), a widely used electrolyte.^{23, 27-28} Our preliminary studies have shown that this IL allows the reversible insertion/desinsertion of lithium into the host electrode material, as will be shown in the present work. In addition, EMITFSI has a stability window capable of exceeding 2.5 V under certain conditions. It is hydrophobic, has a low viscosity (35.6 cP) and a high conductivity (10 mS cm^{-1} at 25°C) compared to other ILs.²⁹ As capacitive electrode, a high surface area mesoporous carbon (MES) was used to facilitate the insertion of the voluminous ions from the IL into the porous structure and to maximize the double layer charge accumulation.¹⁰ As a final step, the properties of the proposed new hybrid cell were evaluated extensively by applying

galvanostatic measurements, while simultaneously recording the voltage and potentials. Conventional systems widely reported in the literature were used as references.

EXPERIMENTAL

Synthesis and characterization of the LiFePO₄. A microwave-hydrothermal method was used to synthesize the LiFePO₄. The NH₄H₂PO₄ (Sigma-Aldrich, Brazil, 99%), CH₃COOLi.2H₂O (Sigma-Aldrich, Brazil, 98%), and FeSO₄.7H₂O salts (Sigma-Aldrich, Brazil, 97%) were dissolved in a mixture (20 mL) containing H₂O/Glycerol (Aldrich, Brazil, 99.5%)/PEG 400 (Merck, Brazil, 98%) (2:2:1 v/v). The resulting solution was placed inside a Teflon reactor of a microwave digestion system (Milistone Start D, Denmark). The hydrothermal synthesis was performed in air atmosphere for 20 min at 180 °C under a self-generating pressure. After the reaction, the resulting light-green precipitate was washed with deionized water until pH 6, filtered, and finally dried at 80 °C for 12 h.

To perform the structural characterization, X-ray powder diffraction (XRD) patterns were collected on a Siemens-D5000 diffractometer (USA), using a Cu tube, in the angular range of $10^\circ < 2\theta < 70^\circ$ at a scan rate of $1.00^\circ \text{ min}^{-1}$.

Scanning electron microscopy (SEM) micrographs at different magnifications were collected using a QUANTA 200 instrument (FEI, USA). The LiFePO₄ sample was deposited on a silicon substrate from a dispersion in isopropyl alcohol.

Synthesis and characterization of the mesoporous carbon. Based on a method well established in the literature,³⁰ 2 g of silica gel (Sigma-Aldrich, 540 m² g⁻¹, 63-210 mesh) were added into an alcoholic solution of p-toluenesulfonic acid (0.5 M) (PTS, Sigma Aldrich, 98%, Spain), and stirred for 1 h at room temperature. The PTS containing silica

was filtered and dried for 3h at 80 °C. Then, 1.9 g of furfuryl alcohol (Sigma-Aldrich, 98%, Spain) was slowly incorporated into the silica/PTS, which was then subjected to an additional heating step at 80 °C for 24 h. Next, the material was heated (inside a quartz tube under a N₂ flow) at 3 °C min⁻¹ up to 800 °C, this temperature being maintained for 1 h. The carbonized material was then added to 50 mL of HF aqueous solution (40% (w/v)) where it was kept for 24 h until all the silica had been removed. Finally, it was filtered and washed with distilled water. The resultant mesoporous carbon (MES) was dried at 120 °C for 2 h. Analysis by energy-dispersive X-ray spectroscopy revealed a residual Si content of less than 3%.

The textural properties of MES were determined using an automatic N₂ adsorption/desorption analyzer at 77 K (Micromeritics ASAP 2420, USA). Degassing was performed at 80 °C for 720 min. The total specific surface area was determined by means of the B.E.T. equation, while the micropore volume, mean pore size and specific surface area of the micropores were calculated by applying the Dubinin-Radushkevich equation. The total pore volume was obtained from the N₂ isotherm at the partial pressure of 0.99. The total mesopore volume was calculated by subtracting the micropore volume from the total pore volume.

The oxygen content was determined directly in a LECO-TF-900 furnace coupled to a LECO-CHNS-932 instrument. Resistivity measurements were performed using the 238 High Current Source Measure Unit (Keithley, USA). Calculation of resistivity depends on the resistance, the geometry and the support used. It was therefore necessary to apply correction factors taken from the cited reference.³¹

Preparation of the electrodes. The MES electrodes were prepared by mixing 90 wt% of the carbon material with 10 wt% of polytetrafluoroethylene (PTFE, Aldrich, USA) as binder. The mixture was prepared in a mortar and pressed into disk-shaped electrodes ($\sim 10.6 \text{ mg cm}^{-2}$ and a thickness of around 0.4 mm).

To prepare the LiFePO_4 cathode layer, a slurry was formed by mixing the active material with carbon black (Erachem, Belgium) and poly(vinylidene fluoride) (PVDF 1012, Solvay, Belgium) in a mixture of acetone (Sigma-Aldrich, 95%, Spain) and N-methyl-2-pyrrolidone (Sigma-Aldrich, 98%, Spain) (20:1 v/v) at 60 °C. The mass ratio of the LiFePO_4 /carbon black/PVDF was 41:5:4. The suspensions were spread on an aluminum current collector by using a doctor blade. After evaporation of the solvent in an oven at 100 °C for 24 h, the foils were transferred to an Ar-filled drybox. The aluminum foil containing the deposited material (used in the standard cells) was cut into disks with a diameter of 7 mm and with a loading capacity in the range of 1 to 3 mg cm^{-2} . For the LiFePO_4 cathode used in the hybrid cells, the slurry was allowed to drip onto cylindrical graphite bars (acting as current collectors with diameter of 1.13 cm^2) and subsequently conditioned in an oven at 60 °C for 24 h. The amount of active material placed on the graphite ranged between 3.5 and 4.4 mg cm^{-2} .

Preparation of the supercapacitor cells. The hybrid SCs were assembled in "T-type" Swagelok[®] cells, with MES as the negative electrode, LiFePO_4 as the positive electrode (deposited on the graphite) and a glass fiber (Whatman, UK) disk as separator. The electrolyte for this cell was prepared with a solution of 1M lithium bis(trifluorosulfonyl)imide (LiTFSI , Io-Li-Tec, 98%, Germany) in EMITFSI ionic liquid (Sigma-Aldrich, 99%, Spain). The hybrid cell has therefore been labelled: $\text{LiFePO}_4|\text{LiTFSI}(1\text{M}), \text{EMITFSI}|\text{MES}$. To record the potential, a silver wire was

employed as pseudoreference electrode. The performance of the cell was compared to a SC cell assembled in a similar way to the hybrid SC, except that MES was used in both electrodes (MES|LiTFSI(1M), EMITFSI|MES).

Standard ion-lithium cells were assembled in a three-electrode T-cell, with lithium metal (MTI Cooperation, China) as the negative electrode, LiFePO₄ (deposited on Al foil) as the positive electrode and a polypropylene-polyethylene-polypropylene membrane (Celgard, USA) as separator. The electrolyte used in this cell was 1 M LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 v/v) (Merck, Brazil) and lithium metal was employed as pseudoreference electrode. This standard cell has been denominated: LiFePO₄|LiPF₆(1M), EC/DMC|Li.

All the cells were assembled and sealed in a dry box containing Argon atmosphere. The electrochemical measurements tests were carried out at ambient temperature in a BioLogic VMP Multichannel Potentiostat/Galvanostat.

Electrochemical characterization. The galvanostatic measurements were performed in a T-cell which records the voltage and potential of both electrodes simultaneously. The cell capacitance (C_{cell}), energy density (E) and power density (P) values were calculated by integrating the galvanostatic discharge profiles (voltage vs. time) and subtracting the ohmic drop by applying equations 1, 2 and 3, respectively.^{10, 32} The specific capacitance of each electrode (C_+ or C_-) was calculated by integrating the discharge profile (potential vs. time) of each individual electrode by means of equations 4 and 5.^{10, 32} The equivalent series resistance (ESR) was determined from the ohmic drop at the beginning of the discharge profile and calculated by means of equation 6. Finally, the coulombic efficiency (ϵ) was calculated from the results of the galvanostatic experiments applying equation 7.

$$C_{cell} = \frac{2I(\int V dt)_{discharge}}{(m_+ + m_-)V_{discharge}^2} \quad (1)$$

$$E = \frac{I(\int V dt)_{discharge}}{(m_+ + m_-)} \quad (2)$$

$$P = \frac{E}{\Delta t_{discharge}} \quad (3)$$

$$C_+ = \frac{2I(\int U_+ dt)_{discharge}}{(m_+)U_{+discharge}^2} \quad (4)$$

$$C_- = \frac{2I(\int U_- dt)_{discharge}}{(m_-)U_{-discharge}^2} \quad (5)$$

$$ESR = \frac{V_{max,charge} - V_{discharge}}{I} \quad (6)$$

$$\varepsilon = \frac{\Delta t_{discharge}}{\Delta t_{charge}} \times 100 \quad (7)$$

where I is the current applied, V is the voltage, U is the potential of the electrodes, m_+ and m_- are the mass of active material in the positive and negative electrodes, respectively, $\Delta t_{discharge}$ is the discharge time, Δt_{charge} is the charge time, $V_{max,charge}$ is the maximum voltage reached by the SC during charging, and $V_{discharge}$ is the maximum voltage discounting the ohmic drop.

Cyclic voltammetry (CV) tests of the hybrid SC were conducted at 1 mV s^{-1} in a 3-electrode configuration in order to evaluate separately the electrochemical behavior of the positive and negative electrodes in the potential ranges determined by the galvanostatic experiments. Electrochemical impedance spectroscopy (EIS) measurements were performed for the global hybrid cell and for the conventional EDLC using a 2-electrode configuration in a frequency range between 0.1 MHz and 0.01 Hz employing an open-circuit potential with an ac perturbation of 5 mV.

RESULTS AND DISCUSSION

Characterization of the electrode active materials: LiFePO₄ and MES. The precursors used in this study for the synthesis of LiFePO₄ are based on the works of Kanamura and Ferrari.^{26, 33} The hydrothermal synthesis was optimized by employing a surfactant (PEG 400) to obtain fine particles so as to minimize both time and temperature. Glycerol was also used in the reaction medium as a reducing agent to prevent the oxidation of Fe²⁺ ions during the synthesis. Figure 1 shows an X-ray diffractogram of the obtained material.

Figure 1. XRD pattern of LiFePO₄ obtained in a microwave-hydrothermal synthesis at 180 °C for 20 min, using a PEG 600/glycerol aqueous solution in the reactor.

The XRD pattern corresponds to the orthorhombic structure of olivine in a single-phase with a *Pnma* space group [JCPDS: 40-1499] and with the absence of crystal impurities. When compared to the crystallographic chart it can be seen that the most intense peaks are related to planes (111)/(201), (020)/(211) and (311). This is relevant for the application of LiFePO₄ as an electrochemically active material as it has been reported in the literature that plane (020) is one of the planes responsible for the insertion of Li⁺ ions. Promoting the growth of the material in this direction will therefore favor the kinetics of the insertion/deinsertion process.³³

Figure 2 shows the SEM images that confirm the formation of LiFePO_4 particles with a platelet-like shape and sizes of around $1\ \mu\text{m}$. The morphology of this material can also be correlated with the XRD pattern. Kanamura et al. studied the relationships between the peak intensities of the diffractogram and the olivine particle shape.³³ According to their experimental results, if the intensity of peak (200) is greater than peak (020) the LiFePO_4 will have a needle-like shape, and when the intensity of the peak (200) is smaller it will have a platelet-like shape. This correlation was confirmed by the present study.

Figure 2. SEM images of the LiFePO_4 sample obtained at 1000x, 10kV (A) and 12500x, 5kV (B).

The electrochemical performance of LiFePO_4 as active cathode was evaluated in standard ion-lithium cells at room temperature. The electrolyte chosen for this experiment was (1M) LiPF_6 dissolved in EC/DMC as this electrolyte has been claimed to show the best performance in the literature on active cathode material and can be considered a good reference.^{26, 34} Figure 3 shows the galvanostatic charge/discharge curves at different current densities (C rates).

Figure 3. Charge/discharge curves of the LiFePO_4 in a standard ion-lithium cell ($\text{LiFePO}_4|\text{LiPF}_6(1\text{M}), \text{EC}/\text{DMC}|\text{Li}$) at different C rates.

In these standard cells the olivine material reveals a capacity value of 154 mA h g^{-1} at C/5. This value corresponds to 90% of its theoretical capacity (170 mA h g^{-1}) of the material and can be considered an excellent result for an uncoated LiFePO_4 . At the lowest C rates evaluated the material suffers an expected loss in capacity. This loss is due to kinetic factors related to the diffusion of Li^+ ions throughout the crystalline structure of the material. For the highest current density evaluated (5C), the capacity values still reach 95 mA h g^{-1} , demonstrating that the synthesized olivine material is capable of a good electrochemical performance.

The textural properties of the MES, as capacitive electrode in the hybrid SC, were determined from N_2 adsorption-desorption isotherms and are summarized in Table 1. Figure S1 shows the isotherms (A) and pore size distribution for MES (B) (Supporting Information).

Table 1. Textural parameters for MES.

S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_{total} ($\text{cm}^3 \text{ g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{ g}^{-1}$)	Mean pore diameter (nm)
1497	1.64	0.54	1.10	2.32

This carbon, resulting from carbonization in silica nano-molds, reveals a high specific surface area ($1497 \text{ m}^2 \text{ g}^{-1}$) similar to that of other carbons commonly employed in conventional SCs.³⁵ High S_{BET} values are important for maximizing the capacitance obtained from an electric double layer mechanism.³⁵ The selection of a mesoporous carbon is clearly due to the use of IL as electrolyte, as this has cations and anions with large diameters (1.5 and 1.6 nm, respectively).²⁷ The carbon material must therefore have a large enough porosity to allow easy access to the ions that make up the electric double layer (more than 67% of the total pore volume is in the mesoporous range). However, the micropore content is still high, resulting in a mean pore diameter of 2.32 nm. In this case, the textural parameters of the MES are, in principle, suitable for use with EMITFSI. In addition, the MES obtained from the carbonization of poly(furfuryl alcohol) is non-graphitizable and its resistivity is high ($315.04 \text{ } \Omega \text{ cm}$) compared to other very conductive carbons (such as CNTs ($0.10 \text{ } \Omega \text{ cm}$) for example) although it is still suitable for use as electrode material with no need for conductive additives.¹⁰ The oxygen content of MES is relatively low (2.9%), and no significant pseudocapacitive processes are to be expected.

Electrochemical study and performance of the hybrid supercapacitor. The results of the electrochemical performance of the hybrid SC are presented and compared with the symmetrical EDLC. The electrolyte used in both cases was 1M LiTFSI dissolved in EMITFSI because lithium salt is needed for the performance of the cathode material that must insert/desinsert the Li^+ ions during the charge/discharge. Figure 4 shows the galvanostatic curves corresponding to the hybrid cell at 0.010 A g^{-1} (A) and the voltammograms for both electrodes at 1 mV s^{-1} (B).

Figure 4. Galvanostatic charge/discharge profiles obtained at 0.010 A g^{-1} for the $\text{LiFePO}_4|\text{LiTFSI}(1\text{M}), \text{EMITFSI}|\text{MES}$. Voltage (left Y-axis) and potential curves for the positive and negative electrodes (right Y-axis) (A). Voltammograms at 1 mV s^{-1} containing the potentials for the positive (red) and negative (blue) electrodes recorded separately (B).

The galvanostatic curves obtained for the hybrid SC clearly reveal fundamental differences with the EDLC (Figure 5). The positive electrode stores energy through a faradaic process (constant potential) where Li^+ ions undergo insertion/desinsertion processes during charge and discharge, whereas the negative electrode displays a purely capacitive behavior with a triangular profile. Cyclic voltammetry (CV) is a classic technique that provides a clearer picture of the different types of electrochemical processes that occur on the electrodes. Figure 4B shows the CV curves obtained in the 3-electrode configuration for the positive and negative electrodes of the hybrid SC. The curve for the positive electrode is typical of a single electron transfer process and in this case it can be considered quasi-reversible due to a wide separation of approximately 0.4 V between the oxidation and reduction peaks, probably due to the slow mass transfer in this viscous medium. In the case of the negative electrode, the voltammogram has a quadrangular shape, which is typical of the capacitive processes that occur during the formation of the electric double layer.

To facilitate discussion of the data and comparison, a symmetric EDLC: MES|LiTFSI(1M), EMITFSI|MES was also evaluated. The galvanostatic curves for this standard cell at 0.01 A g^{-1} are shown in Figure 5. It should be noted however that, although the main goal of this section is to compare both systems, some experimental conditions (e.g. the cell voltage) were different. The voltage of the hybrid system is limited to a maximum of 2.1 V for the performance of the positive electrode, as can be seen by the polarization in the galvanostatic curve for the positive electrode at the end of the charge steps (Figure 4A). On the other hand, the symmetric SC displays a predictable behavior pattern with typical triangular charge/discharge curves in both electrodes and, consequently, in the cell. In this case, the maximum voltage is limited to 2.5 V to ensure that the cell is working inside a comfortable range of potentials, avoiding electrode/electrolyte degradation and demonstrating a high coulombic efficiency. Tables 2 and 3 show the electrochemical parameters calculated from the galvanostatic measurements for the hybrid and EDLC, respectively, operating at their maximum voltages and at the same current densities. The galvanostatic curves for the other current densities can be found in Figure S2 (Supporting Information).

Figure 5. Galvanostatic charge/discharge profiles obtained at 0.01 A g^{-1} for the MES|LiTFSI(1M), EMITFSI|MES. Voltage (left Y-axis) and potential curves for the positive and negative electrodes (right Y-axis).

Table 2. Electrochemical data calculated from the galvanostatic profiles for the LiFePO₄|LiTFSI(1M), EMITFSI|MES cell.

<i>Current density</i> (A g ⁻¹)	<i>C</i> ₊ (F g ⁻¹)	<i>C</i> ₋ (F g ⁻¹)	<i>C</i> _{cell} (F g ⁻¹)	<i>E</i> (W h kg ⁻¹)	<i>P</i> (W kg ⁻¹)	<i>ESR</i> (Ω)	<i>ε</i> (%)
0.010	551.0	160.3	70.9	43.3	10.7	19.5	94.6
0.025	307.3	144.4	54.8	30.2	28.3	15.6	98.2
0.050	213.8	131.5	37.5	22.3	52.3	23.3	98.4
0.100	132.7	106.4	27.8	17.9	102.0	22.5	100.0

Table 3. Electrochemical data calculated from the galvanostatic profiles for the conventional MES|LiTFSI(1M), EMITFSI|MES cell.

<i>Current density</i> (A g ⁻¹)	<i>C</i> ₊ (F g ⁻¹)	<i>C</i> ₋ (F g ⁻¹)	<i>C</i> _{cell} (F g ⁻¹)	<i>E</i> (W h kg ⁻¹)	<i>P</i> (W kg ⁻¹)	<i>ESR</i> (Ω)	<i>ε</i> (%)
0.010	126.4	92.7	26.8	23.1	12.0	18.9	92.3
0.025	130.0	93.6	27.4	23.3	29.8	21.5	95.7
0.050	124.8	90.8	26.4	22.0	57.8	20.1	97.2
0.100	114.2	84.2	24.4	19.6	109.6	18.7	98.1

The electrochemical parameters obtained for the hybrid SC show that the replacement of one capacitive electrode by another of a faradaic type alters the storage capacity of the entire device. In terms of energy density, the hybrid SC is able to yield 43.3 W h kg⁻¹, nearly double that of the EDLC (23.1 W h kg⁻¹, which is also high) at low current densities, despite working at a low voltage. In addition, it is interesting to compare this performance with other hybrid cells containing capacitive and faradaic materials arranged in series. The best aqueous hybrid systems are also capable to overcome 30 W h kg⁻¹ combining activated carbon (capacitive electrode) and MnO₂ (faradaic).³⁶ However, these cells may generate H₂ and O₂ at the negative and positive potential limits, respectively, causing leakage.²² Considering the organic cells, where in most cases the solvent is acetonitrile or mixtures of organic carbonates, they reach the

highest energy densities. Systems that combine activated carbon and faradaic electrodes such as LiMnO_2 and $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ exceed 40 W h kg^{-1} .³⁷⁻³⁸ We also should mention the existence of activated carbon/graphite cells that can exceed 90 W h kg^{-1} , as described in the literature.¹⁸ Unfortunately, these electrolytes are toxic, volatile and flammable, reducing the safety of this type of cell.²²

The potential curves recorded for the positive and negative electrodes during the galvanostatic experiments reveal the reasons behind the improvements in the hybrid cell. It can be seen that, at low currents, the capacitance of the faradaic positive electrode in the hybrid cell (551 F g^{-1}) is much larger than any of the values obtained by the capacitive electrodes, both in the EDLC and in the hybrid SC. This very high capacitance pushes the negative electrode to its maximum capacitance limit (160 F g^{-1}), a value much higher than the values obtained in the EDLC. As a result, the cell as a whole shows a much higher capacitance and energy density.

Despite the high energy density achieved at 0.010 A g^{-1} , the hybrid cell still shows low performance in rate-capability compared to EDLC. When current density is increased tenfold, the values of C_{cell} , and consequently E , decrease markedly reducing to 40% of its initial at 0.100 A g^{-1} . Under the same conditions, EDCL retains about 90% in these parameters.

The rate performance can be understood by the analysis of the evolution of individual capacitance for positive and negative electrodes. At 0.100 A g^{-1} , the values of C_+ and C_- in the hybrid device decrease by 77 and 33%, respectively. While in the symmetric device, the capacitance values decrease by 10% for both electrodes. As a result, the hybrid device performs like a conventional SC, with values of P in the order of 100 W kg^{-1} . This is the weakness of this device, which combines storage mechanisms with very different kinetics in the IL medium, where the response of the faradaic

electrode at high currents is worse. The origin of these differences in performance, especially for the electrode containing LiFePO_4 will be discussed in the next session.

The other electrochemical parameters confirm the excellent compatibility of the $\text{LiFePO}_4/(\text{EMITFSI} + \text{LiTFSI})$ interface, which has a similar resistance to that of the $\text{MES}/\text{EMITFSI} + \text{LiTFSI}$. The *ESR* values of the hybrid SC are similar to those found in the EDLC at all current densities, around $20\ \Omega$. In all cases the cells show optimal conditions of operation (current and voltage) without any excessive degradation of their components. This is reflected in the high values of coulombic efficiency ($>92\%$) obtained in all the experiments.

Capacity performance of the LiFePO_4 in a hybrid supercapacitor based on EMITFSI ionic liquid. In this section the performance of LiFePO_4 is evaluated by comparing it directly with the performance of this cathodic material in a well-known medium: the lithium standard half-cell $\text{LiFePO}_4|\text{LiPF}_6\ (1\text{M}), \text{EC}/\text{DMC}|\text{Li}$. This comparison has been carried out in order to evaluate the capacity of a LiFePO_4 -based cell when it is operating in a real hybrid SC that contains a counter electrode of finite capacitance in an IL medium. It should be pointed out that, unlike the cells described in the previous section (which were constructed using the same LiTFSI/IL electrolyte), the hybrid SC is compared with a cell that works with a low viscosity and a highly conductive electrolyte ($\text{LiPF}_6\ (1\text{M}), \text{EC}/\text{DMC}$) and an infinite capacity counter electrode (metallic lithium). The values of current density are presented as C rates (in accordance with the norm accepted for specialists working in the field of batteries) and A g^{-1} (in accordance with the norm established for SC). The present study can be only carried out using the galvanostatic technique based on the simultaneous determination of potentials and voltage, which allows the curve corresponding to the positive electrode to be

recorded separately. The current densities can then be converted into C rates by taking the absolute current applied by the potentiostat, the theoretical capacity of olivine and the mass of the active material in the cathode. Table 4 shows the capacity results of LiFePO₄ at different C rates (and A g⁻¹) in the two cells: LiFePO₄|LiPF₆(1M), EC/DMC |Li and LiFePO₄|LiTFSI (1M), EMITFSI|MES.

Table 4. Capacity values for LiFePO₄ at different C rates in LiFePO₄|LiPF₆(1M), EC/DMC|Li (standard ion-lithium cell) and LiFePO₄|LiTFSI (1M), EMITFSI|MES.

<i>Current density (A g⁻¹)</i>	<i>C rate</i>	<i>Capacity (mA h g⁻¹) (Standard half-cell)</i>	<i>Capacity (mA h g⁻¹) (hybrid SC)</i>
0.010	C/5	154.7	138.2
0.025	C/2	140.4	90.5
0.050	C	129.8	73.5
0.100	2C	114.9	51.0

The capacity data for the standard cell and hybrid SC can be compared directly because the cathode is the limiting electrode in both cases (the capacity of LiFePO₄ is completely extracted in both cells and the charge is always compensated by the different counter electrodes). At the lowest current densities (C/5) both half-cells present similar performances in terms of capacity. The lowest performance of the cathodic material in IL corresponds to capacities at large current densities.

From the data in Tables 2 and 3 it can be seen that MES shows an improved behavior at high current densities. Therefore, the lower performance of the hybrid device can only be due to the slow exchange of Li⁺ ions into LiFePO₄ in the EMITFSI medium. Hence, in the case of SC which contains the IL, LiFePO₄ is performing below its theoretical maximum capacity. The loss of capacity of the hybrid SC containing an IL liquid electrolyte is the responsible for the low specific energy of the system at high currents, as revealed by the galvanostatic experiments in the previous section. This

probably occurs as a result of the higher viscosity of the EMITFSI (35.6 cP) compared to the mixture of organic carbonates (5.1 cP) which hinders the diffusion of lithium ions.²⁹

³⁹ Another factor that could reduce the capacity of the material is the type of the counter electrode. In the standard cell, metallic lithium has an infinite capacity, but in this hybrid cell the double layer formed at the MES/electrolyte interphase must be able to compensate for the total oxidation of the LiFePO_4 . This is why the negative electrode is even more in demand in the hybrid cell than in the standard cell. At the lowest current density the C values have increased by an additional 70 per cent (Table 2 and 3). Here, it is important to note that the mass ratio of these hybrid systems is very important. In this work, even with an increase in the capacitance required at the interface containing MES in the hybrid SC, the potentials reached by the electrodes are within the electrochemical stability window of the EMITFSI. Therefore, the choice of masses used in each electrode was adequate.

Even taking into consideration the negative features referred to above, the capacitance and the energy density of the $\text{LiFePO}_4|\text{LiTFSI}(1\text{M})$, EMITFSI|MES hybrid cell are high enough for it to be considered as an interesting alternative in the field of electrochemical energy storage devices. The values of the energy density were calculated from the area under the discharge curve (a correct approach) and the mass of the active materials in both electrodes, and those obtained at low current densities are among the best ones ever reported for a hybrid SC with lithium insertion electrodes (Li-ion supercapacitors).⁷ The same strategies used for the optimization of this cathode material in Li-ion batteries could be used to improve the power density in future works.²⁴ For example this could be achieved by the synthesis of smaller particles so as to shorten the diffusion path of lithium ions within the olivine.

Impedance behavior of the hybrid supercapacitor. The complexity of hybrid SCs involving different ion transport phenomena and storage mechanisms can be fully appreciated through EIS measurements. Figure 6 shows a Nyquist diagram of the hybrid and conventional EDLC. Although it is not easy to extract information from the Nyquist curves due to the complexity of the systems under discussion, a comparison of the curve obtained for the hybrid cell with that of the simpler EDLC may help. The curves were obtained using two-electrode cells and, therefore, they are the result of the processes occurring in both electrodes and in the electrolyte.

Figure 6. Nyquist plot for $\text{LiFePO}_4|\text{LiTFSI}(1\text{M}), \text{EMITFSI}|\text{MES}$ (black) and $\text{MES}|\text{LiTFSI}(1\text{M}), \text{EMITFSI}|\text{MES}$ (red).

The first point in the diagram on the Z_{real} axis is obtained at the highest frequency tested and is normally associated with the resistance of the electrolyte. In our opinion, interaction of the electrolyte with the electrode surface must also be contributing to this resistance, as otherwise the resistances would be the same, given that the electrolyte is the same in both experiments. In this case, the resistance of the hybrid cell is slightly larger than that of the symmetric cell and the difference is attributable to the presence of the LiFePO_4 in the first cell. This is the first piece of evidence that the carbon surface

interacts more easily with the IL electrolyte than the inorganic phase of the cathode material.

The diameter of the first semicircle is similar for both electrodes. The diameter of this semicircle is often associated with electrode resistance which is the resistance of the electrode material together with the contact resistance involving the current collectors. For this reason the resistances of the electrodes do not show any significant differences. The first notable difference in the impedance curve is observed with the presence of a second semicircle in the case of the hybrid device that is not observed in the symmetric SC. In view of the differences between the two systems under comparison it can be assumed that this second circle corresponds to the redox process occurring in the cathode of the hybrid cell in this frequency range. The transfer of one electron for the oxidation/reduction of Fe cations would be difficult to take place in an IL medium because the process involves the diffusion and insertion/disinsertion of Li ions in a more viscous medium. The diffusion of the ions is more clearly appreciated in the straight lines that follow the semicircles. In the case of the symmetric cell there is a single straight line (which diverges considerably from the perpendicular) that reflects the problems involved in the formation of the double layer of the viscous IL used as electrolyte. In the hybrid cell there are two different lines. One of them is similar to that obtained in the SC and can be associated with the formation of the double layer in the negative electrode of the hybrid cell. The second line reflects a greater resistance and a larger capacity that is associated with a more restricted diffusion of Li^+ into the crystalline structure of LiFePO_4 .

Cycling performance of the hybrid supercapacitor. In order to be able to operate a hybrid SC it is essential to know its cycling performance. Figure 7 shows the energy

retention and coulombic efficiency of the MES|LiTFSI(1M), EMITFSI|LiFePO₄ subjected to 1000 cycles at 0.025 A g⁻¹ (C/2 in relation to LiFePO₄) (A) and the galvanostatic curves (voltage profiles (B) and potential profiles (C)) corresponding to the cycles 10, 500, and 1000.

Figure 7. Cycling stability and coulombic efficiency of the hybrid SC for 1000 cycles at 0.025 A g⁻¹ (C/2 rate) (A). Galvanostatic charge/discharge curves for different cycles (voltage profiles (B) and potential profiles (C)) at 0.025 A g⁻¹ (C/2 rate).

The hybrid SC developed in the present study work retains 78 and 68% of its initial energy density after 500 and 1000 cycles, respectively, with a coulombic efficiency greater than 98% at C/2 rate. This cell therefore demonstrates an excellent cycling stability although a certain amount of degradation is to be expected for a system containing battery electrodes that become completely degraded before 1200 cycles in

normal conditions.⁹ The cycling performance of LiFePO₄ was also found to be suitable for this type of cell that contains EMITFSI as electrolyte. Hybrid cells with the same configuration (battery-type||EDLC electrode), but different active materials and organic electrolytes show similar cycling stabilities.⁴⁰⁻⁴¹ For further comparison, a complete hybrid SC, reported in the literature, containing Fe₃O₄ as battery-type electrode, 3D-graphene and LiPF₆ dissolved in EC/DEC/DMC as capacitive electrode and electrolyte respectively, is able to retain 70% after 1000 cycles at similar C rates.⁴¹ This shows that EMITFSI is substantially inert towards LiFePO₄ and causes no excessive degradation at the interface. In addition, SEM images of the electrodes were obtained before and after complete degradation of the cell, and showed no significant morphological change in LiFePO₄ particles (Figure S3 – Supporting Information).

The degradation of the cell can be more effectively monitored by analyzing the variation of the potential profiles over a range of cycles (Figure 7C). At C/2, LiFePO₄ initially operates at about 53% of its theoretical capacity and is subject to constant degradation with an increase in its polarization and a decrease in its capacity. The negative electrode maintains its triangular behavior (purely capacitive) without showing any sign of degradation. Despite the continuous degradation of the positive electrode its coulombic efficiency is always very high, close to 98% as can be appreciated in Figure 7A. Although the overall performance of the hybrid cell is acceptable in terms of energy density and long-term performance, further investigation is required to overcome some of the limitations brought to light in this study. The main drawback is the interaction between the cathodic material and the IL which limits its capacity at high currents. Reducing the crystal size to nanometric scale, finding better mass ratios between the two electrodes or testing new IL's with more efficient mass transfer could lead to a significant improvement of future hybrid devices.

CONCLUSIONS

A novel study of a full hybrid SC based on a LiTFSI/EMITFSI ionic liquid electrolyte, LiFePO₄ cathodic material and a mesoporous carbon as anodic electrode has been carried out. The first principles behind the cell's performance were elucidated using cyclic chronopotentiometry to simultaneously record the cell voltage and electrode potentials. The hybrid cell was found to perform well in terms of energy density (providing 43.3 W h kg⁻¹, at 0.010 A g⁻¹) and durability, taking into account the presence of a battery type electrode. It has been demonstrated that the construction of a battery/capacitor hybrid cell with a high energy density using a non-volatile highly stable electrolyte is a feasible enterprise worthy of further investigation.

Supporting Information. N₂ adsorption/desorption isotherms and pore size distribution of the mesoporous carbon, galvanostatic charge/discharge profiles obtained at different current densities for Hybrid SC and for EDLC, SEM images of the LiFePO₄ based electrode before and after cycling.

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