Biliquid Supercapacitors: a Simple and New Strategy to Enhance Energy Density in Asymmetric/Hybrid Devices

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Abstract

A novel strategy for the development of high energy density supercapacitors (SC) is explored. The new devices contain two electrolytes that are different in nature, an aqueous electrolyte in one half-cell and an ionic liquid in the other. These systems, referred to as biliquid SCs, make it possible to combine the best electrode/electrolyte in terms of individual electrode capacitance and cathodic/anodic stability limits. Furthermore, other asymmetries that combine different electrodes, electrolytes and storage mechanisms can be incorporated. Synchronous cyclic chronopotentiometry was used to monitor the performance of these novel complex systems. It is expected that this approach will help scientists working in this field to develop new devices that overcome the energy density limitations of current SCs, thereby extending the scope of their application.

1. Introduction

Energy storage is a main research topic as the development of high energy/high power systems will contribute to the generalization of sustainable and renewable electric production [1-3]. Electrochemical energy storage devices such as batteries and supercapacitors (SCs) are widely used and they present large well defined markets that form part of a multimillionaire business [1, 4-6]. Nevertheless there is a clear need for the further improvement of such devices, especially in terms of their power and energy density, long-term performance, environmental impact and cost [7]. The mechanism of energy storage defines the general properties of each device; whereas batteries are mainly characterized by their high energy densities and present a low power density and poor cyclability, supercapacitors (especially carbon-based double layer SCs) are characterized by their excellent cyclability and present a high power but low energy density [8]. Many efforts have been made in recent years to develop electrochemical systems capable of combining the advantages of each of these devices, maintaining the good cyclability and power densities of SC while enhancing their energy density to rival that of batteries [9, 10].

Many different strategies have been used to develop SCs with improved performance in terms of energy density, via the development of new and more complex devices that are sometimes difficult to classify [9, 11]. The criteria for classification, and more importantly, the criteria for using the appropriate nomenclature and the right equations for calculations have been published elsewhere [12]. The combination of different capacitive materials is probably the easiest way to make a hybrid supercapacitor, for example by combining a carbon material (double layer formation) with a metal oxide or conductive polymer (pseudocapacitance) [11, 13, 14]. Hybrids have also been created by combining double-layer materials with faradaic electrodes,

like V_2O_5 , $Li_2Ti_3O_7$ or MnO_2 , offering the latter the most promising results in terms of electrochemical performance [10, 15]. A different strategy for increasing cell energy density was introduced by Roldan *et al.* in 2010, which involved modifying not the electrodes, but the electrolyte [16]. In their initial study, a cell was built in a *symmetric configuration*, using two identical carbon materials, with a conventional aqueous electrolyte containing an organic compound capable of participating in reversible redox reactions on the carbon surface [16]. Currently, this approach is being widely applied to symmetric and asymmetric cells, using liquid or gel electrolytes that contain a wide range of redox additives [17-19].

The electrochemical performance of SCs (symmetric conventional, containing redox compounds, hybrids, etc.), highly depends on the electrode material which determines capacitance and on the electrolyte selected which determines cell voltage. Different electrolyte media give rise to different voltage windows but also different capacities and power densities [20]. The electric conductivity of the media, the stability at positive and negative potentials and ion size, all affect performance, but other parameters like cost, environmental and security issues are also important when choosing one or another electrolyte [20, 21]. Aqueous media are without doubt the cheapest electrolytes that also yield the highest capacitances and power rates. They can also dissolve a wide range of redox species, in the case of redox-enhanced SCs. But even the best aqueous electrolytes have low operating voltages that seriously limit the energy density [17, 20]. Organic electrolytes have been the most widely used in commercial SCs, mainly due to their relatively high voltage window, although environmental and security issues and cost are a major concern [20]. Finally, ionic liquids are the most promising electrolytes as they can operate at even higher voltages,

but their high viscosities and large ionic size limit their power density and their high cost must also be taken into consideration [20-23].

In this study we present a novel SC concept introducing a new kind of asymmetry, a system with two electrolytes with a completely different chemical nature, that we have named as *biliquid supercapacitors*. In this approach, each electrode is immersed in a specific electrolyte defining two half-cells in the biliquid SCs. To make the right selection of positive and negative electrodes and electrolytes is necessary to know the behavior of each half-cell in symmetric devices. With this previous knowledge, it is possible to select only the best electrode/electrolyte interfaces to build a single cell containing two optimal half-cells. Therefore, at first, biliquid SCs can be designed to overcome the overall capacitance and operational voltage of conventional cells and, consequently, overcome the energy density of systems containing single electrolytes without sacrificing the other properties as the power density. This is the main advantage of this type of cell. It is also expected, as the main challenge for this innovative system, the choice of the appropriate combination of the electrolytes to allow an adequate ionic flow between the phases, maintaining the system's electroneutrality with low resistance.

Other advantages can be expected in the construction of the biliquid systems. It is possible assemble more efficient asymmetric cells with specific electrodes for each electrolyte, using carbon materials with specific textural properties for each type of solvent and ions present in each half-cell. In addition, as already described in this section, the dissolution of active redox species in electrolytes has been extensively studied to increase the energy density of cells [16, 17]. Biliquid SCs can confine different active species to act on each half-cell independently, due to the different affinities and solubilities of the redox molecules with each solvent. Therefore, this new

approach has the potential to solve the problems of diffusion of active redox species present in redox-flow batteries and SCs containing redox electrolytes, preventing the escape of species from a defined half-cell [17, 24, 25]. Finally, an appropriate selection and combination of electrode materials, type of electrolyte, storage mechanism, and redox specific additives for each half-cell increases the possibilities of hybridizing the SCs, to maximize the energy output of the system while ensuring that a good power rate performance is maintained.

Some reversible electrochemical systems reported in the literature operate with two different electrolytes. In redox flow batteries, for example, two electrolytes containing different vanadium salts are separated by an ion exchange membrane [26]. Nevertheless both half-cells are usually aqueous and the separation is required mainly to prevent the vanadium ions in different oxidation of states from mixing [26]. Recently, lithium-air hybrid batteries were developed with two electrolytes (organic and aqueous) separated by a solid electrolyte, which permits the flow of lithium ions between the phases during the operation of the cell [27, 28]. However, such cells require that greater attention is paid to safety and the use of solid electrolytes imposes very high impedances and limitations in ionic conductivity and power density.

In this study a new biliquid SC was built using an aqueous electrolyte in the positive half-cell and an ionic liquid in the negative one (both electrodes composed of carbon materials) separated by a membrane. Different asymmetries and hybridizations were studied to demonstrate the simplicity, security and flexibility of the design of this kind of cells using classic SC materials. The new cells described in this manuscript do not present any extra technological inconvenience that makes them difficult to use in real situations. Biliquid SCs require only the replacement of conventional membrane/separators to delimit the half-cells and to prevent the mixing of the

electrolytes. Finally, an insight into the mechanism of operation of these cells in their most complex assembly is presented. Nevertheless there is still a long way to go before this new concept is fully developed, especially in the understanding of the role that the new interface (electrolyte|membrane|electrolyte) plays in these complex systems, an understanding that would lead to an improvement of the efficiency and long-term behavior of these devices.

2. Experimental Section

2.1. Materials

Commercial multi-walled carbon nanotubes (CNTs, Sigma-Aldrich, Spain) and a mesoporous carbon (MES) synthesized in the laboratory using mesostructured silica as template [29], were employed as active electrode materials. Two ionic liquids (ILs) were used as electrolytes: Ethylammonium nitrate (EAN, Io-Li-Tec, >97%, Germany) and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI, Sigma-Aldrich, >98%, Germany). Solutions of 1.0 M H₂SO₄ (VWR, France) and 1.0 M VOSO₄ (hydrate, Aldrich, 97%, USA) /1.0 M H₂SO₄ were used as aqueous electrolytes.

2.2. Preparation of electrodes and supercapacitor cells

The electrodes were prepared by mixing 90 wt.% of the carbon material and 10 wt.% of polytetrafluoroethylene (Aldrich, USA) as binder. The mixture was prepared in a mortar and pressed into disk-shaped electrodes (weighing approximately 30 mg, with a diameter of 1.13 cm² and a thickness of about 0.4 mm).

Biliquid SCs were assembled in Teflon cells using a cation exchange membrane (Nafion® NRE-212, thickness 0.002 inch, Sigma-Aldrich, Germany) in order to separate the system into two half-cells. Fig. 1 shows a scheme of the cell used. Each half-cell

consisted of a selected electrolyte, a carbon electrode and a current collector (Au), all of which pressed against the membrane pre-fixed inside the cell. In our experiments, the positive half-cell always contained the aqueous electrolyte while the IL is in the negative half-cell. To record the potential, a third reference electrode was immersed in the aqueous medium (Ag|AgCl|3.5M KCl). Conventional symmetric cells containing a single electrolyte were also prepared for comparison purposes, using the same electrodes and current collectors, but in a "T-type" Swagelok® cell with glass fiber separators.

The notation used to facilitate an understanding of these assemblages was as follows. In the case of the more complex systems, containing two electrolytes and a membrane, the cell has been labeled as *positive electrode/electrolyte 1|||electrolyte 2/negative electrode*. In this case, each electrode/electrolyte interface is represented by a single bar (|), while the membrane between the two electrolytes or the electrolyte 1/electrolyte 2 interface is represented by a triple bar (|||). In the case of the conventional cells the notation has been simplified to *positive electrode/electrolyte/negative electrode*.

2.3. Electrochemical characterization

The electrochemical behavior of the devices was evaluated by synchronous cyclic chronopotenciometry, where the cell voltage and the potential of each electrode are recorded simultaneously [12, 30]. For this purpose, the cells (referred to in this paper as *2-3 electrode configuration*) were assembled in a similar way to a two-electrode configuration but with a reference electrode in a third connection, as represented in Fig. 1. Further details on the technique and on the behavior of SC in galvanostatic experiments of this type can be found in supporting information.

In this work all the electrochemical measurements were performed in a BioLogic VMP (USA) device at room temperature. Galvanostatic tests were performed at different current densities (0.1-0.5 A g⁻¹) at the maximum voltage of each cell. From these experiments, the values of specific capacitance for each electrode (C_+ or C_-) were calculated by integrating the discharge profile (potential vs. time) for each individual electrode (in different colors in Fig. S1) by means of the following Eqs [12]:

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

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

where I is the current applied, t is the time and U is the potential for a given electrode, considering only the discharge step.

The specific cell capacitance (C_{cell}) and energy density (E) were calculated by integrating the discharge curve (voltage vs. time) for the cell (hatched area in Fig. S1) by means of the following Eqs [12]:

$$C_{cell} = \frac{2I(\int V dt)_{discharge}}{(m_+ + m_-)V_{discharge}^2} \quad (3)$$

$$E = \frac{I(\int V dt)_{discharge}}{(m_+ + m_-)} \quad (4)$$

where V is the voltage and m_+ and m_- are the mass of active material in the positive and negative electrodes, respectively.

The power density (P) was determined as the ratio between E and the total discharge time according to Eq (5). The equivalent series resistance (ESR) was determined from the ohmic drop at the beginning of the discharge profile and calculated by means of Eq (6):

$$P = \frac{E}{\Delta t_{discharge}} \quad (5)$$

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

where Δt is the discharge time, $V_{max,charge}$ is the maximum voltage reached by the SC during charging, and $V_{discharge}$ is the maximum voltage avoiding the ohmic drop.

Two types of efficiency were considered in this study: the coulombic efficiency (ε) and energy efficiency (η), calculated from the results of the galvanostatic experiments by means of Eqs (7) and (8), respectively:

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

$$\eta = \frac{(\int V dt)_{discharge}}{(\int V dt)_{charge}} \times 100 \quad (8)$$

3. Results and discussion

3.1. Standard Symmetric Supercapacitors

Prior to the investigation of the biliquid supercapacitors, conventional symmetric cells using CNTs as electrode active material were studied for comparative purposes. Fig. 2 shows the charge-discharge profiles at a current density of 0.2 A g^{-1} of the symmetric systems CNT|1M H_2SO_4 |CNT and CNT|EAN|CNT at their maximum operating voltages (1.0 and 1.8 V, respectively), together with their electrode potential profiles. The electrochemical data obtained for these conventional systems are shown in Table 1.

The charge-discharge profile shown in Fig. 2a corresponds to that of an ideal system (see Fig. S1). The specific capacitance of the cell is low (6.7 F g^{-1}) due to the small surface area of the CNTs ($S_{BET} \approx 250 \text{ m}^2 \text{ g}^{-1}$), see textural properties in Fig. S2 and Table S1, supporting information) and, consequently, the energy density is also low (Table 1). Due to the small size of the H_3O^+ and HSO_4^- ions, compared to the average pore diameter of the mesoporous network of the CNTs, the formation of the double layer in aqueous media readily occurs (as the insertion of ions into the pores is not restricted), contributing to low ESR values ($0.5 \text{ } \Omega$). Another consequence of the

easiness of the double layer formation is the symmetry observed in the electrode potential profiles in the aqueous cell, where positive and negative electrodes share half of the cell voltage ($\Delta U_+ \approx \Delta U_- \approx 0.5$ V) and, consequently, their capacitances are very similar. However, the main drawback of using an aqueous electrolyte is the voltage, which is normally limited to 1V [21].

The substitution of the aqueous electrolyte by an ionic liquid (EAN in this study) enables the operating cell voltage to be increased and higher energy density could be anticipated. Nevertheless, significant differences are observed in the charge-discharge profiles (Fig. 2b). First, the voltage profile of the cell is now far from being linear and the behavior of the positive and negative electrodes is rather different (Table 1). These differences are due to the fact that the nitrate ions have greater difficulty forming the double layer in the positive electrode, which results in a lower capacitance and, consequently, in a larger potential window than for the negative electrode ($\Delta U_+ \approx 1.27$ V; $\Delta U_- \approx 0.53$ V), according to Eqn (S2) (supporting information). Therefore, although the cell voltage is wider than in the aqueous media (1.8 vs. 1.0 V), the C_{cell} is much lower (1.8 F g^{-1}), the ESR is higher ($3.9 \text{ } \Omega$) and the total energy density value is very similar to that obtained in the aqueous media.

In light of these results it is clear that both cells have limitations that prevent the increase in the energy density of the device (which is dependent on the capacitance and voltage: $E=0.5CV^2$). The aqueous system, although it provides a higher capacitance, is limited by the electrochemical stability window of water. The cell containing the ionic liquid, despite having a higher operating voltage, is seriously limited by the poor performance of the positive electrode, which results in a lower specific capacitance (4.9 F g^{-1}) and a limited cell specific capacitance.

These results suggest that the system could be optimized by combining the two different electrolytes within the same cell, employing in each half-cell the combination of electrode/electrolyte that best performs in each conventional cell. This is the first time that this type of approach is used. The positive half-cell would contain the aqueous media, as EAN shows a poor performance in this half-cell. EAN could then be used in the negative half-cell where it shows a good performance and is not subjected to limitation of the hydrogen evolution reaction, which is always present in aqueous electrolytes when reaching too negative potentials. Such a cell configuration is a completely new strategy for building complex devices able to exceed the energy densities achieved in the two original symmetric systems.

3.2. *Biliquid-Symmetric Supercapacitor: CNT|1M H₂SO₄||EAN|CNT*

Fig. 3 shows the electrochemical behavior of the first ever biliquid system used as a supercapacitor described in the literature. It has a symmetric assembly, both electrodes being identical and made of the same material and mass, in order to allow it to be compared with the conventional cells. The energy storage mechanism is the same in each electrode, i.e. the electric double layer formation. EAN is used in the negative semi-cell because the positive electrode/electrolyte interface is the limiting one in the CNT|EAN|CNT cell. A Nafion membrane is used to separate each half-cell due to its ability to transport protons [31].

The data in Table 2 show that in this biliquid SC each electrode (positive and negative) operates very close to the maximum values of specific capacitance obtained in the conventional cells previously studied (Table 1). The main limitations of these conventional cells were overcome with the removal of EAN from the positive half-cell and making the new biliquid cell operate at 1,6 V (a higher voltage than that of the

aqueous cell, CNT|1M H₂SO₄|CNT). As a result the energy density of the new cell (CNT|1M H₂SO₄||EAN|CNT) is higher than that of the standard cells. The main drawback is that the *ESR* values are relatively higher for the biliquid SC, which is an inevitable consequence of the use of the membrane.

Certain peculiarities of the novel biliquid SC are worth noting. The use of such different electrolytes in each half-cell leads to an unusually high O.C.P., close to +0.51 V, which is relevant for the long term performance of the cell. While the negative electrode in the IL performs at a comfortable +0.51 V to -0.29 V, the positive electrode is working at very demanding potentials, from +0.51 V to +1.31 V, where both the aqueous media and the carbon materials oxidize with the number of cycles.

There are many different possibilities for improving the performance of this new biliquid SC but it would be essential to limit the potential of the positive half-cell and to increase the potential window of the negative half-cell, by taking advantage of the stability limits of the IL at the negative potentials.

3.3. *Biliquid-Symmetric-Hybrid Supercapacitor:*

CNT|1M H₂SO₄, 1M VOSO₄||EAN|CNT

Our approach to limit the potential of the positive electrode was to add a redox compound to the sulfuric solution to allow this half-cell to perform at constant potential [16]. By using VOSO₄ as inorganic redox electrolyte the potential can be limited to the redox potential of the VO₂⁺/VO²⁺ couple (≈ 0.83 V vs Ag/AgCl). In this way, the cell becomes hybrid, with a different energy storage mechanism in each electrode. The positive half-cell behaves as a battery, working at a constant potential, while the negative half-cell continues to show a capacitive behavior with a change in its potential during charge and discharge. More details about this hybrid behavior are provided elsewhere [12]. Fig. 4 clearly shows the faradaic behavior of the positive electrode, with

a potential plateau corresponding to the vanadium redox reaction, and the capacitive behavior of the negative electrode, with a potential ranging from +0.81 to -0.75 V, as a consequence of which the whole cell shows the triangular shape typical of SCs.

It is worth mentioning that the O.C.P. is fixed by the redox couple at 0.81 V, which is even higher than in CNT|1M H₂SO₄||EAN|CNT but with the advantage that the potential remains almost constant and the positive electrode never reaches the high potential of the previous system (1.31 V). In addition, we emphasize that biliquid systems are more suitable for the use of a redox additive. VOSO₄ is practically insoluble in EAN so the diffusion of the redox species into the half-cell containing the ionic liquid is avoided. As we stated in the Introduction of this paper, the migration of active species is a common problem in other systems such as flow-redox batteries that also use vanadium compounds in their electrolytes [24, 25]. Vanadium species with different oxidation states are able to crossing membranes due to large gradient of concentration [24, 25].

The new *biliquid-symmetric-hybrid SC* yields an energy density of 4.5 W h Kg⁻¹ (Table 3), a value that is more than two-folds that of the former *biliquid-symmetric SC* (1.6 W h Kg⁻¹). An analysis of the quantitative values of capacitance of the positive (1465.7 F/g) and negative (26.7 F/g) electrodes shows that the negative electrode is limiting the cell. As mentioned above, the low specific surface area of the CNTs limits the formation of the double layer, so it would appear reasonable to replace it by an electrode material with higher surface area in order to increase the capacitance of the negative electrode and, therefore, the capacitance and energy of the whole cell.

3.4. *Biliquid-Asymmetric-Hybrid Supercapacitor:*

CNT/1M H₂SO₄, 1M VOSO₄///EAN/MES

In view of the drawbacks of the previous device, the next logical step in order to improve the biliquid SC is to select another carbon material for the negative electrode so as to create an asymmetric system, with different electrode materials in the positive and negative half-cells. A mesoporous carbon with a high specific surface area ($S_{BET} \approx 1350 \text{ m}^2 \text{ g}^{-1}$) was therefore selected as negative electrode. MES was chosen in preference to a microporous carbon because its performance towards electrolytes containing large ions (such as ILs) is better. The main characteristics of MES are summarized in Table S1 (see supporting information). Fig. 5 shows the behavior of the new *biliquid-asymmetric-hybrid SC*. The same energy storage mechanisms are maintained but there is a significant quantitative change, as the charge-discharge time increases substantially. The data in Table 4 reflect the improvements in the electrochemical performance of the cell. The specific capacitance in the negative electrode (C_-) significantly increases (from 26.5 to 102 F g⁻¹) and, consequently, C_{cell} increases from 13.5 to 47.5 F g⁻¹ and E from 4.5 to 15.0 W h kg⁻¹. Nonetheless, the ESR of the device increases from 6.9 to 8.9 Ω , as a result of the lower electrical conductivity of MES in comparison to CNTs (Table S1, supporting information).

In addition to the enhancement in energy density, the power density of this biliquid SC is also significant. Fig. 6 shows the progressive improvement of the electrochemical behavior of the cells described above in terms of energy density (Fig. 6a) and power density (Fig. 6b) for different current densities. The three biliquid cells under study show power densities similar to the two standard cells. Therefore the incorporation of a new interface in the biliquid systems does not harm the power of the cells despite the increase of resistance, reaching values of 300 W kg⁻¹ at 0.5 A g⁻¹. Moreover, the loss of capacitance and, consequently, energy with increasing current

density in the biliquid SCs is smaller than that of the conventional cell containing the IL. The biliquid-symmetric cells, with CNTs in both electrodes, show a decrease in E values of around 29% when the current density is increased from 0.1 to 0.5 A g⁻¹. Under the same conditions, the more complex biliquid SC (CNT|1M H₂SO₄, 1M VOSO₄|||EAN|MES) and the CNT|EAN|CNT cell show a decrease of 34 and 40%, respectively. Finally, Fig. 7 shows the modest long-term performance of this more complex biliquid-asymmetric-hybrid SC, which is able to retain about 70% of its capacitance after 1000 cycles and 50% after 2000 cycles. The hybridization of battery and capacitor materials often undermines the cycling performance of the device [32, 33]. It is well known that systems containing battery electrodes are completely degraded before 1200 cycles [34]. Different hybrid supercapacitors published in the literature are evaluated in about 1000 cycles and they never reach the same performance of the electrochemical capacitors with purely electrostatic mechanism [33-36]. For this reason, the cycling performance for CNT|1M H₂SO₄, 1M VOSO₄|||EAN|MES can be considered acceptable. The origin of degradation of this cell is due to the high potential reached by the positive electrode, which operates at 0.81 V and inevitably degrades the carbon nanotubes. The choice of different electrode and electrolyte materials operating at different potentials may lead to a better performance in future biliquid SCs.

3.5. *Insight into the functioning of the Biliquid Supercapacitor*

After having demonstrated the practical feasibility of these new biliquid systems, their mechanism of operation is discussed, focusing in the most complex assembly presented (CNT|1M H₂SO₄, 1M VOSO₄|||EAN|MES). Fig. 8 shows a scheme of how this biliquid system functions during charging. The behavior of each half-cell is simple and presents no novelties. The negative part contains an IL as electrolyte that forms the

electric double layer as the main mechanism of energy storage (whatever electrode materials are used). The positive part contains a redox electrolyte, in this case the $\text{VO}_2^+/\text{VO}^{2+}$ couple in a sulfuric solution, which stores energy through a reversible redox reaction, using CNTs as an excellent electrode material (high electrical conductivity). It is the combination of these two half-cells what offers new opportunities and challenges.

The whole cell in Fig. 8 operates as follows:

- i) During the charge process, VO^{2+} oxidizes to VO_2^+ on the surface of the CNTs (positive electrode) while, simultaneously, the $\text{C}_2\text{H}_5\text{NH}_3^+$ ions become part of the double layer at the negative electrode. The electronic and ionic movements involving both electrodes generate an excess of positive charge in the aqueous phase and an excess of negative charge in the phase containing the ionic liquid. Therefore, the electroneutrality of the whole cell must be maintained either through the transport of protons (from the aqueous half-cell to the IL) or through the transport of NO_3^- ions (from the IL to the aqueous half-cell). In this particular case, only the transport of protons is feasible due to the membrane selected. During the discharge process, the ionic movement is inverted.
- ii) The transport of protons between the two half-cells is facilitated by the appropriate selection of components. The aqueous phase containing 1.0 M H_2SO_4 has a high concentration of H_3O^+ ions that can cross the Nafion membrane by ion-exchange involving sulfonic acid functional groups ($-\text{SO}_3\text{H}$) [31]. Meanwhile, as EAN is a protic ionic liquid it can accept protons from the aqueous phase according to the following equilibria [37]:

iii) The separation of the electrolytes by the membrane imposes high values of OCP due to the high concentrations of the different species separated into the two half-cells, which leads to an additional electrochemical junction.

In this new biliquid SCs the choice of membrane and electrolytes play an essential role in the operation of the device and must be optimized to minimize the resistance imposed by the new interface and to allow an energetically favorable flow of ions between the different phases.

3.6. *Influence of the electrolyte on the ion-exchange between the two half-cells*

In order to gain a deeper insight into the role that the interface and the electrolytes play in the performance of the biliquid SC, a different IL was used. EAN was replaced by EMITFSI in a new complex cell, CNT|1M H₂SO₄, 1M VOSO₄|||EMITFSI|MES. Important differences in the physical and chemical properties of both ILs need to be pointed out. EMITFSI is hydrophobic, aprotic and immiscible with water, while EAN is hydrophilic, protic and completely miscible with water [37-39] (This is the reason why the latter was initially selected for this study, as it would be more prone to accept protons). Fig. 9 shows the charge-discharge profile of the *biliquid-asymmetric-hybrid SC* using EMITFSI at 0.2 A g⁻¹ and Table 5 presents the calculated electrochemical data.

If the galvanostatic cycles of the cells using EMITFSI (Fig. 9) and EAN (Fig. 5) are compared, there are similarities in the energy storage mechanisms but also some noticeable differences in the behavior of the negative half-cells. The positive electrode maintains the same faradaic mechanism due to the development of the vanadium redox reactions. In the negative electrode the double layer formation continues to be the main mechanism of energy storage, but there is a striking difference when this aprotic IL is used: the charge-discharge profiles of this electrode show a strong deviation from

linearity due to the malfunctioning of the negative half-cell, which is not observed in the system containing EAN.

In order to understand the differences between the two biliquid systems (with EAN and EMITFSI in the negative half-cells), symmetric cells with both ILs as electrolytes and MES as electrodes were assembled (MES|EAN|MES and MES|EMITFSI|MES). Fig. S3 (supporting information) shows the galvanostatic cycles recorded for both systems and their corresponding specific capacitances are compiled in Table S2 (supporting information). The symmetric cell containing EAN shows a standard triangular behavior for a supercapacitor with the negative electrode showing a capacitance value of approximately 100 F g^{-1} , which is the same value as that of the negative electrode in the biliquid system containing EAN in the negative half-cell. It is clear that in this case the use of two electrolytes does not affect the performance of the negative electrode. The symmetric cell containing EMITFSI also shows a triangular behavior with the negative electrode showing a capacitance value of 90.7 F g^{-1} . This result is significant because it demonstrates that there are no problems associated with the formation of the double layer at the EMITFSI|MES interface. The value of C in EMITFSI is a bit lower than that of EAN, but the differences in the size of the ions and viscosity account for this small difference. To explain the poor performance of the negative half-cell in the biliquid system with EMITFSI (Fig. 9), which shows a capacitance value of only 41.1 F g^{-1} and a strong distortion of the charge-discharge curve, the differences in the chemical nature of EAN and EMITFSI must be considered. It is likely that the transport of protons through the membrane into the IL is responsible for this behavior. As mentioned before, EAN is protic and hydrophilic which should facilitate the acceptance of protons. Meanwhile EMITFSI is aprotic and hydrophobic which will limit the movement of protons from the aqueous to the IL media. Therefore,

the transport of ions through the interface to achieve neutrality is a critical factor that must to be taken into consideration when selecting the elements for building the cell (especially the membrane and the two different electrolytes).

3.7. *Efficiency of Biliquid Supercapacitors*

Efficiency is a very important parameter that has not been taken into consideration yet and its study can provide information about the role of the transport of ions through the membrane. In scientific studies on to supercapacitors, coulombic efficiency (ϵ) is usually included in the discussions, normally presenting very high values [40-42]. However energy efficiency (η) is rarely discussed in SCs literature, as for other energy storage devices such as batteries [43, 44]. Generally speaking ϵ is directly related to the charge losses resulting from the degradation process in the cell, such as the decomposition of the electrolyte or electrode, secondary or undesired reactions and self-discharge. It can therefore be expected that pure EDLCs will show a higher ϵ than hybrid SCs where redox reactions are involved. On the other hand η accounts for the losses caused by internal resistances during storage. Therefore, the storage of the small ions from aqueous systems should be more efficient than the storage of ions from IL, due to their smaller size and lower viscosity of the media [38]. In the case of biliquid systems the transport of ions through the interface, so that the ionic charges of the two half-cells are balanced, may also have a great influence in the efficiency, not only because of the difficulty of crossing of the membrane itself but also because of the resistance of the ions of one phase to incorporate in the second phase of a quite different nature.

Table 6 shows the values of ϵ and η in the different electrochemical systems under study. As one might expect, ϵ is very high for the symmetric systems with values close to 99%, both for aqueous electrolytes and for ILs. However this is not the case for

η in the same symmetric systems. The value in the almost ideal aqueous system (with CNTs as electrode material) is very good (92%) but much lower values are obtained for both ILs, ranging from 71% when CNTs are used as electrode material to approximately 57 % when MES is the electrode material. It is worth noting that the use of MES reduces the energy efficiency due to its narrower porosity, which makes the diffusion of the viscous electrolyte even more difficult. The values of ϵ decrease drastically in all the biliquid systems tested (75-85%), probably due to self-discharge processes. On the other hand the values of η seem to vary depending on the IL used. The values are around 50% when EAN is used, similar to those of the symmetric conventional system (57%), but they radically drop to 28% in EMITFSI. As mentioned above the only reason that can explain this behavior is the difficulty or resistance of the protons to move from the Nafion membrane into the hostile EMITFSI media.

4. Conclusions

A novel concept of SCs, referred to as biliquid SCs, have been developed, by assembling a negative half-cell containing an ionic liquid as electrolyte and a positive half-cell with an aqueous electrolyte.

It has been demonstrated that this new concept allows to overcome the energy density of conventional cells, excluding the interfaces that limiting the capacitance, and operating with a new voltage determined by the cathodic stability limit of an electrode and anodic stability limit of the second one. In addition, it has been shown that biliquid SCs are highly flexible as the devices can operate in symmetric, asymmetric or hybrid configurations to optimize their electrochemical performance, without adding any technological complexity in the construction of the cells. The highest cell capacitance

and maximum voltage were reached for the fully asymmetric biliquid SC SC (CNT|1M H₂SO₄, 1M VOSO₄|||EAN|MES), with an energy density of 15.0 W h kg⁻¹.

Synchronous cyclic chronopotenciometry enabled to fully characterize these novel complex systems, allowing us to propose a brief model of their functioning and identifying their limiting aspects. The main challenge of this type of systems lies in the selection of the proper combination of electrolytes that enable a good transport of ions between the two half-cells.

This approach may serve as a basis for scientists working in this field to develop new devices incorporating other asymmetries involving different electrodes, electrolytes and storage mechanisms, in order to enhance energy and power densities and long-term performance.

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Table 1. Electrochemical data calculated from the galvanostatic profiles for the CNT|1M H₂SO₄|CNT and CNT|EAN|CNT cells.

Cell	$E / \text{W h kg}^{-1}$	$P / \text{W kg}^{-1}$	$C_{\text{cell}} / \text{F g}^{-1}$	ESR / Ω	$C_+ / \text{F g}^{-1}$	$C_- / \text{F g}^{-1}$
CNT 1M H ₂ SO ₄ CNT	0.9	92.6	6.7	0.5	24.5	29.7
CNT EAN CNT	0.8	139.4	1.8	3.9	4.9	14.0

Table 2. Electrochemical data calculated from the galvanostatic curves for CNT|1M H₂SO₄||EAN|CNT at 0.2 A g⁻¹.

$E / \text{W h kg}^{-1}$	$P / \text{W kg}^{-1}$	$C_{\text{cell}} / \text{F g}^{-1}$	ESR / Ω	$C_+ / \text{F g}^{-1}$	$C_- / \text{F g}^{-1}$
1.6	126.6	5.0	6.3	21.3	15.9

Table 3. Electrochemical data calculated from the galvanostatic curves for CNT|1M H₂SO₄, 1M VOSO₄||EAN|CNT at 0.2 A g⁻¹.

$E / \text{W h kg}^{-1}$	$P / \text{W kg}^{-1}$	$C_{\text{cell}} / \text{F g}^{-1}$	ESR / Ω	* $C_+ / \text{F g}^{-1}$	$C_- / \text{F g}^{-1}$
4.5	130.4	13.5	6.9	1465.7	26.7

*This value should be considered as charge-capacity due to the faradaic behavior of this electrode.

Table 4. Electrochemical data calculated from the galvanostatic curves for CNT|1M H₂SO₄, 1M VOSO₄||EAN|MES at 0.2 A g⁻¹.

$E / \text{W h kg}^{-1}$	$P / \text{W kg}^{-1}$	$C_{\text{cell}} / \text{F g}^{-1}$	ESR / Ω	* $C_+ / \text{F g}^{-1}$	$C_- / \text{F g}^{-1}$
15.0	117.9	47.5	8.9	837.4	102.0

* This value should be considered as charge-capacity due to the faradaic behavior of this electrode.

Table 5. Electrochemical data calculated from the galvanostatic curves for CNT|1M H₂SO₄, 1M VOSO₄||EMITFSI|MES at 0.2 A g⁻¹.

$E / \text{W h kg}^{-1}$	$P / \text{W kg}^{-1}$	$C_{\text{cell}} / \text{F g}^{-1}$	ESR / Ω	$*C_+ / \text{F g}^{-1}$	$C_- / \text{F g}^{-1}$
11.0	93.2	21.8	9.0	1272.8	41.1

*This value should be considered as charge-capacity due to the faradaic behavior of this electrode.

Table 6. Coulombic (ϵ) and energy (η) efficiencies of symmetric and biliquid systems used in this study.

System	ϵ (%)	η (%)
CNT 1M H ₂ SO ₄ CNT	99	92
CNT EAN CNT	94	71
MES EAN MES	99	57
MES EMITFSI MES	99	58
CNT 1M H ₂ SO ₄ EAN CNT	78	50
CNT 1M H ₂ SO ₄ , 1M VOSO ₄ EAN CNT	74	50
CNT 1M H ₂ SO ₄ , 1M VOSO ₄ EAN MES	73	52
CNT 1M H ₂ SO ₄ , 1M VOSO ₄ EMITFSI MES	84	28

Fig. 1. Scheme of the assembly used to study the supercapacitor containing two electrolytes.

Fig. 2. Galvanostatic charge/discharge profiles obtained at 0.2 A g⁻¹ for the following symmetric cells: CNT|1M H₂SO₄|CNT at 1.0 V (a) and CNT|EAN|CNT at 1.8 V (b). Voltage (left Y-axis) and potential curves for the positive and negative electrodes (right Y-axis).

Fig. 3. Galvanostatic charge/discharge curves obtained at 0.2 A g^{-1} for the *biliquid-symmetric SC*: CNT|1M H_2SO_4 ||EAN|CNT. Voltage (left Y-axis) and potential curves for the positive and negative electrodes (right Y-axis).

Fig. 4. Galvanostatic charge/discharge curves obtained at 0.2 A g^{-1} for the *biliquid-symmetric-hybrid SC*: CNT| 1M H_2SO_4 , 1M VOSO_4 ||EAN|CNT. Voltage (left Y-axis) and potential curves for the positive and negative electrodes (right Y-axis).

Fig. 5. Galvanostatic charge/discharge profiles obtained at 0.2 A g^{-1} for the *biliquid-asymmetric-hybrid SC*: CNT|1M H₂SO₄, 1M VOSO₄||EAN|MES. Voltage (left Y-axis) and potential profiles for the positive and negative electrodes (right Y-axis).

Fig. 6. Energy density (a) and power density (b) of the biliquid SCs at different current densities.

Fig. 7. Cycling performance at 0.2 A g^{-1} for CNT|1M H_2SO_4 , 1M VOSO_4 ||EAN|MES cell.

Fig. 8. Scheme of the biliquid SC during the charge/discharge process.

Fig. 9. Galvanostatic charge/discharge profiles obtained at 0.2 A g^{-1} for the *biliquid-asymmetric-hybrid SC*: CNT|1M H_2SO_4 , 1M VOSO_4 ||EMITFSI|MES. Voltage (left Y-axis) and potential profiles for the positive and negative electrodes (right Y-axis).