Enhancement of Energy and Power Density of Batteries and Supercapacitors: Electrode Hybridization

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***Abstract*— Design and synthesis of electrochemical energy storage devices, which have a long cycle life as well as a high energy and power density, are very important. One of the newest and most promising of energy storage devices that are currently being studied to improve energy storage technologies is the hybrid SC-LIBs with hybrid electrodes. Hybrid SC-LIBs are asymmetric electrodes formed by internal serial hybridization by replacing one of the electrodes of a symmetrical supercapacitor (SC) with a lithium-ion battery (LIB) electrode. It is very important that the charges on both electrodes of the hybrid SC-LIBs are balanced during high-rate charge/discharge operations and that the battery-type electrode contributes to the total capacitance of the device and further increases its working potential. For this reason, the studies focused on hybrid SC-LIBs with hybrid electrodes. These new devices consist of a hybrid SC-LIB electrode and a SC electrode with high power density or a LIB electrode with high energy density. In these devices, which have a wider cell working voltage and a larger capacity, the key factors that reveal the full working potential of the hybrid electrodes are the correct composition and morphological structure of the electrode materials.**

Keywords*— *Supercapacitor, Battery, Hybrid structure, Energy density, Power density.

I. INTRODUCTION

The fact that storage of energy has become a global problem for modern societies increases the demand for high-performance energy storage devices every day. In addition, energy storage devices with high efficiency and low cost are required for continuous use of energy from renewable energy sources such as solar and wind energy [1]. The diversity of energy types and applications indicates the need for different perspectives in the development of energy storage devices. Thanks to strategies for developing new materials and designs in particular, energy storage devices that are aimed at overcoming the challenges of meeting energy needs stand out as the promising systems in global scale. Among the most important energy storage devices of the 21st century are batteries, supercapacitors, and fuel cells. The common feature of all three systems is that they are based on storing the produced energy by the reactions that occur at the electrode and electrolyte interface. In R & D activities, the performance of energy storage devices can be improved by better understanding and improving the electrochemical processes in this interface. In many areas, particularly in smart and portable electronic devices and electric vehicles, it is important to store a lot of energy at low costs. As a result, the energy and power densities of energy storage devices should be increased to a considerable level with the developing technology. The performance of energy storage devices depends on the electrode material, electrolyte, and device design. In this respect, studies on designing battery-type electrodes with new materials are available in the literature. In these studies, it is stated that the material design is made in two ways. The first is balancing the size and morphology of the electroactive particles in the materials with the sizes of the electrolyte ions. The second is the addition of materials with high conductivity to these electroactive particles. Furthermore, the use of aqueous electrolytes as well as organic electrolytes has resulted in a wider working potential range. These advances in electrode material and electrolyte lead researchers to design new hybrid electrode hybrid devices by electrode hybridization.

Current energy storage devices include lead-acid batteries, nickel-metal hybrid batteries, lithium-ion batteries and supercapacitors [2]. These energy storage devices in question differ from one another in cost, cycle life, safety, specific power, and energy density since the energy storage mechanisms of these devices are quite different from each other. Among these devices, the most intriguing are LIBs with high energy density and SCs with high power density [1], [3], [4]. LIBs that have high energy density due to the intercalation and de-intercalation reactions of lithium ions in the active electrode material are widely used in laptops, mobile phones and electric vehicles [5], [6]. However, the Li^+ storage mechanism in the LIB causes a lower power density due to the slowing of solid-state ion diffusion and the faradaic reactions in the bulk electrodes. Moreover, degradation of the electrode structures and volume expansion after cyclic charge/discharge processes reduces the cycle life of LIBs [2], [7]. At this point, electrical double-layer capacitor (EDLC) are of particular interest as materials with high power density and long cycle life due to the high rate of ion transfer (adsorption-desorption) in the active electrode material. However, the fact that the energy densities of the SCs are rather low compared to the LIBs is a significant disadvantage (Table 1) [8], [9].

Table 1. Characteristics of LIB and SC Energy Storage Devices

Parameters	LIB	SC
Energy density (Wh kg^{-1})	20-150	1-10
Power density (W kg^{-1})	<1000	500-10000
Cycle life	~1500	>500000
Efficiency	0.7-0.85	0.85-0.99
Calendar Life (year)	0.5-5	5-20
Charge time	1-5 h	30 sn^{-1} min
Discharge time	0.3-3 h	30 sn^{-1} min

Because the electric charge in the LIB electrodes is stored via redox (faradaic) reactions, the charge storage mechanism on them is a non-capacitive faradaic process. On the contrary, the charge storage mechanism in SCs is capacitive. While the EDLCs show capacitive characteristics, pseudocapacitors exhibit both capacitive and faradaic characteristics (Fig. 1). In SC electrodes, the electric charge can be stored EDL, pseudocapacitive or both [10].

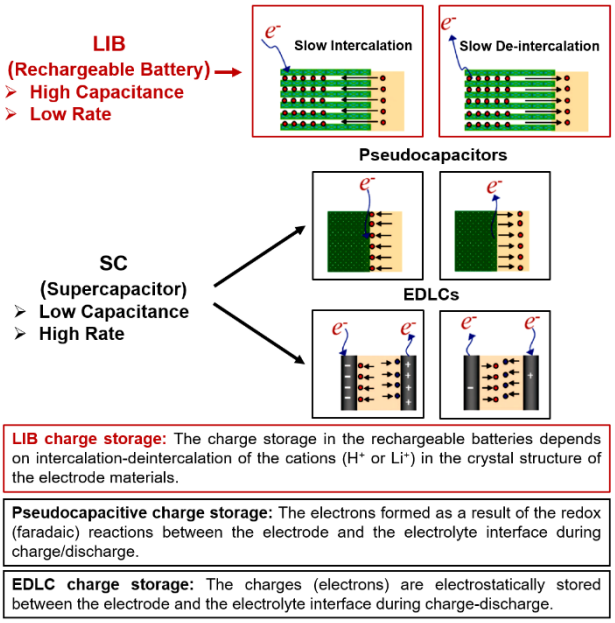


Fig. 1. Demonstration of charge storage mechanisms in LIB and SC [10].

For this reason, new hybrid energy storage devices called "Supercapattery (=**Supercapa**citor + ba**ttery**)" have recently been developed [11], [12] (Fig. 2); they combine the advantages of both capacitive and faradaic charge storage mechanisms and represent a wide range of devices. Researchers plan to produce eco-friendly, low cost and high-performance systems for these new devices by combining SC and LIB, which are complementary of each other thanks to different charge storing mechanisms [13].

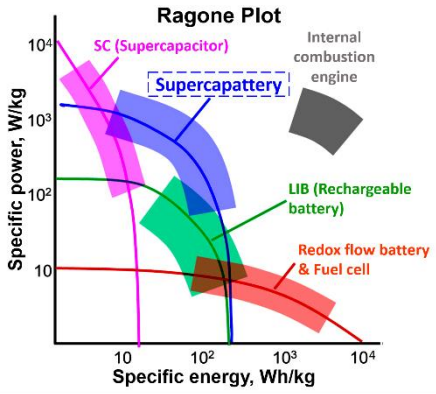


Fig. 2. Ragone plot of energy storage devices [14].

II. ELECTRODE HYBRIDIZATION

As shown in Fig. 3, the charge-potential curve of the single-electrode SC during charge/discharge is linear. However, as the phase change occurs due to the redox reactions during charge/discharge of single-electrode LIB, the potential value is constant as in Fig. 4 according to the phase rule. Therefore, SCs have high power and low energy density, while LIBs have high energy and low power density. That is, the energy stored in the SC is half the energy stored in a LIB [15].

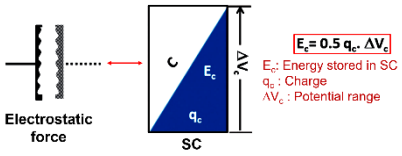


Fig. 3. Charge-potential curve of single-electrode SC in aqueous electrolyte and the corresponding energy storage.

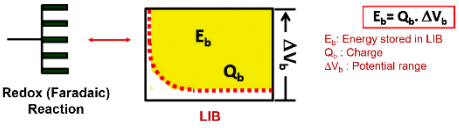


Fig. 4. Charge-potential curve of single-electrode LIB in aqueous electrolyte and the corresponding energy storage.

The performance of the energy storage device is determined by the electrolyte, electrode material and design (hybridization) [1], [16]. This results from the fact that the specific energy and power density values expressing device performance depend on the working potential range and capacity/capacitance of the device [6]. For this reason, some methods schematized in Fig. 5 are being studied to obtain devices with high energy and power density. These methods are the construction of asymmetric electrodes, the use of organic electrolytes and the design of hybrid devices with new hybrid electrodes in a single device [17]. Methods for both constructing asymmetric electrodes and the design of hybrid devices with new hybrid electrodes are investigated within the scope of internal hybridization (Fig. 6) [18].

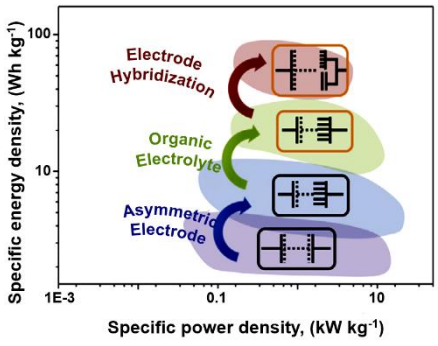


Fig. 5. Development process of specific energy and power density values from symmetrical electrode → asymmetric electrode → organic electrolyte → electrode hybridization [17].

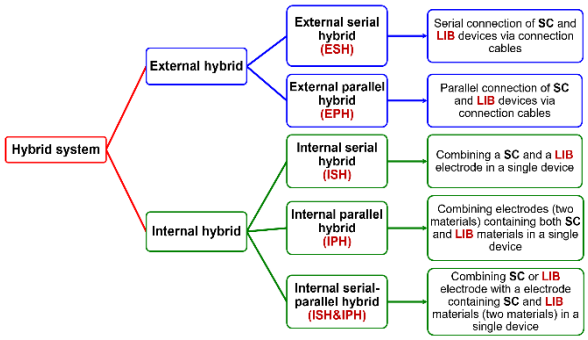


Fig. 6. Different combinations of SC-LIB hybrid structures [18].

CHARGE STORAGE MECHANISM OF HYBRID SC-LIBS

The asymmetric electrodes consist of a SC and a LIB type electrode. Combining these electrodes in a single device is internal serial hybridization (ISH). As shown in Fig. 7 this device, compose of combining the high power density of SC with the high energy density of LIB, is called the hybrid SC-LIB. It is important to use a high working potential (ΔV) to achieve the redox potential (ΔV_b) of the LIB electrode at the initial stage of charging in the hybrid SC-LIB. In this way, the amount of energy stored can be increased according to single-electrode structures. In contrast to the SC electrode, however, the contribution of the LIB electrode to the total capacitance value in the hybrid SC-LIB should be increased. This is due to the fixed electrochemical potential value of the LIB electrode. Furthermore, another disadvantage in hybrid SC-LIBs is that the LIB electrode cannot perform as fast as the SC electrode during charge/discharge. The main reason for this difference between the electrodes is that the charge storage process in the LIB electrode (faradaic) is slower than that of the SC electrode (electrostatic). Thermodynamically, the hybrid SC-LIBs can take full advantage of the different working potential ranges of both electrodes to ensure maximum working potential. In this way, both the specific capacitance and the energy density increase significantly. However, in order to achieve the maximum working potential, it is important to balance the charges stored in both electrodes at high rates in charge/discharge operations [17].

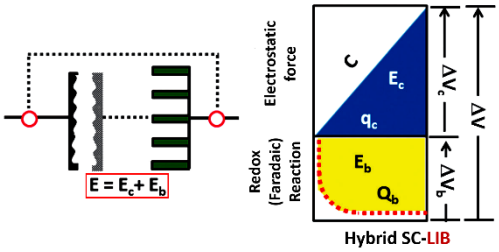


Fig. 7. Charge-potential curve of hybrid SC-LIB in aqueous electrolyte and the corresponding energy storage [15].

Recent research shows that the design of new electrode materials can help balance the low charge transfer kinetics in redox reactions in LIB electrodes [19]–[21]. Electrode material design can be done in two ways. The first is to control the size and morphology of the electroactive particles in the electrode material. The second is the addition of high conductivity materials to this electrode material [22]. The first approach is to shorten the diffusion paths of the charge-balancing ions by the electroactive particles synthesized in the nanosize. Thus, as the charge storage mechanism in the LIB electrodes will improve, solid-state ion diffusion will increase. At the same time, the size and morphology of these electroactive nanoparticles and the size of the electrolyte ions will be balanced. The second approach, which aims to increase the conductivity of the LIB electrode, is discussed in different ways. It is most preferred that these nanoparticles be doped with metals or coated with carbon [6], [23]. Furthermore, the working potential range (ΔV_o) of organic electrolytes in hybrid SC-LIBs is higher than that of aqueous electrolytes (ΔV) (Fig. 8).

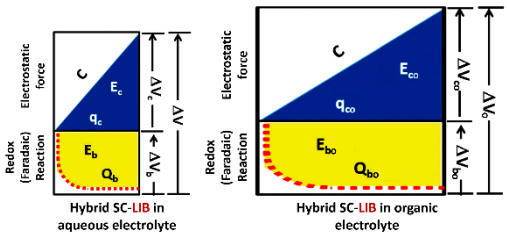


Fig. 8. Charge-potential curve of hybrid SC-LIB in aqueous and organic electrolyte and the corresponding energy storage.

CHARGE STORAGE MECHANISM OF HYBRID ELECTRODE WITH HYBRID SC-LIBS

The new hybrid electrode hybrid device consists of a SC or LIB electrode and a hybrid SC-LIB electrode. The combination of a single-material electrode and a double-material electrode in a single device is called internal serial-parallel hybridization (ISH&IPH). For example, Fig. 9 shows a hybrid electrode hybrid device comprising a SC electrode and a hybrid SC-LIB electrode. In the hybrid SC-LIB electrode, the energy is stored both as faradaic and capacitive. In the initial stage of charging of the hybrid SC-LIB electrode, the SC component stores up to q_1 charge through electrostatic forces until the LIB component reaches the redox potential (ΔV_b). The LIB component is charged with Q_b through the redox reaction until it reaches full charge state. After the full charge (Q_b) of the LIB component, the SC component is again charged up to q_2 through electrostatic forces until the hybrid SC-LIB electrode reaches the maximum potential (ΔV_{bc}). Thus, the amount of charge in the hybrid SC-LIB electrode is equal to the sum of the amounts of charge caused by both the SC ($q_c = q_1 + q_2$) and the LIB (Q_b) component [15].

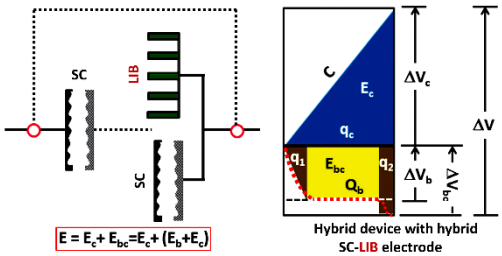


Fig. 9. The charge-potential curve of the hybrid device with hybrid electrode and the corresponding energy storage [15].

On the other hand, the maximum working potential (ΔV) of the hybrid device is equal to the sum of the potentials of the SC electrode (ΔV_c) and the hybrid SC-LIB electrode (ΔV_{bc}). Thus, the total amount of energy stored (E) in this hybrid device is equal to the sum of the energies stored on the SC electrode (E_c) and the hybrid SC-LIB electrode ($E_{bc}=E_b+E_c$). The structural nature of the hybrid SC-LIB electrode allows it to have a higher power density than the LIB electrode since the SC component of the hybrid SC-LIB electrode increases the electron transfer rate of the LIB component even at high-rate charge/discharge operations. The electrochemical performance of the hybrid SC-LIB electrode material depends on the hybridization of SC and LIB components. For this reason, the key factors that reveal the complete working potential compared to conventional electrode materials are the correct composition and morphological structure of the material in hybrid SC-LIB electrode material [15]. Hybrid SC-LIB

electrodes produced for hybrid devices by internal serial hybridization of both LIB and SC components;

- Should work like a single electrode although it consists of double material. Otherwise, this electrode will arrive at the full charge state directly without charging the LIB component due to the faster charge transfer kinetics of the SC component.
- Should have a porous structure and a high surface area for high energy density and good ionic conductivity since the three-dimensional porous network structure increases charge transfer kinetics while maintaining the ionic conductivity of these electrode materials [16].

To improve the electrochemical performance of energy storage devices, these new hybrid-electrode hybrid SC-LIBs will act as milestones in the future [15].

Hybrid SC-LIBs produced from different electrode materials with the same or different charge storage mechanisms are shown in Table 2. Thus, these hybrid SC-LIBs are considered as promising devices in terms of eliminating gaps in their weakness due to the good aspects of both energy storage systems. In addition, the general strategy for the design of electrodes and hybrid SC-LIBs is summarized in Table 2. There are many different options available in the literature regarding electrode materials to be used in the production of hybrid SC-LIBs [24] (Fig. 10).

Table 2. Specific energy density, specific power density and cycling life values of energy storage devices with the same or different charge storage mechanisms [25].

Device	Supercapacitor-battery(Supercapattery)					
	Supercapacitor			Hybrid SC-LIB		Battery
	EDLC	Pseudocapacitor				
	NFCS	NFCS	CFS	NFCS	CFS	NCFS
Electrode Materials	1+1 1+2	1+3	1+1 1+2	1+3	1+2	1+1 1+2
	NFCS	CFS	CFS	NCFS	NCFS	NCFS
Specific Energy (Wh kg^{-1})	6.7 [25], 10.2 [26]	3.6 [27], 14.3 [28]	26.6 [29]	204 [30], 230 [31]	103 [32], 114 [33]	250 [34]
Specific Power (kW kg^{-1})	111.6 [25]	24.7 [27], 0.68 [28]	13 [29]	55 [30]	56 [32]	1.5 [34]
Cycling life	>10000 [26]	>5000 [27]	>5000 [29,35]	>1000 [30]	>1000 [32]	>1200 [34]

NFCS: Non-Faradaic Capacitive Storage = EDLC Storage
CFS: Capacitive Faradaic Storage = Pseudocapacitive Storage
NCFS: Non-Capacitive Faradaic Storage = Battery-Type Storage
1+1: Symmetrical device of the same electrode material;
1+2: Asymmetrical device of different materials with the same storage mechanism;
1+3: Asymmetrical device of different materials with different storage mechanism.

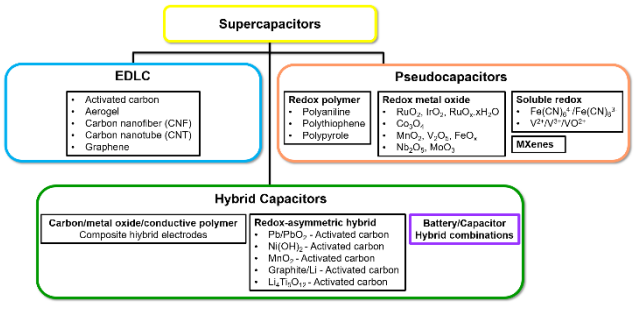


Fig. 10. Classification of supercapacitors [24].

The mass and charge of the electroactive nanoparticles in the positive and negative electrode materials in the hybrid SC-LIBs should be in equilibrium as indicated in the Equation (1). That is, the amount of charge stored on both electrodes must be equal [14].

$$Q_- = m_- Q_{sp-} = m_+ C_{sp+} \Delta E_+ = Q_+ \rightarrow \frac{m_+}{m_-} = \frac{Q_{sp-}}{C_{sp+} \Delta E_+} \quad (1)$$

where, $\mathbf{Q_+}$:charge at positive electrode, $\mathbf{Q_-}$:charge at negative electrode, $\mathbf{m_+}$:mass of electroactive nanoparticles in the positive electrode, $\mathbf{m_-}$:mass of electroactive nanoparticles in the negative electrode, $\mathbf{Q_{sp}}$:specific charge, $\mathbf{C_{sp}}$:specific capacitance and $\mathbf{\Delta E}$:potential range. The CV curves of the battery, EDLC and hybrid SC-LIB are given in Fig. 11. The reason for the observation of peaks in CV curves is that the charges on both electrodes in the batteries (or pseudocapacitors) are stored by faradaic redox reactions. For both electrodes in EDLCs, CV curves are rectangular since the charges are stored electrostatically. However, the charges in the hybrid SC-LIBs are stored by faradaic redox reactions in one of the electrodes while the other is electrostatically stored. Therefore, two different CV curves are observed in hybrid SC-LIBs. Peaks are observed in one of these curves while the other is rectangular.

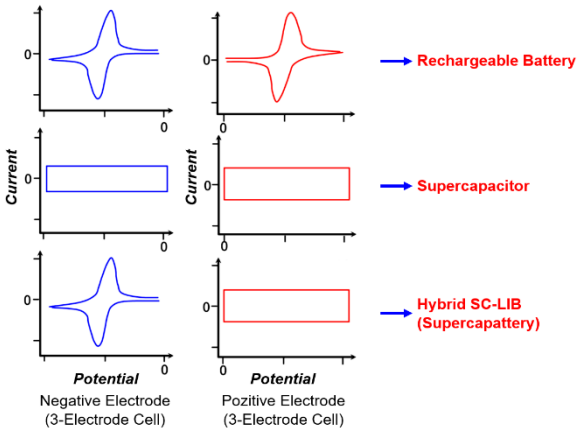


Fig. 11. Cyclic voltammetry (CV) curves of rechargeable battery, supercapacitor and hybrid SC-LIBs [14].

As seen in Fig. 12, the minimum voltage value during discharge in the supercapacitor (U_{min}=0) and hybrid SC-LIBs ($U_{min} \geq 0$) is decreased to zero, while the minimum voltage value ($U_{min} >> 0$) during the discharge in the batteries cannot be decreased to zero due to the possibility of irreversible reactions. Because the minimum discharge potential in the hybrid SC-LIBs is greater than or equal to zero ($U_{min} \geq 0$), the energy stored in these devices is calculated by the Equation (2) [14].

$$E = \frac{C_{sp,device}}{2}(U_{max}^2 - U_{min}^2) \quad (2)$$

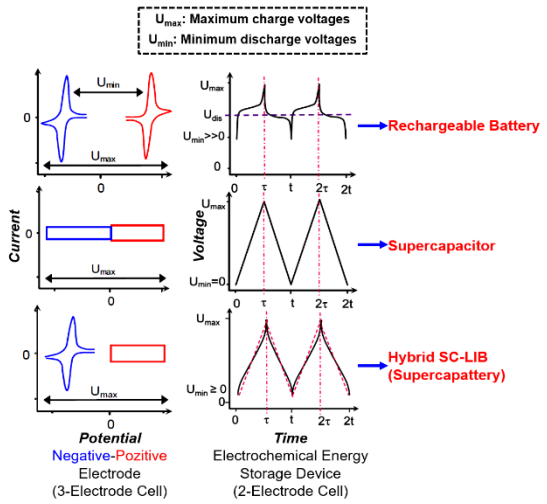


Fig. 12. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves of rechargeable battery, supercapacitor and hybrid SC-LIBs [14].

The GCD curves and electrode-device potential ranges of some hybrid SC-LIBs composed of different electrode materials are given in Fig. 13(a-c). As shown in Fig. 13(a), the negative electrode in the hybrid SC-LIBs with different charge storage mechanism is lithium metal or LiC_6, while the positive electrode is activated carbon. The negative electrode in the hybrid SC-LIBs with the same charge storage mechanism in Fig. 13 (b) is lithium metal or LiC_6, while the positive electrode is pseudocapacitive. In the hybrid SC-LIBs with the same charge storage mechanism, the negative electrode is the battery-type, while the positive electrode is pseudocapacitive (Fig. 13(c)). Thus, hybrid SC-LIBs with hybrid electrodes can be constructed by combining different combinations of capacitive (EDL, Pseudo, EDL: Pseudo) and battery-type electrode materials (Fig. 14).

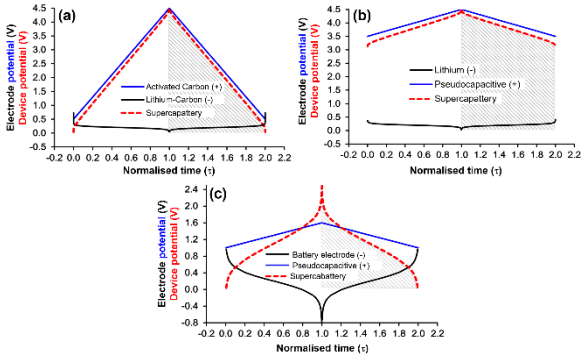


Fig. 13. Galvanostatic charge-discharge curves and electrode-device potential ranges of hybrid SC-LIBs consisting of different electrode materials [25], [37], [38].

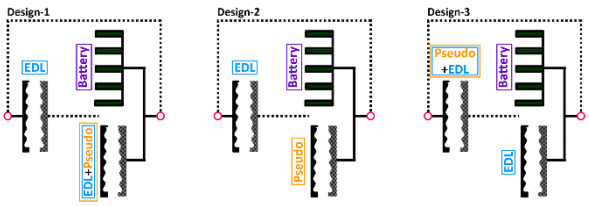


Fig. 14. Different designs of hybrid SC-LIBs with hybrid electrodes.

CONCLUSION

Carrying out many experimental studies has become inevitable to design and manufacture hybrid SC-LIBs with hybrid electrodes. The reason for this is that a better understanding of the surface chemistry between the SC and LIB components will ensure overcoming the challenges in the combination of high energy and power density in a single device. In particular, it is important that the current collector-electrode and electrolyte interfaces with the electroactive nanoparticles have a highly homogeneous distribution to increase charge transfer. Nanoparticles present in porous structures and in redox active materials can, capacitively or not, be used in the production of these devices since the charge can be stored both in capacitive and faradaic ways. This helps derive excellent electrochemical results from the right hybridization of highly polarized (positive and negative charge) SC and LIB components in the device.

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