



# **Battery-Type Lithium-Ion Hybrid Capacitors: Current Status** and Future Perspectives

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Abstract: The lithium-ion battery (LIB) has become the most widely used electrochemical energy storage device due to the advantage of high energy density. However, because of the low rate of Faradaic process to transfer lithium ions (Li<sup>+</sup>), the LIB has the defects of poor power performance and cycle performance, which can be improved by adding capacitor material to the cathode, and the resulting hybrid device is also known as a lithium-ion battery capacitor (LIBC). This review introduces the typical structure and working principle of an LIBC, and it summarizes the recent research developments in advanced LIBCs. An overview of non-lithiated and pre-lithiated anode materials for LIBCs applications is given, and the commonly used pre-lithiation methods for the anodes of LIBCs are present. Capacitor materials added to the cathodes, and suitable separator materials of LIBCs are also reviewed. In addition, the polarization phenomenon, pulsed performance and safety issues of LIBCs and electrode engineering for improving electrochemical performance are systematically analyzed. Finally, the future research and development direction of advanced LIBCs is prospected through the discussion of the existing problems of an LIBC in which the battery material in the composite cathode is LiNi<sub>x</sub>Co<sub>w</sub>Mn<sub>1-x-v</sub>O<sub>2</sub> (NCM).

**Keywords:** lithium-ion battery capacitor;  $\text{LiNi}_x \text{Co}_y \text{Mn}_{1-x-y} \text{O}_2$ ; polarization phenomenon; pulsed performance; safety; electrode engineering

# 1. Introduction

With the growing problems of global warming and environmental pollution caused by carbon emissions, the development of renewable energy and clean energy has gradually become the focus of attention. As a link in the conversion, storage and use of energy, electrochemical energy storage devices have been widely applied in fields such as electric vehicles, electronic products, smart grids and large-scale energy storage [1,2]. At present, the most commonly used electrochemical energy storage device is the lithium-ion battery (LIB). An LIB stores/releases energy by a reversible lithium-ions (Li<sup>+</sup>) intercalation/deintercalation process on the cathode and anode through Faraday reaction, which has the advantage of high energy density. Intercalation/deintercalation is actually the process through which Li<sup>+</sup>/lithium compounds gain/lose electrons on the cathode or anode and are converted into lithium compound/Li<sup>+</sup>. In addition, the LIB is also flexible and lightweight, thus suitable for electric and hybrid vehicles [3].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The anode materials commonly used in LIBs include lithium titanate (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LTO) and carbon-based materials, such as graphite, hard carbon (HC), soft carbon (SC), etc., while the cathode materials are usually lithium cobalt oxide (LiCoO<sub>2</sub>, LCO), lithium iron phosphate (LiFePO<sub>4</sub>, LFP), lithium manganate (LiMn<sub>2</sub>O<sub>4</sub>, LMO), ternary materials (LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> and LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>1-x-y</sub>O<sub>2</sub>) and other lithium-containing compounds [4,5]. The first material used to prepare automotive batteries was layered transition metal oxide LCO, which has the characteristics of high tapped density and good cycle stability, but low specific capacity (about 140 mAh g<sup>-1</sup>) makes it fail to meet the mileage requirements of the growing development of electric vehicles [6]. Olivine-shaped LFP material has a high theoretical capacity (about 170 mAh g<sup>-1</sup>), high oxidation potential, high stability in a long-term cycle, good rate performance and high temperature resistance, but it has the disadvantages of poor conductivity, low tapped density and high cost [7]. Spinel LMO is characterized by low cost, good safety and low-temperature performance, but its cycle performance and high-temperature performance are poor [8].

Lithium nickel-cobalt manganate LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> (NCM), also known as ternary material, is an oxide material containing three transition metal elements (Ni, Co, Mn) [9]. The general crystal structure of NCM is shown in Figure 1 [10], similar to that of LCO, which is a layered structure of  $\alpha$ -NaFeO<sub>2</sub>. The space group of NCM is R-3m, and it belongs to the hexagonal crystal system. Transition metal ions occupy the 3b site, and lithium ions occupy the 3a site, while oxygen ions occupy the 6c sites in Wyckoff notation. Six oxygen ions surround one transition metal ion to form the octahedral structure of MO<sub>6</sub>, and Li and the transition metal layer are alternately arranged to form a Li<sup>+</sup> transport channel [11,12]. The different contents of Ni, Co and Mn make NCM exhibit different properties: (1) the introduction of excessive nickel ions can improve the specific capacity of the material, but it will aggravate  $Ni^{2+}/Li^+$  cation mixing and make the cycle stability worse [13]; (2) the introduction of excessive manganese ions can reduce the cost and improve the safety and stability of the material, but it will lead to the destruction of the layered structure of the material [14]; (3) the introduction of excessive cobalt ions can reduce the cation occupation, stabilize the layered structure, and improve the conductivity and power performance, but it will reduce the specific capacity of the material and increase the cost. The synergistic effect of Ni, Co and Mn makes NCM combine the advantages of high specific capacity of LiNiO<sub>2</sub>, high conductivity of LCO, low cost and good stability of LMO. Therefore, NCM has become the cathode material used in most commercial LIBs.



Figure 1. Schematic view of the layered NCM crystal structure [10].

 $\text{LiNi}_x \text{Co}_y \text{Al}_{1-x-y} \text{O}_2$  (NCA) has the advantages of high reversible specific capacity, low cost and structural stability due to the replacement of Mn with Al, which makes it successfully applied in Tesla Model 3 and other electric vehicles [15]. Despite the current problems of poor thermal stability and strict preparation conditions, NCA remains a promising alternative to the next generation LIB with high energy density.

However, due to the sluggish Faradaic reaction rate and the accompanying side reactions between the cathode and electrolyte, the LIB has the disadvantages of low power density, poor cycle stability, and safety issues that cannot be ignored [16]. In order to overcome these problems, a variety of methods have been proposed and adopted, including metal doping to improve electrochemical performance [17–19], surface coating to enhance interface stability [20–24], preparation of single crystal structure to enhance the mechanical strength of material [25–27], and design of electrode engineering to optimize device performance [28–31]. In addition, the electrochemical performance of LIBs can be improved by adding capacitor material to the cathode material, and the resulting hybrid device is also commonly referred to as an X-based lithium-ion battery capacitor (LIBC), in which X is the battery material in the composite cathode (X can be LCO, LMO, LFP or NCM). In this article, the research progress of LIBCs in recent years is reviewed, and the development trend of LIBCs is prospected. It is worth noting that the focus of this review is mainly on NCM-based LIBCs due to the advantages of the NCM material and the large amounts of recent research work on NCM-based LIBCs.

#### 2. Structure and Working Principle

LIBC is a new type of energy storage device composed of a bifunctional material cathode with the coexistence of battery material and capacitor material, and a battery material anode. The cathode is usually a combination of the LCO, LMO, LFP or NCM material with activated carbon (AC) [32–35]. The typical structure of the LIBC is shown in Figure 2a, in which the cathode material is composed of NCM and AC, and the anode material is soft carbon (SC). The composite cathode stores/releases energy through the adsorbing/desorption of anions by the electric double-layer formed on the AC surface and the reversible Li<sup>+</sup> intercalation/deintercalation process in the NCM material. Compared with LIB, the capacitor material added to the composite cathode of the LIBC can rapidly store/release energy through the physical adsorption/desorption process, which greatly improves the power performance and cycle stability of the energy storage device [36,37]. Although the energy density will be slightly reduced after adding capacitor material to the cathode, the power density of the energy storage device can be significantly improved by adjusting the relative content of the battery and capacitor material in the cathode and other methods [38].



**Figure 2.** (a) Schematic diagram of the structure and working principle of a typical LIBC; (b) Measurement configuration of segmented cathode structure for monitoring current contribution; (c) Voltage profile and current contribution upon galvanostatic charge and discharge processes [39].

Although the cathode of a LIBC contains two active materials, the reaction rate and the capacity contribution of battery material and capacitor material are different. In order to

study the specific working process and energy storage mechanism of LIBC, Guo et al. [39] prepared (33 wt.% LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM111) + 67 wt.% AC)//pre-lithiated SC LIBCs. Since the composite structure cannot be used to directly monitor the current contribution of two materials in the cathode of the LIBC upon galvanostatic charge and discharge processes, a special segmented cathode measurement configuration (Figure 2b) was designed, which shows the usefulness of the multi-electrode configuration in the experimental test, as demonstrated in ref. [40]. The specific test method is as follows: two current transmitters were used to connect to the AC electrode and the NCM electrode, respectively, and the signals of the two transmitters were collected through the Paperless Tester. It can be observed from the experimental results shown in Figure 2c that the current only flows into the AC electrode when the charge process begins, which indicates that the composite cathode of the LIBC transfers energy only through the physical process at this time. With the increase in voltage, the current flowing into the AC electrode decreases, while the current flowing into the NCM electrode gradually increases. As the current flowing into the NCM electrode increases to the maximum, it slowly decreases, but it is always greater than the current flowing into the AC electrode. The total current flowing into the two materials remains constant during the whole process. The variation trend of the current contribution upon the discharge process is opposite to that upon the charge process.

Combining the above results with Figure 2a, the specific working process of the LIBC can be obtained: when the charge process begins, electrons flow from AC in the cathode to the positive electrode of the power supply under the action of the external electric field. AC is positively charged due to the loss of electrons, so the anions in the electrolyte are electrostatically adsorbed to the AC surface, forming the electric double layer [37,41,42]. NCM starts to deintercalate Li<sup>+</sup> when the voltage increases to a certain value. Throughout the charge process, Li<sup>+</sup> in the electrolyte is continuously intercalated in the anode material, which comes partly from the Li<sup>+</sup> in the electrolyte that has not reached charge balance after  $PF_6^-$  adsorbed to AC and partly from the Li<sup>+</sup> that diffuses into the electrolyte after deintercalation from NCM. When the discharge process begins, electrons flow back to the cathode from the external circuit under the action of external electric field. In order to maintain the charge balance,  $PF_6^-$  on the AC surface starts to be desorbed, while Li<sup>+</sup> starts to be intercalated in NCM. Throughout the discharge process, Li<sup>+</sup> is continuously deintercalated from the anode material. On the one hand, the LIBC stores/releases energy quickly by physically adsorbing/desorbing anions through AC in the low-voltage range, which increases the power performance of the device. On the other hand, it can be seen from Figure 2c that most of the energy of the LIBC is transferred by Li<sup>+</sup> intercalation/deintercalation process in NCM, which greatly improves the energy density of the device. Therefore, the synergistic effect of battery material and capacitor material enables the LIBC to combine the advantages of both the LIB and electrochemical capacitor.

Moreover, in order to further understand the principle of the AC addition to improve the power density of LIBC, Han et al. [43] explored the mechanism of AC in the  $(LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 (NCM622) + AC)$  composite cathode in promoting charge transfer and accelerating the reaction kinetics by the time-of-flight secondary ion mass spectrometry, X-ray photoelectron spectroscopy and Comsol simulation analysis. It can be concluded from Figure 3a that the mechanism of AC can be divided into three stages. Stage I: Figure 3b shows the electrolyte uptake percentage versus time, which demonstrates that the addition of AC allows more electrolyte to be pre-absorbed into the electrode that reduces the ionic transport resistance. Stage II: The addition of AC increases the electronic conductivity of the composite electrode to about three times that of the original one (Figure 3c). Stage III: Comsol simulation results based on the porous electrode theory (Figure 3d) reveal that with the addition of AC, the concentration polarization is alleviated at high rates, resulting in a more uniform reaction distribution and faster reaction kinetics, which ultimately improves the utilization of active materials near the current collector. Dark colors in Stage III indicate the high degree of reaction and light colors represent the low degree of reaction or no reaction in the electrode.



**Figure 3.** (a) Mechanism of AC in promoting charge transfer and accelerating the reaction kinetics; (b) Electrolyte uptake percentage; (c) Electronic conductivity; (d) Simulation results of Comsol [43].

# 3. Advanced LIBCs

#### 3.1. Anode Material

3.1.1. Non-Lithiated Anode Material

Since Du et al. [44] actually prepared an LIBC with LCO and AC as the composite cathode and a nanostructured LTO as the anode, in 2004, its excellent electrochemical performance and broad application prospects have attracted more and more scholars into research on LIBCs, and the literature on LCO-based LIBCs, LFP-based LIBCs and LMO-based LIBCs has thus emerged. Until 2013, Sun and co-workers [35] used LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (NCM523), with the merits of high capacity, good rate performance and low cost, and AC as composite cathodes, and graphite, with the advantages of low redox potential and high theoretical capacity, as anodes to prepare electrochemical energy storage devices, and they proposed an NCM-based LIBC for the first time. The hybrid device can achieve a specific energy of 36.2 Wh kg<sup>-1</sup> at a specific power of 39.1 W kg<sup>-1</sup>, and even 8.9 Wh kg<sup>-1</sup> at 2.38 kW kg<sup>-1</sup> (all based on the mass of the cathode active material). The improvement of the electrochemical performance benefits from: (1) the formation of a better conductive network between AC and conductive agent to improve conductivity, (2) the porous structure of AC to absorb and hold electrolyte, shortening the ion transport pathway, and (3) the synergistic effect of AC and NCM. The excellent electrochemical performance of the hybrid device shows great potential.

In order to improve the power characteristics, graphite was substituted for the highpower battery material HC as the anode material of the LIBC in some studies. Xia et al. [45] prepared (NCM523 + AC)//HC LIBCs, and they investigated the effect of ethanol extraction method and the use of composite conductive agent on the electrochemical performance of the devices. The ethanol extraction method is used to eliminate the solvent to reduce the effect of N-methyl-2-pyrrolidone (NMP) on device performance. The purpose of designing carbon black (Super P, SP)/carbon nanotubes (CNT)/graphene (G) composite conductive agent is to: (1) add CNT to form conductive bridge between active particles to reduce internal resistance and (2) add graphene to form three-dimensional conductive network to improve electron transfer in all directions and thus improve the rate performance. In the voltage range of 2.5–4.2 V, the hybrid device with the weight ratio of AC: NCM = 1:3 in the cathode has the energy density of 66.6 Wh kg<sup>-1</sup> at 83.4 W kg<sup>-1</sup> and 21.5 Wh kg<sup>-1</sup> at 6.5 kW kg<sup>-1</sup>, while in the voltage range of 2.8–4.0 V, the device has the energy density of 50.0 Wh kg<sup>-1</sup> at 79.5 W kg<sup>-1</sup> and 13.2 Wh kg<sup>-1</sup> at 4.8 kW kg<sup>-1</sup>. Moreover, the hybrid device exhibits excellent cycle stability with energy retention rates of 99.06% and 96.45% after 1000 cycles at the rate of 14C and 50C in the voltage range of 2.8–4.0 V, respectively.

The electrochemical performance of an (NCM111 + AC)//AC LIBC by directly using AC as the anode material was investigated in detail by Lee et al., in 2018 [46]. It can be found from the scanning electron microscopy (SEM) image of the cathode shown in Figure 4a that the AC particles are uniformly distributed around the NCM particles. The good dispersion is beneficial to increase the electronic conducting pathways and improve conductivity of the cathode. Figure 4b displays cyclic voltammogram (CV) curve of the hybrid device at the scan rate of 10 mV s<sup>-1</sup>. The curve shows the capacitive characteristics of AC in the low-voltage range, and a pair of wide redox peaks in the high-voltage range, which corresponds to the Li<sup>+</sup> intercalation/deintercalation process in NCM. The energy storage mechanism of the composite cathode can be expressed by the following equation:





**Figure 4.** (NCM111 + AC)//AC LIBCs: (a) SEM image of the composite cathode; (b) CV curve; (c) Rate performance; (d) Cycle performance [46].

Finally, the hybrid device has a capacity retention of 91.6% at a high current density of  $5 \text{ A g}^{-1}$  (compared to the specific capacity at the current density of  $0.5 \text{ A g}^{-1}$ ) and a capacity retention of 98.9% after 9000 cycles at  $3 \text{ A g}^{-1}$  (Figure 4c,d). The improved rate performance and cycle performance benefit from the high conductivity and the semi-permanent lifetime of the AC material. The hybrid device can reach the energy density of 42 Wh kg<sup>-1</sup> and the power density of 7989 W kg<sup>-1</sup>. Moreover, mesocarbon microbeads (MCMB) were used as the anode to fabricate (LFP + AC)//MCMB LIBC, reported in ref. [47]. The hybrid device with 30 wt.% LFP in the composite cathode was found to have the best electrochemical performance, and its specific energy was maintained at 69.02 Wh kg<sup>-1</sup> at the rate of 4C after 100 cycles.

In addition to carbonaceous materials, spinel-like LTO, which does not generate strain during Li<sup>+</sup> intercalation/deintercalation and has a high Li<sup>+</sup> diffusion coefficient, is also commonly used as the anode material for LIBs [48,49]. The diffusion coefficient reflects the reaction rate of Li<sup>+</sup> intercalation/deintercalation in the electrode material,

and is the main parameter to characterize the kinetic of the electrode material. The higher the diffusion coefficient, the better performance of the material at high currents. Zhu and his colleagues [50] prepared LTO and NCM111 by solid-phase reaction and assembled (NCM111 + AC)//LTO LIBCs. It is found that the device with 10% NCM in the composite cathode within a voltage window of 1–2.5 V has a specific capacitance of 178.6 F  $g^{-1}$  at the current density of 80 mA  $g^{-1}$ , which is greater than other hybrid devices with different NCM content, and it still has the retention rate of 92.5% after 50 cycles (Figure 5). Improving the stability of NCM and LTO in the electrolyte is expected to further enhance the cycle performance of hybrid devices. Chen et al. [51] doped an appropriate amount of multi-walled carbon nanotubes (MWCNTs) in the LTO anode, and used the (NCM111 + AC) composite cathode to construct LIBC. The results show that the hybrid device has a maximum specific energy of 52.2 Wh kg $^{-1}$  and a maximum specific power of 993.2 W kg $^{-1}$  (based on the active mass of a single electrode) in the voltage range of 1.5–2.8 V. The capacity retention rate is 92.2% after 5000 cycles at the current density of  $0.4 \text{ Ag}^{-1}$ . The main reasons for the improvement of electrochemical performance are discussed. (1) The carbon nanotubes present a one-dimensional hollow tubular structure, which can provide more adsorption space and increase the rate of Li<sup>+</sup> intercalation; (2) One-dimensional carbon nanotubes are uniformly distributed in the middle of LTO, establishing a good conductive network structure; (3) In addition, MWCNTs will absorb some Li<sup>+</sup> during the reaction process to form the electric double layer to improve the rate performance of the device.



**Figure 5.** (NCM111 + AC)//LTO LIBCs: (**a**) Charge and discharge voltage profile; (**b**) Cycle performance [50].

Moreover, LTO is also widely used as the anode material of an LFP-based LIBC and LMO-based LIBC. Chen et al. [52] prepared LIBCs using LFP + AC as the composite cathodes and LTO as the anodes. In the voltage range of 1-2.6 V, a hybrid device with 30 wt.% LFP + 70 wt.% AC cathode can provide a specific capacity of 69.5 mAh  $g^{-1}$  at the current density of 0.5 A  $g^{-1}$ , 42% higher than that of the AC//LTO hybrid device, while its power density is the same to that of AC//LTO hybrid device. A novel LIBC composed of a segmented LFP + AC cathode and a segmented LTO + AC anode (Figure 6a) was developed by Lee et al. [53]. It is able to fully exploit the synergistic effect of both Faradaic and non-Faradaic reactions. The hybrid system can achieve an energy density of 48.5 Wh kg<sup>-1</sup> at a power density of 167.7 W kg<sup>-1</sup>, and an energy density of 4.9 Wh kg<sup>-1</sup> even at a high-power density of 5243.2 W kg<sup>-1</sup> (Figure 6b). Hu et al. [54] constructed an (LMO + AC)//LTO LIBC and further investigated its electrochemical performances. The CV profiles of the LIBC and LMO//LTO LIB used for comparison in the voltage range of 1.2–2.8 V are shown in Figure 6c, and the scan rate is  $0.2 \text{ mV s}^{-1}$ . It can be observed that the LIBC has a larger response current in the low-voltage range compared with LIB, which reflects the double-layer capacitive behavior. In addition, the LIBC shows two pairs of redox peaks in the high-voltage range, which corresponds to the Li<sup>+</sup> intercalation/deintercalation reaction of LMO. Therefore, the LIBC has both the high capacity from the LIB and the high rate capability of electrochemical capacitor. At the high rate of 4C, the LIBC with 30 wt.% LMO in the cathode can reach an energy density of 16.47 Wh  $kg^{-1}$ , and the capacity loss does not exceed 7.95% after 5000 cycles.



**Figure 6.** (LFP + AC)//(LTO + AC) LIBCs: (a) Schematic diagram of a hybrid device with segmented cathode and segmented anode; (b) Ragone plot. The red star represents the requirement of hybrid electric vehicles (HEVs) [53]. (c) CV profiles of the (LMO + AC)//LTO LIBC and the LMO//LTO LIB [54].

# 3.1.2. Pre-Lithiated Anode Material

The low initial coulomb efficiency of carbonaceous anode is due to the fact that most of the Li<sup>+</sup> deintercalated from the cathode during the initial charge and discharge process will be consumed when the solid electrolyte interphase (SEI) film is formed on the cathode surface. These Li<sup>+</sup> become irreversible losses and will not be intercalated or adsorbed back to the cathode. Therefore, it is necessary to pre-lithiate the carbonaceous anode to reduce the irreversible capacity loss.

Pre-lithiation for anode is a process to supplement Li<sup>+</sup> by providing lithium source to the anode material before the energy storage device works, usually achieved by electrochemical (EC), external short circuit (ESC), and internal short (IS) methods [55]. At present, the anodes of LIBCs are usually pre-lithiated through EC and IS methods. Sun et al. [56] used a three-electrode structure (Figure 7a) to pre-lithiate HC anode through the EC method. Figure 7c shows a schematic diagram of the EC method, where Li metal is used as counter electrode and HC is used as working electrode. An external power supply is then used for discharging so that Li<sup>+</sup> from Li metal passes through the separator and the perforated Cu foil to be finally intercalated in the anode. The voltage profile of pre-lithiation process for HC anode is revealed in Figure 7b, and it can be observed that pre-lithiation process can not only supplement Li<sup>+</sup>, but also reduce the anode potential range, thereby increasing the cathode potential range without changing the cell voltage range, ultimately significantly increasing the energy density of the hybrid device. Compared with the EC and ESC methods, the IS method, which brings the Li source and anode directly into contact, is considered to be a faster and more effective method [57], as shown in Figure 7f. Shellikeri et al. [58] pre-lithiated HC anodes of LIBCs with LFP + AC composite cathodes by pressing the Li metal strip directly on the surface of HC (Figure 7d), and the weight of the Li metal strip is about 7–8% of the HC electrode active material weight. The hybrid device shows excellent rate performance and cycle performance with the capacity retention of 94% after 1000 cycles at 1C, and 92% after 100,000 cycles at 60C (Figure 7e).



**Figure 7.** (NCM523 + AC)//pre-lithiated HC LIBCs: (**a**) Schematic structure of three-electrode LIBC; (**b**) Voltage profile of pre-lithiation process for HC anode [56]; (**c**) Schematic diagram of the EC method. (LFP + AC)//pre-lithiated HC LIBCs: (**d**) HC anode (A) loaded with Li metal strips; (**e**) Cycle performance [58]; (**f**) Schematic diagram of the IS method.

HC material was pre-lithiated and then used as anode material to prepare (NCM523 + AC)//pre-lithiated HC LIBCs in [56]. Hybrid devices with NCM accounting for 0, 25%, 50% and 75% of the cathode active material are denoted as LAC, LAN25, LAN50 and LAN75, respectively. The cell voltage and electrode potential profiles of LAN25 at a current density of 25 mA  $g^{-1}$  in the voltage range of 2.0–4.0 V are shown in Figure 8a. It can be found that both the cathode potential and voltage profiles have a plateau characteristic, which indicates that HC has been effectively pre-lithiated. The differential capacity versus potential (dQ/dV) profiles in Figure 8b show that an NCM-based LIBC has a pair of wide redox peak. In addition, the influence of the mass ratio of the cathode to the anode on device performance (Figure 8c,d) was also studied. The results show that the cathode and anode potentials do not change much with the mass ratio. The specific capacity based on the total mass of the cathode and anode active material and the mass of HC increases with the increase in the mass ratio, while the specific capacity based on the mass of (AC+NCM) decreases slightly with the increase in the mass ratio. In Figure 8e, the Ragone plot of LAN25 with an optimal mass ratio of 1.2 displays that the hybrid device has an energy density of 75.6 Wh kg<sup>-1</sup> at 41.7 W kg<sup>-1</sup> and 28.5 Wh kg<sup>-1</sup> even at 6.9 kW kg<sup>-1</sup> (both based on the total mass of the cathode and anode active material). LAN25 with the mass ratio of 0.75 exhibits excellent cycle performance with a capacity retention rate of over 98% and a coulombic efficiency of nearly 100% throughout the cycle after 20,000 cycles at the current density of 0.5 A  $g^{-1}$  in the voltage range of 2.5–3.9 V (Figure 8f). Moreover, Zheng et al. [59] assembled a hybrid device using pre-lithiated HC as the anode and LCO + AC as the cathode, which can achieve a synergistic balance between energy and power. At low C-rate (power density of 60 W  $kg^{-1}$ ), the hybrid device shows an energy density of about 150 Wh kg<sup>-1</sup>; when providing a low energy density (21 Wh kg<sup>-1</sup>), the hybrid device can reach a power density of  $1000 \text{ W kg}^{-1}$ .



**Figure 8.** (NCM523 + AC)//pre-lithiated HC LIBCs: (**a**) Cell voltage and electrode potential profiles; (**b**) differential capacity versus potential profiles; (**c**) potential versus mass ratio profiles: (A) the maximum and (B) the minimum potentials of cathode, and (C) the maximum and (D) the minimum potentials of anode; (**d**) specific capacity versus mass ratio profiles; (**e**) Ragone plot; (**f**) Cycle performance [56].

With the advantages of high specific capacity, excellent rate and cycle performance, and easy preparation, graphitizable SC is a common anode material for LIBs and LICs [60]. Du et al. [61] designed a special segmented anode structure (Figure 9a) and prepared (NCM111 + AC)//pre-lithiated SC LIBCs. Figure 9b shows the cell voltage and electrode potential profiles of an LIBC with 67% NCM in the cathode (LIBC67) at the rate of 0.2C, where the voltage window is 2.5–4.0 V. It can be observed that the voltage profile can be divided into two parts: in the low-voltage range with capacitive characteristics, the capacity is mainly provided by AC; in the high-voltage range of 3.01–4.13 V for the cathode and 0.13–0.51 V for anode ensures that the device operates without electrolyte decomposition at the cathode interface and Li plating on the anode surface, thanks to the effective pre-lithiation of the anode. According to Figure 9c,d, LIBC67 has a specific energy of 173.3 Wh kg<sup>-1</sup> at 26.91 W kg<sup>-1</sup> (based on the total mass of the cathode and anode active material), and after 10,000 cycles, at 10C, the capacity retention exceeds 80% and the coulombic efficiency is maintained at around 100%.



**Figure 9.** (NCM111 + AC)//pre-lithiated SC LIBCs: (**a**) Schematic diagram of a hybrid device with segmented cathode structure; (**b**) cell voltage and electrode potential profiles of LIBC67; (**c**) Ragone plot; (**d**) Cycle performance [61].

# 3.2. Capacitor Material in Cathode

As mentioned above, AC is the most widely used capacitor material in the composite cathode of LIBCs due to its porous structure, large specific surface area, and good electronic conductivity. However, compared with AC, Chen et al. [62] concluded that carbon aerogel (CA) with higher conductivity, more mesopores, and smaller particle size is more suitable for composite cathode of LIBC. They prepared (NCM622 + CA)//pre-lithiated HC LIBCs by mixing several types of CA materials with NCM622. The comparison of physical properties of CA (materials A, B and C) with different structures and control AC (material D) are shown in Figure 10a, where it can be obtained that material B has higher conductivity, smaller particle size distribution and a mesoporous structure supplemented by micropores. Figure 10b–d demonstrate the electrochemical performance of a hybrid device with material B as the capacitor material of the composite cathode. The capacity of this LIBC is 97.3 mAh  $g^{-1}$  at 10C, and the specific energy can reach 323.8 Wh  $kg^{-1}$  (based on the mass of the cathode). In addition, it also shows less polarization and excellent cycle performance. The specific surface area and pore structure are important factors for CA to improve the cycle stability and rate performance of the electrode while maintaining the high capacity of NCM: (1) Porous carbon can promote the uniform distribution of charge; (2) Large specific surface area is favorable for electrostatic adsorption; (3) Mesoporous structure is conducive to storing more electrolyte and accelerating ion transport.



**Figure 10.** (**a**) Physical properties of several porous carbon materials; (NCM622 + CA)//pre-lithiated HC LIBCs: (**b**) Rate performance; (**c**) Cyclic voltammetry curves; (**d**) Cycle performance [62].

Yan et al. [63] prepared the composite cathode of LFP and interconnected mesoporous carbon, and coupled it with the HC anode to construct LIBC. The hybrid device achieves an energy density of 131 Wh kg<sup>-1</sup> at the mass ratio of 2:1 for the cathode to anode, and 90 Wh kg<sup>-1</sup> at a power density of 25 kW kg<sup>-1</sup>. The excellent electrochemical performance is attributed to the effective amorphization of the LFP by the interconnected mesoporous carbon, which allows it to bypass the undesired severe phase transition process in the crystalline LFP to achieve an ultrafast ion intercalation mechanism.

The development of some novel materials makes them promising candidates to replace AC as the capacitor material for the composite cathode in an LIBC [64–66]. Graphene is a novel two-dimensional material with high specific surface area and electrical conductivity. The intrinsic capacitance of single-layer graphene can reach 550 F  $g^{-1}$ , which is the upper limit of electric double layer capacitance for all carbon-based materials [67]. Liu et al. [68] mixed 10% mesoporous graphene prepared by the self-propagating high-temperature method with 90% NCM to construct a composite cathode, which achieves a high discharge capacity of 76.7 mAh  $g^{-1}$  at the high rate of 5C. Mesoporous graphene acts as both an active material and a conductive additive, and its rich mesoporous structure, high electrical conductivity and Li<sup>+</sup> diffusion rate improve the rate performance of the electrode. NCM111 + graphene + CNT composite cathode was prepared through the wet chemical method by Li et al. [69]. Graphene and CNT construct a three-dimensional conducting network, which enhances the electron and ion transport rates and significantly improves the dynamic performance of the composite cathode. As a result, the composite cathode has a specific capacity of 134 mAh  $g^{-1}$  at the high rate of 3C, excellent cycle performance and small electrochemical polarization.

#### 3.3. Separator

As a component in the composition of the cell that separates the cathode and anode, provides porous pathways for ions to pass back and forth in the electrolyte, and can effectively control the diffusion of by-products, the choice of separator plays a crucial role in the electrochemical performance of the device [70–73]. Commonly used separators for LIBs include porous polymer membranes, nonwoven separators and composite separators [74]. Porous polymer membranes have good porosity as well as great mechanical strength and electrochemical stability, but are prone to shrinkage at higher temperatures leading to device short circuits. The combination of porous polymer membranes can produce multilayer separators, which have a high-temperature shut-off property and can be converted to nonporous membranes at high temperatures [75-77]. The advantages of nonwoven separators are low cost and thermal stability, but the pore size of nonwoven separators is large. In order to prevent the growth of lithium dendrites through the pores, the thickness of the separators must be increased [78]. Composite separators are prepared by incorporating inorganic additives into porous or nonwoven separators, which have excellent wettability, thermal stability and thermal conductivity. However, the tensile strength of composite separators is generally lower than that of ordinary polymer membranes [79–81]. In addition, cellulose has great potential to become a separator material due to its low price and environmentally friendly advantages, but its large pore size and poor mechanical strength still need to be improved [82,83].

In order to select the separator material suitable for LIBC, Sun et al. [84] prepared four (75 wt.% NCM523 + 25 wt.% AC)//graphite coin cells, in which the separators were nonwoven polypropylene (PP) mat, porous PP membrane,  $Al_2O_3$ -coated PP membrane and cellulose paper, respectively. The nonwoven and cellulose separator is composed of micro/submicron fibers with fiber diameters of about 2–6 µm and 0.1–1 µm, respectively. The nanofibers connect adjacent crystalline regions and form a three-dimensional network in the PP separator. The  $Al_2O_3$ -coated PP membrane is a composite separator, where micron-sized  $Al_2O_3$  particles are grown on the porous PP membrane, and the gap between adjacent  $Al_2O_3$  particles provide pathways for ion transport. Various electrochemical tests were performed on the four cells, and it was found that the device with the nonwoven PP mat had the highest specific capacity. Although the composite separator had improved thermal stability and wettability, its specific capacity and rate performance were reduced. The cellulose paper has a better affinity for the electrolyte, but the low specific capacity and high self-discharge rate limit its practical application.

#### 3.4. Polarization Phenomenon

Although LIBCs can improve the power performance of LIBs, mixing the battery material with the capacitor material at the same electrode level results in a significant polarization phenomenon in the hybrid device. It is noticed from Section 3.1 that the charge plateau voltage of LIBCs is significantly higher than the discharge plateau voltage upon the galvanostatic charge and discharge processes, which represents electrochemical polarization and energy loss [85–87].

Du et al. [61] attributed the polarization to the unfavorable interactions between capacitor material and battery material. In order to verify the conjecture, AC and NCM were arranged separately in the two segments of the anode, and LIBCs with segmented bi-material cathodes were prepared (Figure 9a). The galvanostatic charge/discharge profiles and differential capacity versus potential curves of the half-cells with different cathode structures at 0.2C in the voltage range of 2.5–4.2 V are depicted in Figure 11a,b, respectively. It can be seen that the voltage profile of the segmented cathode is obviously more symmetrical than that of the composite cathode, and the difference in plateau voltage between the charge and discharge processes of the segmented cathode is much smaller than that of the composite cathode, which is 40 mV for the former and 280 mV for the latter. In addition, the LIBC with the segmented cathode has a larger capacity and better rate performance, which benefits from the elimination of the unfavorable interactions between AC and NCM.



**Figure 11.** Polarization phenomenon of LIBCs: (**a**) Charge/discharge profiles, and (**b**) differential capacity versus potential curves of the half-cells with different cathode structures [61]; (**c**) CV curves [62]; (**d**) Charge/discharge profiles under different voltage range [88].

Chen et al. [62] found that the introduction of porous carbon with high conductivity, mesoporous structure, and small particle size (Figure 10a) can reduce the polarization of the composite cathode, as shown in Figure 11c. The differences between the redox peak potentials of five cathodes are 265 mV (NCM), 255 mV (A3), 230 mV (B3), 235 mV (C3), 265 mV (D3), respectively. The cathode prepared by mixing NCM with material B with a higher conductivity, more mesoporous structure and smaller particle size has the smallest redox peak potential difference.

Hagen and his colleagues [88] suggested that the surface area of AC is active in the high-voltage range and the reactions between AC and lithium salt-based organic electrolyte at a high voltage will lead to the increase in polarization. Figure 11d displays the charge/discharge profiles of LIBCs with 40 wt.% NCM523 + 60 wt.% AC as composite cathode and pre-lithiated HC as anode in the voltage range of 2.2–3.8 V and 2.2–4.2 V. With the increase in the upper voltage limit, the capacity of the hybrid device increases by 21.4%, but the coulombic efficiency decreases from 100% to 88.9%. Therefore, the selection of an appropriate operating voltage range plays a crucial role in reducing the polarization of an LIBC and extending the service life of the device. Finally, the polarization phenomenon of selected NCM-based LIBCs is revealed in Table 1.

### 3.5. Pulsed Performance

Due to the synergistic effect of the battery material and capacitor material in the composite cathode and the special recharging phenomenon [34], an LIBC is considered to be a promising energy storage device for pulsed applications. In order to study the recharging phenomenon of LIBC, Guo et al. [39] used a segmented cathode structure (Figure 2b) to test the current contribution of each material in the bifunctional material cathode in an LIBC during the rest period after the discharge process, and the experimental results are shown in Figure 12a. It can be observed that the current flows from the NCM electrode to the AC electrode at the end of the discharge process, which indicates that the NCM electrode recharges the AC electrode. The reason for this phenomenon is that due to the large polarization of the NCM electrode, the potential of the NCM electrode will recover

to a larger value at the end of the discharge process, which will result in a voltage difference between the NCM and AC electrode, as shown in the inset of Figure 12a. Furthermore, Figure 12b reveals the current contribution of the NCM and AC electrode of this LIBC for the pulsed discharge with an amplitude of 10C (the applied duty cycle is 10%). The NCM electrode provides a capacity about 1.663 mAh to the AC electrode during all rest periods at 10C pulsed discharge, which accounts for 35.9% of the total pulsed discharge capacity provided by the AC electrode (4.63 mAh), indicating that the recharging phenomenon has a significant role in improving the pulsed discharge performance of LIBC.

Cell	Voltage/V	Scan Rate or C-Rate	Voltage Plateau Difference/mV	Cyclability	Ref.
(75% NCM523 + 25% AC)//graphite	2.5-4.0	$0.5 {\rm ~mV~s^{-1}}$	300	/	[35]
(33% NCM111 + 67% AC)//Li	2.5-4.2	0.2C	280	/	[61]
Segmented (33% NCM111 + 67% AC)//Li	2.5-4.2	0.2C	40	/	[61]
Segmented (NCM111 + 67% AC)//pre-lithiated SC	2.5-4.0	/	/	More than 80% at 10C after 10,000 cycles	[61]
(96% NCM622 + 4% CA)//Li	2.5-4.2	$0.5 {\rm ~mV~s^{-1}}$	230	72.79% at 1C after 300 cycles	[62]
(96% NCM622 + 4% CA)//pre-lithiated HC	2.5-4.2	$0.5 \mathrm{~mV~s^{-1}}$	130	71.6% at 0.1C after 500 cycles	[62]
(90% NCM111 + 6.7% graphene + 3.3% CNT)//Li	2.5-4.6	$0.1~\mathrm{mV~s^{-1}}$	440	93.8% at 1C after 50 cycles	[69]

 Table 1. Polarization phenomenon of selected NCM-based LIBCs.



**Figure 12.** NCM-based LIBC: (**a**) Recharging phenomenon; (**b**) Current contribution of each branch for the pulsed discharge [39]. (**c**) Pulsed discharge voltage profile; (**d**) Voltage drop profile of a single pulse at SOC of 0%; (**e**) Specific energy for the increasing pulse amplitude [61].

Du et al. [61] analyzed the pulsed performance of an LIBC based on the prepared (NCM111 + AC)//pre-lithiated SC hybrid devices. The pulsed discharge voltage profile of LIBC, at the rate of 40C, is recorded in Figure 12c, and the voltage drop profile of a single pulse at the state of charge (SOC) of 0% is shown in Figure 12d. The LIBC shows a narrow voltage drop in the first and middle stages of the discharge process, indicating lower internal resistance and polarization. However, the voltage drop of the LIBC becomes larger at the SOC of 0%, but it is still lower than that of LIB. Figure 12e presents the specific energy

of different devices for the increasing pulse amplitude. It can be seen that the LIBC has a higher specific energy than the LIB at a higher pulse amplitude, and a much higher specific energy than LIC when the pulse amplitude is lower than 160C. The specific energy of the LIBC at a 100C-rate pulsed discharge condition is 74.0 Wh kg<sup>-1</sup>, higher than that provided at a galvanostatic discharge at 100C (64.67 Wh kg<sup>-1</sup>, Figure 9c), which is attributed to the synergistic effect between AC and NCM and the special recharging phenomenon in pulsed applications. In addition, Xia et al. [56] found that NCM-based LIBCs maintained a relatively stable state during the high-rate pulsed discharge cycle except for the activation process of the first dozens of cycles, showing excellent high-power pulsed performance.

Cericola and co-workers [36] comparatively studied the effects of duty cycle (DC) as well as pulse amplitude on LTO//LMO LIB, AC//AC double-layer capacitor, LTO//AC and AC//LMO electrochemical capacitors, (19% LTO + 81% AC)//(28% LMO + 72% AC) (LTO/LMOz24) and (50% LTO + 50% AC)//(50% LMO + 50% AC) (LTO//LMOz50) LIBCs. The profiles of pulsed specific current versus specific energy are shown in Figure 13, where the applied pulse amplitude is expressed as the specific current. It can be found that the energy densities of LIBCs are higher than that of the double-layer capacitor and electrochemical capacitors but lower than that of the LIB at low-pulsed specific current; however, LIBCs have the highest energy density at high-pulsed specific current and high duty cycle, which benefits from the recharging phenomenon. The increase in duty cycle does not significantly affect the performance of LIBCs and capacitors, but it degrades the performance of the LIB. An LIBC is the most suitable energy storage device for pulsed charge/discharge application scenarios in all the cases considered.



**Figure 13.** The profiles of pulsed specific current versus specific energy for the different systems. Pulsed charge: duty cycle (DC) of (**a**) 2%, (**b**) 10%, and (**c**) 50%; Pulsed discharge: DC of (**d**) 2%, (**e**) 10%, and (**f**) 50% [36].

## 3.6. Safety Issues

Battery material has brought some safety issues while increasing the capacity of the composite cathode of an LIBC, such as cation mixing [89], microcracks and structural

degradation [90], surface side reactions [91], and thermal runaway [92]. The capacity failure mechanism of an NCM-based LIBC during cycling was analyzed in detail by Zhao et al. [93], in 2020, as shown in Figure 14a. During cycling, the lithium residues on the NCM surface react with the solvent to form a complex gel, which forms an irregular electrode coating and poor adhesion to the current collector. Side reactions also occur when NCM is in contact with the electrolyte, forming polycarbonates, LiF,  $Li_x PF_y$  and  $Li_x PF_y O_z$  compounds on the surface. As the cycle number increases, a trace amount of water in the electrolyte reacts with  $LiPF_6$  to form HF, which will corrode metal ions in NCM. On the one hand, the dissolution of metal ions will lead to the structural degradation of NCM, resulting in a significant decrease in the energy density of the material. On the other hand, the dissolved metal ions will react with some components in the electrolyte and migrate, producing substances such as fluorides, oxides or metals that accumulate on the surface of NCM or adhere to AC. The increase in by-products and surface deposits seriously deteriorates the conductivity and electrochemical performance of the electrode. In addition, the experimental results show that some dissolved metal ions may migrate to the anode and deposit on the HC surface, leading to the destruction of the SEI film structure, which makes the electrochemical performance of the electrode further degraded. In order to solve the capacity failure problem, the atomic layer deposition method is proposed to coat  $Al_2O_3$ film on the surface of NCM. The  $Al_2O_3$  coating can not only inhibit the dissolution of metal ions, but also reduce the stress interaction caused by anisotropic volume changes in NCM during cycling. Figure 14b indicates that the LIBC assembled by the  $Al_2O_3$  coated NCM composite cathode showed excellent rate performance and cycling stability.



**Figure 14.** NCM-based LIBC: (**a**) Capacity failure mechanism; (**b**) Rate performance and cycle performance [93]. (**c**) Cycle performance; (**d**) Discharge profiles at different currents [94].

Similarly, Hagen et al. [94] prepared (25 wt.% NCM523 + 75 wt.% AC)//pre-lithiated HC pouch LIBCs and tested the stability of NCM during cycling at different currents (Figure 14c,d). It was found that at the current of 0.5 A (4.4C), which is a low rate, the contribution of NCM to the capacity of the LIBC gradually attenuates during cycling, that is, NCM degrades during cycling, which may be caused by cathode material disorder through lattice expansion and contraction during Li<sup>+</sup> intercalation and deintercalation processes. However, at high rates (above 18C), the LIBC still has good capacity retention even after more than 20,000 cycles. This may be due to the reduced production of oxygen vacancies within the material at high-rate cycling, which traditionally would cause compressive stress. This work shows that the LIBC can be used in some practical applications that can still provide sufficient energy at higher currents, filling the blank space between the LIB and LIC.

Since electrochemical energy storage devices do not always operate at relatively suitable temperature conditions, it is necessary to study the effect of temperature on their electrochemical performance [95]. Figure 15 displays the cell voltage and electrode potential profiles of LIBCs upon galvanostatic charge and discharge processes in the cell voltage range of 1.5–4.0 V at different temperatures. As the temperature decreases, the specific capacity decreases. In addition, the lower potential limit of anode decreases with the decrease in temperature. The lower potential limit of anode is obviously lower than 0 V at -40 °C, which increases the risk of Li dendrite formation and growth on the surface of the anode. The performance degradation at low temperatures can be attributed to the poor fluidity of electrolyte and the increase in the activation energy for Li<sup>+</sup> diffusion and intercalation in the anode. However, the operating temperature of the LIBC is not as high as possible, and high temperatures tend to lead to electrolyte decomposition. Therefore, the selection of a suitable operating temperature range is beneficial to ensure the stable performance of the LIBC.



Figure 15. Temperature performance of NCM-based LIBC [95].

Since the safety issues cannot be ignored, the thermal runaway behavior of LIBs has been extensively studied [96–98]. Due to the addition of battery material to the cathode, the LIBC is inevitably accompanied by increased safety concerns. In view of the safety issue, Wu and co-workers [99] investigated the over-heating-triggered thermal runaway characteristic of a large-format pouch cell LIBC based on the (NCM622 + AC)//HC system and plotted the schematic diagram of thermal runaway of the fully charged LIBC based on the experimental results (Figure 16). The schematic diagram of thermal runaway can be divided into five stages: (1) The temperature rise in the stage I is attributed to the external heating of the adiabatic rate calorimeter (ARC). (2) In the stage II, the LIBC starts to self-heat, and the ARC stops external heating. At this time, the anode generates the SEI film and produces a small amount of gas. When the temperature rises to 100  $^{\circ}$ C, the SEI film decomposes, and the electrolyte and the anode react. The vaporization of the low boiling solvent in the electrolyte leads to the reduction in capacitance as well as the expansion of the pouch cell. At about 130 °C, the aluminum plastic film breaks out. (3) The decrease in the temperature rising rate in the stage III is attributed to the release of gas caused by the rupture of the aluminum plastic film. In addition, the decomposition of separator and electrolyte, the reaction between the electrolyte and the anode, and the decomposition of NCM occur in the cell. The decomposition of NCM releases oxygen and generates a large amount of heat, resulting in a rapid increase in the temperature rising rate. At 249 °C, the thermal runaway occurs. (4) In the stage IV, the temperature rises sharply to 490.9 °C. This stage is regarded as the thermal runaway stage. At this time, the cell produces a large amount of gas and ejects out smoke, but no fire or explosion occurs. (5) The stage V is the cooling stage. At the end of cooling, the cell is severely damaged. This study shows that battery material in cathode is the root cause of the thermal runaway of LIBC, which provides meaningful information for understanding the thermal runaway mechanism of LIBC.



Figure 16. Schematic diagram of thermal runaway of NCM-based LIBC [99].

The above results indicate that studies on the safety of LIBs are expected to play a certain reference role and inspire the related research on LIBCs. For example, Qi et al. [100] probed heat generation and release issues of an LIB with nickel-rich NCM cathode and found that the contribution from the ohmic effect and surface impedance increases with the increase in discharge rate when mass transport and charge transfer have a dominant effect on the total polarization heat. Additionally, the polarization heat also continues to increase as SOC decreases, due to the increase in mass transfer overpotential. In addition, heat accumulation and delayed heat release effects of LIBs have also been revealed, which may lead to an undetectable but dangerous internal temperature increase at high discharge rates. The findings of this study provide some insight into the safe and rational design of LIBs and even LIBCs.

# 3.7. Electrode Engineering

Since the cathode contains two active materials, the design of electrode engineering plays a critical role in the electrochemical performance of LIBC. Increasing the proportion of battery material in the composite cathode usually increases the energy density of LIBC,

while increasing the proportion of capacitor material usually increases the power density. By adjusting the relative content of battery material and capacitor material in the cathode, hybrid devices with different properties can be prepared to meet different practical needs. The increase in AC content will reduce the cell capacity but improve the rate performance and cycle performance. However, when the AC content is too high, in order to achieve an ideal capacity ratio of cathode to anode, the thickness of the cathode will increase due to the low theoretical capacity and tap density of AC. This will increase the internal resistance and electrochemical polarization, and it will deteriorate the overall performance of the device [56]. Yan et al. [101] compared the electrochemical performance of (LFP + AC)//pre-lithiatedHC LIBCs with different LFP contents, and found that with the increase in battery material contents in the cathode, the energy density of the device increased, but the power density as well as cycle performance deteriorated (Figure 17). When the LFP contents are 60% and 80%, the energy density of hybrid devices is almost close to the use specification (red line in Figure 17b) after only 10,000 cycles at high-rate. This is due to the fact that when the battery material content occupies the major part of the composite cathode, most of the current load and strain are concentrated in the battery material. Unlike the capacitor material, the battery material is not able to withstand a high rate and long-term current impact, which ultimately affects the power performance and cycle performance of the device.



**Figure 17.** LIBCs with different battery material contents in the cathode: (**a**) Ragone plot; (**b**) Cycle performance [101].

Compared to the strategy of excessive anode capacity, the design of appropriate capacity ratio of cathode to anode is more likely to enable the hybrid device to display the optimal electrochemical performance. Hagen et al. [88] calculated the capacity ratio of cathode to anode based on the reversible Li<sup>+</sup> intercalation and deintercalation specific capacity of the anode active material, as shown in Equation (2):

$$C_{\rm C}/C_{\rm A} = \frac{m_{\rm NCM}c_{\rm NCM} + \frac{m_{\rm AC}c_{\rm AC}(v_{\rm max} - v_{\rm OCV})}{(3.6s \cdot A)}}{m_{\rm HC}c_{\rm HC_{\rm T}}}$$
(2)

where  $m_{\rm NCM}$ ,  $m_{\rm AC}$  and  $m_{\rm HC}$  represent the active mass of NCM, AC and HC, respectively.  $c_{\rm NCM}$  is the specific capacity of NCM, and  $c_{\rm AC}$  is the specific capacitance (F g<sup>-1</sup>) of AC.  $c_{\rm HC_r}$  is the reversible Li<sup>+</sup> deintercalation specific capacity of HC.  $V_{\rm max}$  is the maximum cell operating voltage, and  $V_{\rm ocv}$  is the open circuit voltage of the cell. Their previous work [101] showed that the capacity ratio of cathode to anode of AC//HC LIC with the best electrochemical performance was 0.14. Therefore, the optimal capacity ratio is 0.14 when the NCM content is 0. Based on this, the optimal capacity ratio for different NCM contents can be calculated. As the NCM content increases from 0 to 60%, the capacity ratio increases from 0.14 to 0.71.

Optimizing the content or composition of inactive components is also a method to improve the electrochemical performance of hybrid devices. For instance, the use of carbon black (SP)/carbon nanotube (CNT)/graphene (G) composite conductive agent can enhance the electrochemical performance by forming a better three-dimensional conductive network [45]. It is not unique, as Guan et al. [102] also found that the addition of graphene to the composite cathode of (LFP + AC) allowed the cathode to exhibit an excellent high-rate performance and highly efficiency capacitive-battery characteristics. This is attributed to the hierarchical porous architecture of AC and the three-dimensional conductive network constructed by the graphene, which provides abundant pathways for Li<sup>+</sup> diffusion and fast electron transfer. As a result, the composite cathode exhibits a high specific capacity of 66 mAh g<sup>-1</sup> at the high rate of 100C and a high capacity retention of 82% after 3000 cycles. Furthermore, the selection of suitable thickness and areal density of the electrode and electrode preparation methods, etc., also belong to the scope of electrode engineering [56,103,104].

#### 4. Summary and Perspectives

Lithium-ion battery capacitors have been widely studied because of the advantages of both lithium-ion batteries and electrochemical capacitors. An LIBC stores/releases energy through the adsorption/desorption process of capacitor material and the Li<sup>+</sup> intercalation/deintercalation process of battery materials, which is a promising energy storage device. This review briefly introduces the structure and working principle of the typical LIBC, and summarizes the research progress in recent years of material system, separator, polarization phenomenon, pulsed performance, safety issues and electrode engineering. Despite great advances in LIBCs, much attention should be still paid to the existing shortcomings and problems. The NCM material is considered to be one of the most promising battery materials due to its high specific capacity, low cost and high conductivity, and the proliferation of studies on an NCM-based LIBC in recent years also signifies its great advantages. Based on this, the research and development direction of NCM-based LIBCs (Figure 18) is prospected to explore and discuss the solutions to the existing shortcomings and problems of advanced LIBC:



Figure 18. Schematic illustration of the research and development direction of NCM-based LIBC.

The proposed NCM-based LIBCs have shown great potential in terms of energy density, rate performance and cycle performance (Table 2), but still need to be further improved. In fact, the energy density and power density (both based on the total mass of the cathode and anode material) of LIBCs still do not exceed 300 Wh kg<sup>-1</sup> and 10 kW kg<sup>-1</sup>. The use of new capacitor cathode materials (such as graphene, carbon nanotubes, carbon aerogel, etc.) and anode materials (such as silicon-based materials, mesocarbon microbeads, etc.) is expected to expand the material system of LIBCs and take the electrochemical performance to a higher level. Nickel-rich (Ni  $\geq$  80%) NCM material has a high theoretical capacity, but as far as we know, there is currently no LIBC that uses nickel-rich NCM as the battery material of the composite cathode. In addition, it is unreasonable to compare the performance of high-Ni NCM-based LIBCs and low-Ni NCM-based LIBCs from different

studies, because their preparation methods and calculation basis are not exactly the same. Therefore, the comparison of the electrochemical performance of different LIBC systems also needs further investigation.

Cathode	Anode	Voltage/V	Power Density/ (kW kg <sup>-1</sup> )	Energy Density/(Wh kg <sup>-1</sup> )	Ref.
75% NCM523 + 25% AC	graphite	2.5-4.0	2.38	36.2	[35]
75% NCM523 + 25% AC	HC	2.5-4.2	6.5	66.6	[45]
25% NCM523 + 75% AC	pre-lithiated HC	2.0-4.0	6.9	75.6	[56]
75% NCM523 + 25% AC	pre-lithiated HC	2.2-3.8	4.2	20	[94]
60% NCM523 + 40% AC	pre-lithiated HC	2.2-3.8	5	42	[88]
67% NCM111 + 33% AC	pre-lithiated SC	2.5-4.0	/	173.3	[61]
90% NCM111 + 10% AC	AC	0-2.8	7.989	42	[46]
12.5% NCM111 + 87.5% AC	LTO/MWCNTs	1.5-2.8	0.993	52.2	[51]
96.25% NCM622 + 3.75% CA	pre-lithiated HC	2.5-4.2	/	323.8	[62]

Table 2. Structure and performance of selected NCM-based LIBCs.

Although most of the separators for LIBCs are polypropylene separators at this stage, the development of other modified separators and composite separators is expected to provide a new application direction. Electrochemical polarization is an important reason hindering the commercialization and industrialization of LIBC. By taking the approaches of special cathode structures, porous carbon with better physical properties and reduced voltage ranges, electrochemical polarization has been reduced. However, there are still problems such as complicate cell structure, high cost and significant sacrificed energy density. Therefore, the mechanism and the resolution of polarization phenomenon of LIBCs need to be further investigated. Pulsed behaviors of LIBCs have been studied, including recharging phenomenon and voltage drop of a single pulse and so on, which explains the reason why LIBCs have an excellent pulsed performance. Before an LIBC can be put into practical research in pulsed applications, the simulation analysis of the pulsed behaviors of the LIBC is also an interesting research direction. Battery material is considered to be the main cause of capacity degradation and thermal runaway of LIBC, and its performance can be improved by some methods such as surface coating and element doping. The studies on LIBs are expected to play a certain reference role and inspire the related research on LIBCs.

The electrochemical performances of hybrid devices can be greatly improved by electrode engineering, such as selecting the appropriate ratio of battery material to capacitor material, the appropriate capacity ratio of cathode to anode, and the contents of conductive agents and binders, etc. Although there is still a lot of room for progress in the research on LIBCs at this stage, there is no doubt that their great application prospects determine that they will be one of the important development directions for new energy storage devices.

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