From Li-Ion Batteries toward Na-Ion Chemistries: Challenges and Opportunities

Kudakwashe Chayambuka, Grietus Mulder, Dmitri L. Danilov, and Peter H. L. Notten*

Among the existing energy storage technologies, lithium-ion batteries (LIBs) have unmatched energy density and versatility. From the time of their first commercialization in 1991, the growth in LIBs has been driven by portable devices. In recent years, however, large-scale electric vehicle and stationary applications have emerged. Because LIB raw material deposits are unevenly distributed and prone to price fluctuations, these large-scale applications have put unprecedented pressure on the LIB value chain, resulting in the need for alternative energy storage chemistries. The sodium-ion battery (SIB) chemistry is one of the most promising “beyond-lithium” energy storage technologies. Herein, the prospects and key challenges for the commercialization of SIBs are discussed. By comparing the technological evolutions of both LIBs and SIBs, key differences between the two battery chemistries are unraveled. Based on outstanding results in power, cyclability, and safety, the path toward SIB commercialization is seen imminent.

1. Introduction

2019 was a year of the crowning achievement for lithium-ion batteries (LIBs) because of the Nobel Prize in chemistry award to John Goodenough, M. Stanley Whittingham, and Akira Yoshino,[1] a long-awaited, meritorious recognition to the inventors of the versatile energy storage device, which, nowadays, powers anything from microsensors to electric vehicles. Granted, the limitation to only three recipients is a restriction of the Nobel committee; we must equally acknowledge other scientists, some of whom will be mentioned in this essay, whose key contributions led to the development of one of humanity’s greatest achievements of the last century.

Based on the discoveries of the aforementioned Nobel laureates, LIBs were commercialized in 1991 by SONY and immediately experienced a double-digit growth in sales.[2] It took only 6 years for the LIB market share to surpass that of incumbent battery technologies, the likes of nickel–cadmium (NiCd) and nickel–metal hydride (NiMH) batteries.[3] This phenomenal growth was made possible by the rise in portable consumer electronic devices (e.g., cassette recorders, discmans, personal care appliances, and mobile phones). The problem was powering these devices off-grid for long periods of time.[4] The lightweight and high energy density characteristics of LIBs made them ideal for these applications. This also meant that there was no direct competition between LIBs and existing battery technologies; for example, the sales in NiCd and NiMH in Japan did not decline as a result of the exponential growth in LIB sales.[1] Evidently, a new market segment had emerged and the LIB was an idea whose time had come.

Since the first commercial LIB, portable consumer electronics have drastically evolved, in form and function. Often, we cite Moore’s law, an observation that the number of transistors on an integrated circuit doubles, about every 2 years.[5,6] This means, computing speed has roughly doubled biennially, giving rise to “smart” devices. The battery energy density needed to run these complex devices has also increased, albeit at a slower rate. This is because of fundamental chemical limitations, and increasing the useful energy density of batteries has proved to be an enormous challenge.[7] Nevertheless, there remains room to improve other battery properties such as cost, cycling stability, safety, environmental toxicity, and cell design.[8–11]

An outstanding feature of LIBs is their ability to continually find new applications. Of late, battery electric vehicles (BEVs) pioneered by Tesla Inc., BYD, and Nissan have been successfully commercialized, powered by LIBs.[12] A Tesla model S with an on-board battery pack of 100 kWh has a driving range of 600 km, certified by the U.S. Environmental Protection Agency.[13] The global fleet of electric cars and busses currently stands at 4 million, a number that is expected to reach...
50–200 million by 2028.\cite{14} This transition toward electric mobility (e-mobility) is driven by clean energy policies, with the aim to become climate neutral.\cite{15} Bigger LIB installations of the megawatt-hour scale are anticipated in the stationary storage sector.\cite{16} While in these applications, the battery weight and footprint are not primary considerations, LIBs are nevertheless expected to play a leading role. This is because other LIB performance metrics, such as cycling efficiency, high power, and deep discharge capability, are important requirements for profitable grid ancillary services.\cite{17}

Although no apparent performance limit has been identified for the LIB technology, it has however become difficult to source raw materials such as lithium carbonate and cobalt.\cite{18-21} As the size of battery packs and number of installations increase, mining companies find it increasingly difficult to match the demand. As a case in point, in 2015, the price of lithium carbonate nearly tripled within a period of 10 months, due to demand from the e-mobility sector.\cite{22} The problem is that lithium carbonate is scarce and unevenly distributed;\cite{23} nearly half of the 2015 global production came from South America. For a compound whose economic stake is rapidly increasing, this is problematic because of global supply risk shortage and overexploitation at the source. Moreover, cobalt and graphite, the other vital constituents of LIBs, are classified as critical raw materials by the European Union (EU).\cite{24} The recent large-scale deployments of LIBs have therefore put greater pressure on an already congested value chain, resulting in price fluctuations. It is therefore necessary and urgent to invest in research efforts on alternative, beyond lithium technologies, to overcome the overreliance on scarce resources.

Fortunately, over the last decade, research interest in sodium-ion batteries (SIBs) has gained momentum.\cite{25} This is primarily because SIBs fundamentally hold the greatest potential to match the performance of LIBs.\cite{26} Sodium and lithium are two neighboring members of the group 1 elements, also known as alkali metals. They both have one loosely held electron in the valence shell and thus readily form first oxidation states Li$^+$ and Na$^+$.\cite{27} As electrochemical carriers, there is not much of a difference between Li$^+$ and Na$^+$, in terms of the standard electrode potential; Na ($\approx\,$2.71 V vs the standard hydrogen electrode (SHE)) is only 300 mV higher than Li ($\approx$3.04 V vs SHE). At the time of discovery and development of lithium intercalation compounds, the structural and electrochemical properties of sodium compounds were equally explored.\cite{28} Although lithium compounds showed superior electrochemical properties, the availability and cost of sodium compared to lithium were expected to shift fortunes in favor of sodium.\cite{29} However, due to the relatively small production volumes of early LIB cells, lithium production limits were never tested. In addition, battery energy density is of primary importance in portable electronic device applications.\cite{30} As a result, the research and commercialization of LIBs grew exponentially, somewhat at the expense of SIBs. In the past decade, however, due to concerns of lithium supply shortage and the needs for alternative, sustainable battery technologies, research in SIBs is well and truly revived.

While the recent SIB revival efforts have led to remarkable discoveries in sodium insertion compounds, it is equally imperative for SIBs to evolve into an economic success and thus significantly contribute to the clean energy transition. In this essay, we analyze the driving forces which have propelled different development paths of room-temperature rechargeable batteries based on lithium and sodium. Particular attention is
on the properties of candidate room-temperature, organic-electrolyte-based SIBs, in order to answer the question: can SIBs replace LIBs? For the interested reader, several in-depth reviews have recently emerged on both SIBs\(^{30-33}\) and LIBs.\(^{34-37}\) The remarkable progress in SIBs is attributed to the scientific knowledge in solid-state materials, gained in developing LIBs (which has also been useful in developing SIBs). In addition, similarities in electrode architecture have allowed the same industrial processing techniques for both SIBs and LIBs.\(^{38,39}\) This combination of positive factors has put wind in the sails of the SIB technology, wind that is expected to carry SIBs to commercial success.

### 2. Shared History of SIB and LIB

The reversible electrochemical intercalation reaction of layered TiS\(_2\) with lithium in a Li//TiS\(_2\) cell was first reported by Whittingham in 1976.\(^{40}\) Sodium and lithium were found to be equally capable of intercalating in TiS\(_2\), as well as in other transition-metal dichalcogenides.\(^{41}\) Due to the low open-circuit voltage of TiS\(_2\) cathode, \(\approx 2.2\) V versus Li\(^+/\)Li, and the instability of metallic lithium anode, the Li//TiS\(_2\) cell could not be developed into a functional device.

To address shortcomings at the cathode side, Goodenough and co-workers\(^{42-45}\) proposed the layered metal-oxide family of compounds in the 1980s. The chemical composition is LiMeO\(_2\), in the case of lithium and NaMeO\(_2\), in the case of sodium (Me = Co, Ni, Cr, Mn, or Fe). Pioneering works by Delmas and co-workers in the early 1980s led to discoveries of NaMeO\(_2\) compounds.\(^{28,44,45}\) In terms of cell voltage, Goodenough co-workers’ discoveries were groundbreaking. For example, LiCoO\(_2\) (LCO) has an open-circuit voltage of 4.0 V, nearly double that of TiS\(_2\). In general, the electrochemical properties of lithium-based compounds were superior to those of the sodium-based compounds.

The anode of choice however, remained either metallic lithium or sodium.\(^{31}\) Because these highly electropositive metal anodes react with the electrolyte, these cells were unstable. Furthermore, during plating and stripping cycles, dendrites grow uncontrollably. Dendrite growth is the main cause of internal short-circuits and battery-related fires. For safety reasons, the use of metal anodes is not recommended. As an alternative, Scrosati proposed a low-voltage intercalation anode to replace the metal anodes.\(^{46,47}\) This marked the birth of the “rocking-chair” battery, in reference to the shuttling of ions between two interaction electrodes. In the case of lithium, Yazami and Touzain discovered that carbonaceous materials had the ability to intercalate lithium at a desirably low voltage and high gravimetric capacity.\(^{48}\) This allowed Yoshino to make the first LIB using a soft carbon anode and LiCoO\(_2\) cathode;\(^{49}\) a device which was commercialized by SONY in 1991.\(^{51}\) Unfortunately in the case of sodium, intercalation in soft carbons and graphite resulted in approximately ten times less capacity.\(^{50}\) This became a bottleneck and a second major setback for the commercial prospects of SIBs.

Following the decision by SONY, the period between the years 1990 and 2000 witnessed a sharp decline in SIB research.\(^{51}\) During the same period, the market share and value of LIBs skyrocketed. Cobalt prices rose sharply and were moderated by sales of U.S. Government stockpiles.\(^{52}\) Scarcity and ethical concerns around cobalt extraction motivated the search for cheaper alternatives.\(^{47}\) This resulted in the synthesis of new types of metal-oxide structures such as the spinel LiMn\(_2\)O\(_4\) (LMO),\(^{53}\) and the olivine LiFePO\(_4\) (LFP).\(^{54}\) Co substitution in nickel oxides was also found to increase structural stability and this resulted in mixed metal-oxides, such as LiNi\(_{1-x}\)Co\(_x\)Mn\(_2\)O\(_4\) (NCA) and LiNi\(_{1-x}\)Mn\(_x\)Co\(_2\)O\(_4\) (NMC), toward the end of 2000.\(^{55-57}\)

In spite of the decline in SIB research, there were intensive developments in high-temperature sodium batteries.\(^{58}\) The sodium–sulfur (NaS) systems operating between 300 and 350 °C were developed by the Ford Motor Company and then through a joint Japanese consortium of TEPCO and NGK.\(^{59}\) A slightly lower temperature variant of NaS, the sodium–nickel chloride battery, commonly known as ZEBRA cells, first appeared.\(^{60,61}\) The ZEBRA cells operate between 250 and 300 °C and were first developed by Zeolite Battery Research Africa, from where the name ZEBRA is derived. A common feature of these battery systems is the molten sodium anode and ceramic separators. Application areas include stationary grid energy storage,\(^{62}\) e-mobility,\(^{63}\) and space missions.\(^{64}\) They serve as proof of the feasibility of large-scale, sodium-based energy storage. Nevertheless, the high operating temperature brings other problems, such as corrosion issues and low energy efficiency.

The rejuvenated interest in room-temperature SIBs began with the discovery of Na intercalation in hard carbon (HC) by Stevens and Dahn, in the year 2000.\(^{65,66}\) HC anode in SIB has a low voltage and high gravimetric capacity of 300 mAh g\(^{-1}\), close to that of graphite in LIBs (372 mAh g\(^{-1}\)). Although this discovery proved to be a turning point in revived research interest in SIBs, it did not spark an immediate rush toward commercialization, because of an apparent lack of incentives to replace lithium at the time. A patent-based analysis reveals that the rise in SIB patent filings only began 12 years later, in 2012.\(^{30}\) It can therefore be concluded that the driving force to replace LIBs with SIBs is the supply risk shortage, as a result of large-scale applications of LIBs.

Since 2010, there has been an unprecedented progress in SIB cathode materials. The total number of cathode materials reported in the 3 years between 2010 and 2013 nearly equals the total number that existed before.\(^{25}\) The three main families of SIB cathode materials are the layered metal-oxides, polyanion compounds, and Prussian blue analogs (PBA).\(^{30}\) The goal is to make cheap SIBs (with similar performance characteristics as LIBs), which explains the choice of earth-abundant elements such as, iron, manganese, and magnesium in the composition of the cathode materials. As for the anode, HC remains the prominent choice because of cheap and abundant precursors.

In 2015, the first “18650” (18 mm diameter, 65 mm height) cylindrical SIB cells were developed through the French network for electrochemical energy storage (RSEF),\(^{67}\) a collaboration of the French National Center for Scientific Research (CNRS), the French Alternative Energies and Atomic Energy Commission (CEA), and the Collège de France.\(^{58}\) Giant leaps toward SIB commercialization have been undertaken mostly by startup companies and over ten such companies have since emerged.\(^{68}\)
Spearheading these efforts is Faradion Limited, Tiamat, and HiNa. UK-based Faradion was founded in 2011 and is among the first to commercialize SIBs. Currently, Faradion is developing and commercializing 1–5 Ah SIB pouch cells based on proprietary layered metal-oxide cathode, Na1.1Ni0.3Mn0.5Mg0.05Ti0.05O2 (NMMT) and commercial HC anode. French-based Tiamat is a spinoff company from RS2E, founded in 2017. The company has continued the path of cylindrical SIB cells based on the polyanionic compound cathode, Na3V2(PO4)2F3 (NVPF) and HC anode. According to their website, Tiamat has produced over 10 000 SIB cells. Finally, Chinese-based HiNa was founded in 2017 as a spinoff from the Institute of Physics Chinese Academy of Sciences (IoP-CAS). They currently produce SIB pouch cells based on proprietary Na0.9[Cu0.22Fe0.30Mn0.48]O2 cathode and anthracite-based HC anode. In April 2019, HiNa announced the largest SIB module to date, a 100 kWh (30 kW power) battery installation in the Liyang city in China, for energy arbitrage by load shifting.

### 3. Comparison of SIB and LIB Cells

As outlined above, the electrochemical properties of LIBs and SIBs are similar. As a result, the same manufacturing processes and protocols can be used in the production of both battery types. However, there are some differences in the materials used and the operational characteristics.

---

**Figure 1.** Shared history of LIB and SIB illustrating the technological evolutions and drivers in different decades. a) Illustration of a Li//LiCoO2 cell. b) Illustration of a Na//NaCoO2 cell. c) Illustration of a graphite//LiCoO2 battery. d) Illustration of the Ford Ecostar, which was designed to use NaS batteries. e) A Nokia 3310 portable device, powered by LIB. f) Commercial ZEBRA battery for grid energy storage applications. g) 2010 Nissan Leaf model powered by LIB. h) Illustration of a HC//Na3V2(PO4)2F3 cell. i) Illustration of a grid-scale LIB installation. j) HiNa SIB installation in Liyang city in China. (d) Reproduced with permission. Copyright 2020, Ford Motor Company. (f) Reproduced with permission. Copyright 2003, Elsevier B.V. (g) Reproduced with permission. Copyright 2020, Nissan Motor Corporation. (j) Reproduced with permission. Copyright 2019, Wiley-VCH.
systems. This means, no additional capital expenses would be incurred by LIB manufacturers, should they decide to produce SIBs. As such, SIB manufacturing has been described as “drop-in” replacement, which partly explains the remarkable rate at which the technology has evolved. The next frontier for SIBs is to “drop-in replace” LIBs in large-scale and emerging applications. For this, they need to either match or exceed the performance metrics of LIBs, which include power, energy density (volumetric and gravimetric), cyclability, safety, and cost.

3.1. Physical Features

Judging by physical appearance, there is not much of a difference between a SIB and LIB. Cylindrical LIBs are commonly of the 18650 format and similar SIB cells are currently produced by Tiamat. To the best of our knowledge, they remain the only manufacturer of cylindrical SIBs to date. Other manufactures have opted for pouch cells, which have a variable footprint. Inside the cells and apart from chemical compositions, the composite electrode coatings also look similar. This is because the same conductive carbon filler and binder materials are used in both cell chemistries. The only physical difference is the type of current collectors. In LIBs, copper and aluminum foils are used as anode and cathode current collectors, respectively, while in SIBs, aluminum foils are used as current collectors for both electrodes. This is because sodium does not alloy with aluminum current collectors at the anode. This reduces the material costs and weight of SIBs, because aluminum is cheaper and less dense than copper. Figure 2a,b shows a schematic representation of the main components of LIBs and SIBs, respectively.

Using the same current collector has other advantages. Chief among them is the ability to discharge and store a SIB at 0 V, without degradation. This highly safe characteristic has been demonstrated by Faradion, through their patent on the safe storage and/or transportation of sodium-ion cells at 0 V Another advantage is the ease to recycle SIBs wherein, current collectors, tabs and casings are entirely composed of aluminum. The foil separation step is therefore easier; and the ability to safely discharge the battery pack to 0 V reduces electrical and chemical hazards. Finally, making SIB bipolar electrodes becomes inherently facile and opens up the possibility of high-voltage SIB cells.

3.2. Electrolytes

The aprotic electrolyte solvents used in LIBs and SIBs are the same. This is an advantage for both technologies from a cost perspective; SIBs can ride on the economies of scale of aprotic electrolytes and make them cheaper. Solvents that are common to both LIBs and SIBs include ethylene carbonate (EC), propylene carbonate (PC), dimethoxyethane (DME), and dimethyl carbonate (DMC). A mix of two or three solvents is needed to obtain optimal electrolyte properties such as viscosity, conductivity, and electrochemical stability window.
systematic studies on the optimization of electrolytes for SIBs and LIBs have been carried out. Differences with LIB electrolytes arise in the salt. Whereas LiPF$_6$ is the most frequently used salt in LIBs, NaPF$_6$ is frequently used in SIBs. The typical salt concentration is 1 M (i.e., 1 mol dm$^{-3}$), due to optimal conductivity and viscosity at this concentration. There were some unsuccessful attempts to use NaClO$_4$ salts which were abandoned due to explosion hazards. Early NaPF$_6$ salts had purity issues and resulted in turbid electrolytes. This impacted negatively the performance of half-cells and sodium reference electrodes. These are some of the practical challenges in developing a new battery chemistry. Nevertheless, high-purity, battery grade NaPF$_6$ is commercially available at a price four times cheaper than LiPF$_6$. For comparison, the price of LiPF$_6$ is $≈8.9$ € g$^{-1}$ while that of NaPF$_6$ is $2.2$ € g$^{-1}$ (Sigma–Aldrich, 2020 price level for 500 g). This price disparity is due to differences in the cost of upstream, alkali-metal carbonates (Li$_2$CO$_3$ and Na$_2$CO$_3$), although the synthesis routes for the two salts are similar.

3.3. Energy Density, Power, and Cyclability

Since inception, SIBs have demonstrated energy densities comparable to commercial LIBs. The energy density of the first generation 18650 cells was 90 Wh kg$^{-1}$ which was already impressive while, pouch cell SIBs from Faradion and Novasis Energies have ≈150 and 130 Wh kg$^{-1}$, respectively. As reference, the first Sony LIB had an energy density of 80 Wh kg$^{-1}$ while state-of-the-art LIBs have ≈150–200 Wh kg$^{-1}$. Although state-of-the-art SIBs have energy densities in the lower range of LIBs, improvements can be expected with new anode and cathode material discoveries, in the same way the LIB technology evolved. Besides this expectation, the power rate capability of SIBs has been outstanding and in some cases superior to LIBs. Figure 2c illustrates the rate performance of a 55 Wh kg$^{-1}$ cylindrical SIB at room temperature. These power-optimized SIBs reach 10 C rate (i.e., full discharge in 6 min), with 84% capacity retention. Pouch cells from Novasis Energies have shown equally excellent rate capabilities i.e., 10 C rate with 84% capacity retention.

Another performance metric is the cyclability of the cells. Electric vehicle battery test standards define the battery end-of-life as 80% initial/nominal capacity retention. Different conditions of temperature, (dis)charge rate, and depth of discharge (DoD) are known to affect the cyclability of LIBs. Temperature extremes (above and below 25 °C), high (dis)charge rates (above 1 C rate), and high DoD (above 80%) reduce the number of battery cycles. The cyclability of pouch and cylindrical SIBs has recently been explored under different conditions. Figure 2d illustrates the long-term cycling performance of 75 Wh kg$^{-1}$ SIB cylindrical cells at room temperature. These SIBs exhibit an outstanding cyclability, close to 4000 cycles at 1 C rate and 100% DoD. The cyclability of LFP in these conditions is, in general, ≈2000 cycles. High-temperature cycling of SIBs has also been impressive, Novasis Energies pouch cells cycled at 45 °C and 1 C rate show 200 cycles with 95% capacity retention. Therefore, SIBs have the ability to operate in a wide range of ambient conditions, and their cyclability rivals that of state-of-the-art LIBs.

3.4. Safety

Several abuse and tolerance tests, such as crush, nail penetration, and accelerating rate calorimetry (ARC), have been performed on pouch and 18650 SIB cells. A Novasis Energies Pouch cell, which has undergone nail penetration test, is shown Figure 3b. Although the nail piercing is visible, the SIB did not catch fire during the abuse test, due to the absence of oxygen generation from the PBA cathode. Remarkably, both crush tests and nail penetration tests on short-circuited (shorted) SIB cells did not show any temperature variation; another proof of the importance of transport and storage at 0 V.

During the ARC test, the cells are heated gradually to evaluate their self-heating temperature. The self-heating temperature is indicated by a temperature plateau wherein the cell temperature is sustained by internal exothermic reactions. Figure 3c compares the ARC test of NMC (LIB) to Sumitomo SIB, based on HC//NaFe$_{0.4}$Mn$_{0.3}$Ni$_{0.3}$O$_2$. The self-heating temperature is lower in the case of the LIB (165 °C) and higher for SIB (260 °C), indicating superior thermal stability of the SIB. Figure 3d compares the ARC test of both LCO and LFP Li-ion batteries to Faradion SIB cells. Similarly, the SIB shows a delayed start of self-heating and a significantly lower self-heating rate.

Due to the numerous cases of LIB fires, battery safety is of utmost importance to battery shipping companies. Airlines, in particular, are obliged to follow stringent regulations regarding onboard LIBs, which follows two catastrophic LIB failures in 2013, which forced the grounding of the Boeing 787 Dreamliner. In the case of LIBs, blanket LIB regulations have been applied by extension. However, as demonstrated by the safety test results, SIBs have superior thermal stability and abuse tolerance. Results of shorted SIBs warrant reclassification of SIB transport regulations, and experts can borrow from the regulations of shorted asymmetric capacitors, which can be transported as airfreight.

3.5. Cost

SIBs have ignited interest because of their low-cost potential for grid applications. Therefore, the cost factor has been a subject of investigation in recent studies. The benchmarking task is made difficult by the different maturity levels of the two energy storage technologies. Therefore, methods and results should be understood in this context. Vaalma et al. proposed a simple approach, wherein, components of a LiMn$_2$O$_4$/synthetic graphite cell are swapped to construct a hypothetical NaMn$_2$O$_4$/synthetic graphite cell. Disregarding the fact that such an SIB cell is inconceivable (because Na does not intercalate in graphite), this approach provides a quick and rational comparison of the material costs. The results show a 12.5% cost reduction in the SIB compared to the analogous LIB.
However, battery cost analysis is not a simple question of material costs and must be addressed in a holistic approach. Auxiliary features such as cell design, electrode coating thickness, and porosity are significant cost factors, and their impact varies with battery chemistry. Novák and co-workers\cite{95} applied an energy-cost model to compare the costs of SIBs and LIBs. This model considers material costs, processing costs, and administrative overheads. The cost of a HC//NVPF SIB cell was 320 $ \text{kWh}^{-1}$, while that of the graphite//LFP LIB cell was 280 $ \text{kWh}^{-1}$. It is revealing that, in spite of cheap material costs per kWh, SIBs emerged more expensive than LIBs. The inclusion of auxiliary features, such as processing costs and overheads, results to that date (2015 report) in more expensive SIBs.

A more detailed battery cost analysis is based on the Argonne National Laboratory’s BatPac model.\cite{98} This model includes cell design features, cell depreciation, and warranty on top of material and processing costs. Numerous studies have used BatPac in LIBs and recently in SIBs.\cite{80,97} Peters et al.\cite{80} performed the BatPac analysis to determine the costs of an 18650 SIB composed of the Faradion recipe active materials, i.e., HC//NMNT. The calculated costs of the SIB, LFP, and NMC cells were 223, 229, and 168 € \text{kWh}^{-1}, respectively. Therefore, the SIB cell was cheaper than the LFP battery while the NMC battery was the cheapest. These results highlight a second important factor of battery cost analysis, the energy density of the active materials. High energy density materials have a twofold effect of reducing both the material cost per kWh and the processing costs to reach a target cell energy. It should be highlighted that, of the three cells benchmarked, NMC had the most expensive materials. Therefore, the endeavor to make cost-competitive SIBs should be accompanied with an outlook for high energy density active materials.

### 3.6. e-Mobility and Stationary Applications

LIBs are the power behind the growth in BEVs. While the high-power rating of LIBs allows fast acceleration of electric vehicles, the driving range is limited by the capacity of the battery pack. Within the chassis of the vehicle, there is a limited volume in which to fit a battery pack. Battery weight is not the foremost consideration in BEV design because the driving range on the motorway is impacted by aerodynamics.\cite{99} Therefore, the range anxiety issues in BEVs can be addressed by vehicles with less drag coefficients and batteries with higher volumetric energy density.

![Superior thermal stability and safety of SIBs compared to commercial LIBs.](image)

Figure 3. Superior thermal stability and safety of SIBs compared to commercial LIBs. a) Cylindrical SIBs undergoing nail penetration test. b) SIB pouch cell with four thermocouples after nail penetration test showing no flames.\cite{82} c) ARC test of a SIB compared to NMC showing a high self-heating temperature for SIB. d) ARC test of a SIB compared to LCO and LFP showing a low self-heating rate of the SIB. a) Reproduced with the permission.\cite{92} Copyright 2019, the United Nations. b) Reproduced with permission.\cite{38} Copyright 2018, Wiley-VCH c) Data from ref. [73]. d) Data from ref. [105].

Based on the energy-cost model, the volumetric energy density of a HC//NVPF SIB is $\approx 400 \text{ Wh L}^{-1}$, while that of a graphite//NCA cell used in a Tesla BEV is $\approx 700 \text{ Wh L}^{-1}$.\cite{95} It is evident that state-of-the-art SIBs cannot address the range problems in BEVs. That is not to say however that they cannot find niche applications, such as low-speed electric vehicles and quadricycles (four-wheeled microcars). HiNA has pioneered the development of low-speed electric vehicles, powered by SIBs.\cite{71} It is also worthwhile to mention demonstrator e-scooters and e-bikes made by Tiamat and Faradion, respectively.
In stationary applications, batteries will play the key role of integrating renewable energy sources into the grid. As mentioned before, the battery weight and footprint are not major factors yet, LIBs are expected to play a leading role. Several large-scale battery installations have been announced recently; notable mentions include a 6.6 MWh (5.6 MW) LIB installation by SAFT that is set to become the largest LIB in Nordic countries and the Tesla Megapack battery, a container-sized LIB pack with a capacity of up to 3 MWh.\textsuperscript{[100,101]} In the case of SIBs, the 100 kWh battery by HiNA is currently the largest battery pack.\textsuperscript{[68]}

Battery sizing for grid applications is a question of selecting the right battery chemistry for the given grid application or duty cycle. Grid applications include time shifting in day ahead market, congestion relief, flexible ramping, and frequency regulation. In the time shifting and congestion relief applications, a high battery capacity is required, while in the ramping and frequency regulation applications, high battery power is required. Studies show that SIB and LIBs have the highest electrical energy storage efficiency (above 90%), in deep discharge applications, while lead-acid and NiCd batteries have the lowest.\textsuperscript{[27]} Because revenue generation per MWh scales linearly with battery efficiency, SIBs and LIBs are therefore the most profitable,\textsuperscript{[27]} thus explaining the interest in LIBs in stationary applications. However, outstanding performances for SIBs can be found in time shift applications, due to their high DoD and long cycle life as previously discussed.

### 4. Technological Trend Analysis and Outlook for SIB

Based on the current trajectory, LIBs will indeed face resource challenges. Eventually, LIB demand will surpass production limits, resulting in price increases. While other sources of lithium can be found, for example seawater, the extraction costs, in low-concentrated brines, are exorbitant and approximately five times the current costs.\textsuperscript{[19]} Other alternatives would be LIB recycling, as well as battery-life extension of retired BEV cells, because they still have ≈80% of their nominal capacity remaining at the end-of-life. These efforts are encouraged and noteworthy efforts include, for example, Umicore’s ultrahigh temperature (UHT) process,\textsuperscript{[102,103]} with an installed LIB recycling capacity of 7000 metric tons per year and the EU-funded Circusol project for second-life batteries.\textsuperscript{[104]} Nevertheless, environmental concerns regarding the use of leaching chemicals in battery recycling need to be addressed.\textsuperscript{[22]}

The SIB technology can however offer viable alternatives to complement LIB applications, the most promising being stationary storage applications. As revealed in this essay, prototype SIBs are comparable to state-of-the-art LIBs, in terms of energy density, rate capability, and cyclability. In addition, based on thermal stability studies, the safety features of SIBs are superior to LIBs. Although SIBs are generally cheaper, in terms of material costs, the challenge is to drive the processing costs to competitive levels. Current strategies include use of thick electrode coatings and lower salt concentration electrolytes.\textsuperscript{[105]} Both strategies exploit the higher conductivity of sodium-based electrolytes. Economies of scale can be further expected to play a major role, when the SIB technology reaches mature levels.

We should also highlight the long cycle life of SIBs, which can offset high upfront investments and make them cost attractive in large-scale, stationary applications.

Technological trend analysis based on patent numbers usually follows the four successive stages: i) predevelopment (emerging), ii) take-off (growth), iii) acceleration (maturity), and finally iv) stabilization (saturation).\textsuperscript{[106,107]} The predevelopment stage is characterized by an exponential rise in annual patent numbers while the growth stage is characterized by a drop in patent numbers, as companies consolidate and commercialize the technology. A patent trend analysis on the LIB technology revealed that the LIB technology entered the maturity stage in 2009.\textsuperscript{[106,107]} The saturation stage in LIBs remains to be seen because of emerging LIB applications in e-mobility and stationary storage markets. A similar analysis of the SIB technology was first carried out in 2017.\textsuperscript{[50]} Based on a monotonous and sharp increase in annual patent fillings, it was concluded that the SIB technology was still in the emerging stage.

However, since 2017, annual SIB patent numbers have been on a decline, which marks the entrance in the growth stage. Such a drop in patent numbers is attributed to the curtailment of research as companies focus on commercialization.\textsuperscript{[107]} Combining these patent trends with the positive results seen in prototype SIBs, there is reason to expect commercial SIBs in the near future.

Startup companies working toward SIB commercialization, beside the already mentioned companies, include Nanorion Energy (formerly Alveo Energy)\textsuperscript{[108]} and Altris AB.\textsuperscript{[109]} While startups in the early stages of seed capital are battling to manage the burn rate and overcoming the “valley of death,” the growing number of companies is another positive sign. This likely guarantees the success and commercialization of the SIB technology in the coming years. Several EU-funded projects such as NAIADES,\textsuperscript{[110]} NAIMA,\textsuperscript{[111]} and Ecodesign Batteries\textsuperscript{[112]} have brought together contributions from EU industries, research institutes, and universities to develop SIBs. The EU next-generation battery targets include long cycle life, improved recyclability (for a circular economy), and the substitution of critical raw materials. By 2030, energy storage costs are expected to fall below 0.05 € KWh$^{-1}$ per cycle and the SIB technology promises to meet these targets.

In terms of roadmaps, it appears there are different strategies being pursued. Some hope SIBs will eventually replace LIBs as cheaper and resource-abundant alternative, while others find no reasons to justify the replacement strategy and instead believe SIBs should identify as a separate class of batteries.\textsuperscript{[12]} By taking lessons from the historical development of LIBs, it is evident that a battery technology needs a matching application, a fact illustrated by the first LIBs, which evolved together with portable electronic devices. To avoid the pitfall of giving the right technological solutions to wrong and misplaced policies, it is important to identify target applications and aim for the most satisfying long-term outcome. Catching up to an established technology such as LIB is undoubtedly an enormous task, which is justified by the need to avert lithium supply risk shortage. Besides that, leapfrogging and going beyond LIBs, in areas such as solid-state batteries,\textsuperscript{[112]} rechargeable metal–air batteries,\textsuperscript{[113]} ionic-liquid-based batteries,\textsuperscript{[114]} and aqueous electrolyte-based batteries\textsuperscript{[114,115]} is another opportunity in fundamental research, to exploit the subtle yet unique properties of SIBs, for future applications.
5. Conclusions

So, can SIBs replace LIBs and become economically competitive? SIBs have, in a short period of time, demonstrated matching performance metrics with LIB and potential to replace them in large-scale stationary applications. SIBs have evolved with the guiding mindset of earth-abundant elements and have achieved a high performance/cost ratio. Outstanding performances of SIBs are in power, cyclability, recyclability, and safety (due to 0 V storage and transportation). Furthermore, encouraging signs in patent trends point toward an evolution from the emerging stage to the growth stage. SIBs, however, face challenges toward commercialization because of high costs per kWh and direct competition with an incumbent technology in applications.

The revived research in SIBs is justified by needs for sustainable and environmentally benign energy storage solutions. Going forward, it is necessary for this technology to catch up to LIBs by building on the success of prototype batteries toward commercialization. Cutting-edge differences can be found in the subtle differences with LIBs, which could propel SIBs beyond LIBs. All these are potential avenues for new discoveries in fundamental and applied research, which await to be exploited.

Acknowledgements

D.L.D. has received funding from the European Union’s Horizon 2020 Research and Innovation Program under Grant Agreement No. 769900-DEMOBASE. K.C. and G.M. are grateful for the support from the European Union’s Horizon 2020 Research and Innovation Program under Grant Agreement No. 646433-NAIADES.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

battery commercialization, lithium-ion batteries, sodium-ion batteries

Received: April 15, 2020
Revised: May 15, 2020
Published online: August 12, 2020

[1] The Royal Swedish Academy of Sciences, “The Nobel Prize in Chemistry 2019. NobelPrize.org,” https://www.nobelprize.org/prizes/chemistry/2019/press-release/ (accessed: June 2020).
[2] K. Ozawa, Solid State Ionics 1994, 69, 212.
[3] R. Brodd, Electrochem. Soc. Interface 1999, 8, 20.
[4] Sony, “Keywords to understanding Sony Energy Devices,” http://www.sonyenergy-devices.co.jp/en/keyword/ (accessed: December 2016).
[5] G. E. Moore, Proc. IEEE 1998, 86, 82.
[6] D. Takahashi, Forty Years of Moore’s Law, The Seattle Times, San Jose, CA 2005.
[7] M. M. Thackery, C. Wolverton, E. D. Isaacs, Energy Environ. Sci. 2012, 5, 7854.
[8] H. Maruyama, H. Nakano, M. Ogawa, M. Nakamoto, T. Ohta, A. Sekiguchi, Sci. Rep. 2015, 5, 13219.
[9] H. Wu, D. Zhuo, D. Kong, Y. Cui, Nat. Commun. 2014, 5, 5193.
[10] S. Nieto, S. B. Majumder, R. S. Katyar, J. Power Sources 2004, 136, 88.
[11] European Commission, “Ecodesign preparatory Study for Batteries,” https://ecodesignbatteries.eu/ (accessed: May 2020).
[12] Statista, “Worldwide BEV sales by brand 2019,” https://www.statista.com/statistics/666130/global-sales-of-electric-vehicles-by-brand/ (accessed: May 2020).
[13] US DOE, “Fuel Economy,” https://www.fueleconomy.gov/(accessed: April 2020).
[14] I. Tsiropoulos, D. Tarvydas, N. Lebedeva, Batteries for Mobility and Stationary Storage Applications Scenarios for Costs and Market Growth, Publications Office of the European Union, Luxembourg 2018.
[15] European Commission, “A European Green Deal,” https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en (accessed: April 2020).
[16] InsideEVs, “Total To Build France’s Largest Li-ion ESS Using Saft Batteries,” https://insideevs.com/news/406987/total-france-largest-battery-ess-saft/ (accessed: April 2020).
[17] D. M. Davies, M. G. Verde, O. Mnyshenko, Y. R. Chen, R. Rajeev, Y. S. Meng, G. Elliott, Nat. Energy 2019, 4, 42.
[18] C. Grosjean, P. H. Miranda, M. Perrin, P. Poggi, Renewable Sustainable Energy Rev. 2012, 16, 1735.
[19] J. Speirs, M. Contestabile, Y. Houari, R. Gross, Renewable Sustainable Energy Rev. 2014, 35, 183.
[20] D. Kushnir, B. A. Sandén, Resour. Policy 2012, 37, 93.
[21] C. Wadia, P. Albertus, V. Srinivasan, J. Power Sources 2011, 196, 1593.
[22] D.-W. Kim, J. R. Park, N.-K. Ahn, G.-M. Choi, Y.-H. Jin, J.-K. Yang, J. Korean Cryst. Growth Cryst. Technol. 2019, 29, 91.
[23] E. A. Olivetti, G. Ceder, G. G. Gaustad, X. Fu, Joule 2017, 1, 229.
[24] S. Bobba, P. Claudiu, D. Huygens, P. Alves-Dias, B. Gawlik, E. Tzimas, D. Wittmer, P. Nuss, M. Grohol, H. Saveyn, F. Burouei, G. Orveillon, T. Hamor, S. Slavko, F. Mathieux, M. Gislev, C. Torres De Matos, G. A. Blengini, F. Ardente, D. Blagoeva, E. Garbarino, Report on Critical Raw Materials and the Circular Economy, Publications Office of the European Union, Luxembourg 2018.
[25] D. Larcher, J.-M. Tarascon, Nat. Chem. 2015, 7, 19.
[26] A. Porouch, M. R. Palacin, Philos. Trans. R. Soc., A 2019, 377, 20180297.
[27] Y. Marcus, Ion Properties, CRC Press, Boca Raton, FL 1997.
[28] C. Delmas, J.-J. Bracconier, C. Fouassier, P. Hagenmuller, Solid State Ionics 1981, 3–4, 165.
[29] S. Bach, N. Baffier, J. P. Pereira-Ramos, R. Messina, Solid State Ionics 1989, 37, 41.
[30] K. Chayambuka, G. Mulder, D. L. Danilov, P. H. L. Notten, Adv. Energy Mater. 2018, 8, 1800079.
[31] C. Delmas, Adv. Energy Mater. 2018, 8, 1703137.
[32] A. Eftekhar, D.-W. Kim, J. Power Sources 2018, 395, 336.
[33] Q. Liu, Z. Hu, M. Chen, C. Zou, H. Jin, S. Wang, S.-L. Chou, Y. Liu, S.-X. Dou, Adv. Funct. Mater. 2020, 30, 1909530.
[34] M.-S. Balogun, W. Qiu, Y. Luo, H. Meng, W. Mai, A. Onasanya, T. K. Olaniji, Y. Tong, Nano Res. 2016, 9, 2823.
[35] A. Mauger, C. M. Julien, Ionics 2017, 23, 1933.
[36] F. Schipper, D. Aurbach, Russ. J. Electrochem. 2016, 52, 1095.
[37] M. Winter, B. Barnett, K. Xu, Chem. Rev. 2018, 118, 11433.
[38] A. Bauer, J. Song, S. Vail, W. Pan, J. Barker, Y. Lu, Adv. Energy Mater. 2018, 8, 1702869.
[39] S. Roberts, E. Kendrick, Nanotechnol. Sci. Appl. 2018, 11, 23.
[40] M. S. Whittingham, Science 1976, 192, 1126.
[41] W. B. Johnson, W. L. Worrell, Synth. Met. 1982, 4, 225.
A. D. Patricia, B. Darina, P. Claudiu, A. Nikolaos, Cobalt: demand-supply balances in the transition to electric mobility, Publications Office Of The European Union, Luxembourg 2018.

R. J. Gummow, A. De Kock, M. M. Thackeray, Solid State Ionics 1994, 69, 59.

A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada, J. B. Goodenough, J. Electrochem. Soc. 1997, 144, 1609.

Z. Liu, A. Yu, J. Y. Lee, J. Power Sources 1999, 81–82, 416.

M. Yoshio, H. Noguchi, J. Itoh, S. Okada, T. Mouri, J. Power Sources 2000, 90, 176.

M. S. Whittingham, Chem. Rev. 2004, 104, 4271.

K. B. Hueso, M. Armand, T. Rojo, Energy Environ. Sci. 2013, 6, 734.

T. Oshima, M. Kajita, A. Okuno, Int. J. Appl. Ceram. Technol. 2004, 1, 269.

J. L. Sudworth, J. Power Sources 1994, 51, 105.

A. Hartenbach, M. Bayer, C.-H. Dustmann, in Molten Salts Chemistry (Eds: F. Lantelme, H. Groult), Elsevier, Oxford 2013, pp. 439–450.

R. Benato, N. Cosciani, G. Crugnola, S. Dambone Sessa, G. Lodi, C. Parmeggiani, M. Todeschini, J. Power Sources 2015, 293, 127.

R. Stepler, Pop. Sci. 1993, 242, 32.

W. Aufer, The PB sodium sulfur cell for satellite battery applications, Paper presented at 32nd International Power Sources Symposium, Cherry Hill, NJ, June 1986.

D. A. Stevens, J. R. Dahn, J. Electrochem. Soc. 2000, 147, 1271.

D. A. Stevens, J. R. Dahn, J. Electrochem. Soc. 2001, 148, A803.

J. Ayre, “18650 Sodium-Ion Battery Developed At RS2E,” https://cleanotechnica.com/2015/12/01/18650-sodium-ion-battery-developed-at-rs2e/ (accessed: April 2020).

Y.-S. Hu, S. Komaba, M. Forsyth, C. Johnson, T. Rojo, Small Methods 2019, 3, 1900184.

CNRS, A Start-Up for Much Faster Batteries, http://www.cnrs.fr/en/start-much-faster-batteries (accessed: June 2020).

Tiamat, “Powerful, fast charging, enduring cells thanks to sodium-ion,” http://www.tiamat-energy.com/ (accessed: April 2020).

X. Rong, L. Xiaxiang, Q. Xingguo, Z. Quan, K. Weihe, T. Kun, H. Youngsheng, Energy Storage Sci. Technol. 2020, 9, 515.

K. Smith, J. Treacher, D. Ledwoch, P. Adamson, E. Kendrick, ECS Trans. 2017, 75, 13.

S. Kuze, J. Kageura, S. Matsumoto, T. Nakayama, M. Makidera, M. Saka, T. Yamaguchi, T. Yamamoto, K. Nakane, Sumitomo Kagaku 2013, 1, 11.

J. L. Murray, Bull. Alloy Phase Diagrams 1983, 4, 407.

J. Barker, C. J. Wright, Storage and/or Transportation of Sodium-Ion Cells WO2016027082A1, 2016.

K. Xu, Chem. Rev. 2014, 114, 11503.

A. Ponrouch, E. Marchante, M. Courty, J.-M. Tarascon, M. Rosa Palacín, Energy Environ. Sci. 2012, 5, 8572.

J. Fondard, E. Irisarri, C. Courrèges, M. R. Palacín, A. Ponrouch, R. Dedvyvère, J. Electrochem. Soc. 2020, 167, 070526.

K. Kubota, S. Komaba, J. Electrochem. Soc. 2015, 162, A2538.

J. F. Peters, A. Peña Cruz, M. Weil, Batteries 2019, 5, 10.

T. Placke, R. Kloepsch, S. Dühnen, M. Winter, J. Solid State Electrochem. 2017, 21, 1939.

ISO 12405–4, Electrically propelled road vehicles—Test specification for lithium-ion traction battery packs and systems—Part 4: Performance testing, ISO, Geneva, Switzerland 2018.

IEC 61982, Secondary batteries (except lithium) for the propulsion of electric road vehicles - Performance and endurance tests, IEC, Geneva, Switzerland 2012.

IEC 62660–1, Rechargeable Cells Standards Publication Secondary lithium-ion cells for the propulsion of electric road vehicles. Part 1: Performance testing, IEC, Geneva, Switzerland 2010.

SAE J2288, Life Cycle Testing of Electric Vehicle Battery Modules, SAE, Warrendale, PA 2008.

N. Omar, M. A. Monem, Y. Firooz, J. Salminen, J. Smekens, O. Hegazy, H. Gaulous, G. Mulder, P. Van den Bossche, T. Coosemans, J. Van Mierlo, Appl. Energy 2014, 113, 1575.

L. Mu, S. Yu, Y. Li, Y.-S. Hu, H. Li, L. Chen, X. Huang, Adv. Mater. 2015, 27, 6928.

T. Broux, F. Fauth, N. Hall, Y. Chatillon, M. Bianchi, T. Bamine, J.-B. Leriche, E. Suard, D. Carlier, Y. Reynier, L. Simonin, C. Masquelier, L. Croguennec, Small Methods 2019, 3, 1800215.

G. Yang, J. Shi, C. Shen, S. Wang, L. Xia, H. Hu, H. Luo, Y. Xia, Z. Liu, RSC Adv. 2017, 7, 26052.

J. Wang, P. Liu, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, P. Finamore, J. Power Sources 2011, 196, 3942.

X. Wang, P. Adelmann, T. Reindl, Energy Procedia 2012, 25, 135.

Sub-Committee of Experts on the Transport of Dangerous Goods, Sodium-ion batteries — comments on document ST/SG/AC.10/C.3/2019/35, UNECE 55th session, Geneva July 2019.

O. S. Mendoza-Hernandez, S. Taniguchi, H. Ishikawa, K. Tanaka, S. Fukuda, Y. Sone, M. Umeda, EES Web Conf. 2017, 16, 07001.

N. Williard, W. He, C. Hendricks, M. Pecht, Energies 2013, 6, 4682.

E. Berg, C. Villeviede, D. Streich, S. Trabesinger, P. Novák, J. Electrochem. Soc. 2015, 162, A2468.

Y. Kim, K.-H. Ha, S. M. Oh, K. T. Lee, Chem. - Eur. J. 2014, 20, 11980.

C. Vaalma, D. Buchholz, M. Weil, S. Passerini, Nat. Rev. Mater. 2018, 3, 18013.

P. A. Nelson, K. C. Gallagher, I. D. Bloom, D. W. Dees, Modeling the Performance and Cost of Lithium-Ion Batteries for Electric-Drive Vehicles, Argonne National Laboratory (ANL), Lemont, IL 2012.

D. MacKay, Sustainable Energy—without the Hot Air, UIT, Cambridge 2008.

Tesla, “Megapack,” https://www.tesla.com/megapack (accessed: April 2020).

Saft Batteries, “Making the most of Nordic wind power,” https://www.saftbatteries.com/media-resources/our-stories/making-most-nordic-wind-power (accessed: April 2020).

H. Morel, Presented at Capital Markets Event on Recycling, Umicore, November 2010.

Umicore, “Our recycling process,” https://csm.umicore.com/en/recycling/battery-recycling/our-recycling-process (accessed: April 2020).

Circusol, “Second-life batteries,” https://www.circusol.eu/en/topics/second-life-batteries (accessed: April 2020).

J. Barker, R. J. Heap, N. Roche, C. Tan, R. Sayers, J. Whiteley, Y. Lui, Commercialization of Faradion’s High Energy Density Na-Ion Battery Technology, Faradion Limited, Sheffield, UK 2016.

R. Wagner, N. Preschitschek, S. Passerini, J. Leker, M. Winter, ECS Meet. Abstr. 2014, MA2014-01, 78.

R. Wagner, N. Preschitschek, S. Passerini, J. Leker, M. Winter, J. Appl. Electrochem. 2013, 43, 481.
[108] Natron Energy, “Natron Energy—Prussian Blue Sodium Ion Battery Technology,” https://natron.energy/ (accessed: April 2020).
[109] Altris, “We enable the next generation of batteries,” https://www.altris.se/ (accessed: April 2020).
[110] EU H2020 Program, “Naiades, Sodium ion batteries,” http://www.naiades.eu/ (accessed: April 2020).
[111] NAIMA, “New Na-ion cells to accelerate the European Energy Transition,” https://naimaproject.eu/ (accessed: April 2020).

[112] C. Zhao, L. Liu, X. Qi, Y. Lu, F. Wu, J. Zhao, Y. Yu, Y.-S. Hu, L. Chen, 
Adv. Energy Mater. 2018, 8, 1703012.

[113] X. Xu, K. S. Hui, D. A. Dinh, K. N. Hui, H. Wang, Mater. Horiz. 
2019, 6, 1306.

[114] J.-K. Kim, F. Mueller, H. Kim, S. Jeong, J.-S. Park, S. Passerini, 
Y. Kim, ChemSusChem 2016, 9, 42.

[115] S. T. Senthilkumar, H. Bae, J. Han, Y. Kim, Angew. Chem. 
2018, 130, 5433.

[116] C.-H. Dustmann, J. Power Sources 2004, 127, 85.