

Brief review on Na-ion Batteries

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Declaration

I declare that the literature review titled “Brief review on sodium- ion battery” has been carried out by me in Chemistry Department, School of Chemical Sciences, Goa University. The Information derived from the literature been duly acknowledged in the text and a list of references is provided.

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Certificate

This is to certify that the dissertation entitled “Brief review on sodium- ion battery” is bonafide work carried out by Mr. Reis Estrocio under my supervision in partial fulfillment of the requirement for the award for the degree of Master in Science in Chemistry at the School of Chemical Sciences, Goa University

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1.1. Introduction

During the 1970s and early 1980s, the sodium-ion battery was developed concurrently with the lithium-ion battery. By the 1990s, however, it was evident that lithium-ion batteries held greater commercial promise, and interest in sodium-ion batteries had waned[1]. The increased demand for and cost of lithium-ion battery raw materials prompted a rebirth of interest in sodium-ion batteries in the early 2010s. The widespread adoption of renewable energy will necessitate an increase in the production of low-cost, energy-efficient energy storage systems. As intermittent renewable energy generating technologies such as wind, solar, and wave become more prevalent and integrated into the electrical grid, battery technology will need to be extended to large-scale storage. While lithium-ion battery technology is fairly mature, there are still concerns about lithium battery safety, lifetime, and low-temperature performance. Furthermore, as the use of large format lithium batteries spreads, rising demand for Li commodity chemicals combined with geographically limited Li mineral reserves will drive up prices[2].

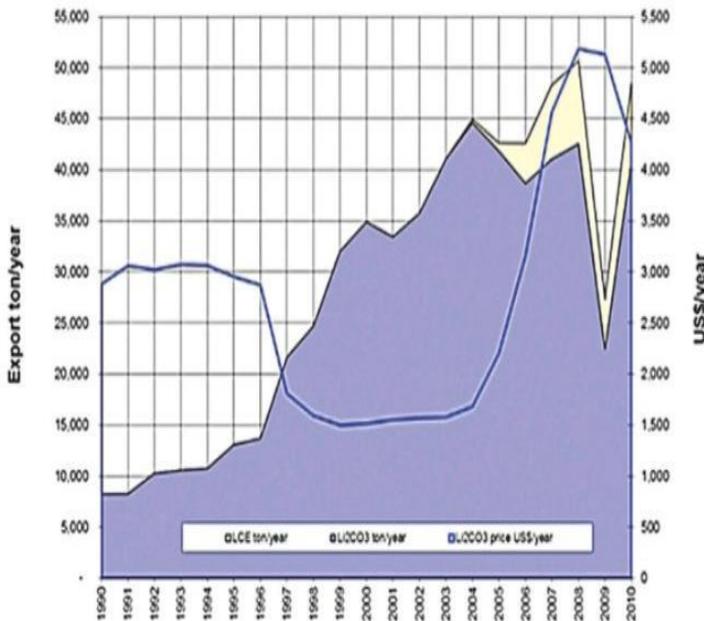


Figure 1. Fluctuation of the price and production of Li_2CO_3 over time. The sharp rise in price in the mid-2000s was caused in part by increases in demand for lithium batteries. Reproduced with permission. [4] Copyright 2012, The Lithium Site

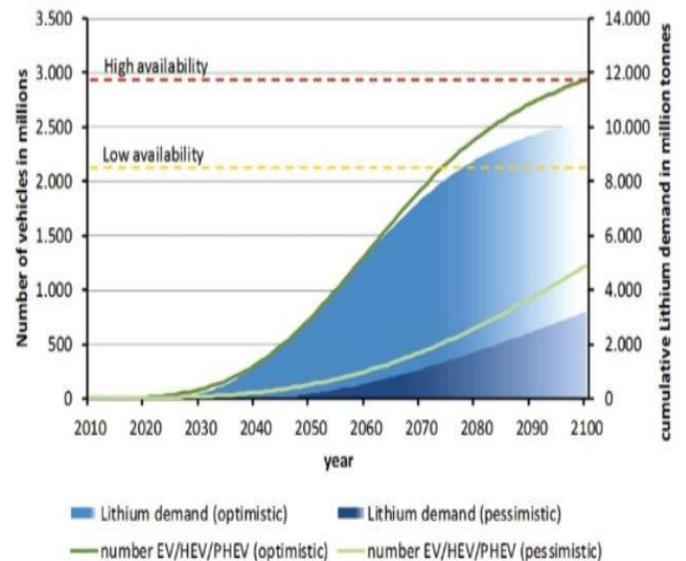


Figure 2. Lithium demand and availability and number of electric vehicles (EVs), hybrid electric vehicles (HEVs) and plugin hybrid electric vehicles (PHEVs) over time. In low availability of lithium/optimistic EV/HEV/PHEV production scenarios, lithium could run out in the near future. Reproduced with permission. [4] Copyright 2012, Research Center for Energy Economics.

Battery manufacturing now consumes roughly one-quarter of the world's production of lithium-containing precursor materials, contributing to a steep rise in the price of Li_2CO_3 during the first decade of this century (Figure 1) [2]. The widespread use of Li ion batteries for traction applications is expected to add to the pressure; in some scenarios, lithium supplies are expected to run out in the near future (Figure 2). If these batteries are used for large-scale energy storage, supplies are likely to be even more limited. Although new sources of lithium are being investigated, and the metal can be recycled once. On contrast, sodium (Na) metal, which is right below Li in the periodic table, is the sixth most abundant element [3] in the earth's crust (2.6 percent) and has a uniform geographic distribution with a limitless number of dissolved salts in seawater. Sodium may have a considerable cost advantage due to its enormous abundance. Furthermore, although most LIBs use cobalt in the cathode, sodium-ion batteries (NIBs) rely less on such a costly, poisonous, and rare element¹. Lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs) have comparable cell chemistry (Table 1). Sodium has a lower open circuit potential (E°) and charge-storage capacity (for metal electrodes) than lithium, but it is abundant and has a very low cost.

Table 1: Comparison between Lithium and Sodium

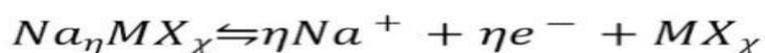
| Properties | Lithium | Sodium |
|---------------------------------------|---------|--------|
| Cation size (Radius \AA) | 0.76 | 1.06 |
| Atomic weight (g mol^{-1}) | 6.9 | 23 |
| Electronic cell structure | 2,1 | 2,8,1 |
| Melting point $^\circ\text{C}$ | 180.54 | 97.2 |
| Cost, carbonates $\text{\$ ton}^{-1}$ | 5000 | 159 |
| E° (vs SHE) | -3.05 | -2.71 |

1.2 Conventional sodium-ion battery (NIB) build-up

Sodium-ion battery cells include a cathode primarily based totally on a sodium-containing material, an anode (now no longer always a sodium-primarily based material), and a liquid electrolyte containing dissociated sodium salts in polar or aprotic solvents. During charging, sodium ions are extracted from the cathode and inserted into the anode whilst the electrons journey via the outside circuit; at some stage in discharging, the opposite system takes place in which the sodium ions are extracted from the anode and re-inserted within the cathode anode the, electrons traveling via the outside circuit doing beneficial.

As addressed by several researchers and expressed in the chemical equation below [1], [2], [4]–[8] the intercalation/deintercalation processes entail the interstitial insertion/removal of Na into a host crystals lattice.

Because the forward and backward reactions have identical transition states, this reaction is highly reversible. However, the radius of a sodium atom (1.06) is greater than that of a lithium atom (0.76). When sodium is injected into the host electrode material lattice, it can create several crystallographic phases, resulting in a partial loss of reversibility. $\text{Na}_{1-x}\text{MO}_2$ (M: transition metals such as Fe, Co, Mn, Ti, Cr, etc.) and their derivatives have been discovered.



1.2.1 Cathode materials

Cathode preparation has been synthesized and examined. A few metal fluorides, including associated compounds, have also been explored (metal: Fe, V, Ti, Co [9] and Mn). Phosphates and fluorophosphates like NaFePO_4 , $\text{Na}_2\text{FePO}_4\text{F}$, as well as pyrophosphates like $(\text{MoO}_2)_2\text{P}_2\text{O}_7$ and $\text{Na}_2\text{FeP}_2\text{O}_7$, have been investigated.

a. Sulphides

Large galleries in layered sulphides allow Na cations to be intercalated. Early research focused mostly on binary metal sulphides, the most notable of which is TiS_2 , the canonical intercalation electrode [10], [11]. The Ti(IV)/(III) redox couple has a redox potential of 1.8–2.0 V vs. Na, which is about 0.3 V lower than the LiTiS_2 system.

In comparison to Na_xTiS_2 , novel layered oxides and recently described framework poly-anionic cathodes enable substantially higher operating voltages (> 2.0 V) for Na cells. Other sulphides for ambient temperature non-aqueous Na batteries have lower voltage and are better used as anodes; Ni_3S_2 (0.8 V vs. Na) [12], and Cu_2S (1.0 V vs. Na) are notable examples.

b. Fluorides

The performance of perovskite transition metal fluorides (usually FeF_3) in Na batteries have been studied. When the Na reacts with the material electrochemically, it fills the A site in the ABO_3 perovskite structure, reducing the Fe to Fe (II). This reaction takes place at a voltage of

around 2 V vs. Na[13]. The voltage curve has a lot of hysteresis, yet at a low current rate of 0.2 mA cm^{-2} , the capacity can approach 240 mg^{-1} . Ball milling the FeF_3 to fine particle sizes is also essential as it encouraged reactivity in the Elec electrochemical system because the material was generated in the charged state, the next step was to chemically manufacture NaFeF_3 in the discharged state utilizing a solution-phase nanomaterial synthesis[14]. In a Na cell, NaFeF_3 can be charged to 4.5 V and then cycled reasonably between 1.5 and 4.5 V as a discharge material.

c. Oxides

Orthorhombic $\text{Na}_{0.44} \text{MnO}_2$ (i.e . $\text{Na}_4 \text{Mn}_9 \text{O}_{18}$) has large S-shaped tunnel structures and is electrochemically active to reversible Na electrochemical reaction as shown by Sauvage[15] and also the earlier work of Doeff in Na-metal polymer cells[16]. The open framework allows Na^+ to cycle into and out of obtainable octahedral sites with relative ease. Although this compound can provide relatively high capacity because of cycling ca. 0.6 Na (160 mAh g^{-1}), this full capacity is just accessible in half-cells where the additional Na does not present within the starting material provided by the anode. A revisit of $\text{Na}_{0.44} \text{MO}_2$ oxides within the type of nanowires was recently reported for Na batteries[17]. Although the specific capacity of 128 mAh g^{-1} was under previous reports for this material, the mixture of the high-aspect-ratio active nanomaterial with low electrode loading ($\sim 2 \text{ mg cm}^{-2}$) improved rates and provided remarkable capacity retention (77% after 1000 cycles at 0.5 C), thus demonstrating the effectiveness of nanosizing for Na electrochemical systems. Some early work on the sodium insertion into the spinel λMnO_2 showed that the fabric converts to other MnO_2 structures, including $\text{Na}_{0.44} \text{MnO}_2$ and therefore the layered $\text{Na}_{0.7} \text{MnO}_2$, during cycling[18]. Complete rearrangement of

the oxide lattice framework should occur to accommodate Na in these structures since Na won't fit into the spinel tetrahedral sites.

d. Phosphates and Sulfates

As documented in the Li ion battery literature, olivine-structured Li transition metal phosphates (LiFePO_4) were widely reported and subsequently used in the battery industry following the important discovery that these This material has the electromagnetic properties[19]. The lack of sodium ion electrochemical studies of sodium transition metal phosphates for Na batteries is disappointing despite the synthesis of several types of these phases. Instead, many of these studies only looked at the electrochemical ion exchange of Na with Li inside a Li ion cell and the subsequent experiment in a Li battery. [20]. Almost all of the Na would be reversibly cyclic from this structure, and an actual capacity of 10 mAh g^{-1} has been demonstrated. Almost no research on phosphates in liquid Na ion cells is truly water-free (no metallic Na), except for the pioneering work on NaVPO_4F in addition to the strong carbon anode[21], also the cathode of this layer, was synthesized using an exciting topological reaction from the precursor of the ammonium cation $\text{NH}_4\text{M PO}_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Fe, Ca, Mg}$)[22]. Unfortunately, the iron substitution in this structure leads to a decrease in the electrochemical efficiency and only 0.6 Na can be cyclized in $\text{NaMn}_{1/2}\text{Fe}_{1/2}\text{PO}_4$, which has a specific capacity could be 93 mAh g^{-1} . The deleterious effects of substituting manganese for iron in $\text{Na}_2\text{FePO}_4\text{F}$; During this study, the poor electrical conductivity of the oxyanion cathode materials was solved by using thermal synthesis to generate nano-sized particles with better performance in Na cells compared with those of larger sizes. Super small. These materials show a capacity of 110 mAhg^{-1} [23]. The NASICON type $(\text{A}_n\text{M}_2(\text{XO}_4)_3)$; $\text{X} = \text{Si}^{4+}, \text{P}^{5+}, \text{S}$

⁶⁺, Mo ⁶⁺, As ⁵⁺, etc.), and their structures are known to be used as Na ion conductors, their use as a cathode in Na cells is very rare.

e. Vanadium oxide.

Vanadium oxides with layered (α - V_2O_5 and $Na_{1+x}V_3O_8$) or burrow (β - $Na_xV_2O_5$) structures have been shown to reversibly cycle up to 1.6 Na (225 mAh g^{-1}), the normal cell potential is low and limits maintenance is poor[24], [25], interestingly, electro-deposited V_2O_5 accomplished an extremely high limit (250 mAh g^{-1}) in Na cells for more than 300 cycles[26]. This nanostructured fabric reversibly converts from a disordered, cantilevered shape within the deintercalated layers to a bilayered shape while Na is inserted. $Na_{0.33}V_2O_5$ nanorods have additionally been examined as cathodes in Na cells, imparting 142 mAh g^{-1} [27]. However, the hassle related to those vanadium oxides is that they may be intrinsically synthesized within the charged country.

Therefore, a supply of sodium is required for the cathodes to perform efficaciously in a Na-ion format. Sodium vanadium oxides organized within the discharged regions, including the layered oxides Na_xVO_2 ($x = 0.7, 1$) also are stated to cycle ca . 0.5 Na reversibly (a hundred thirty mAh g^{-1})[28], [29]. Voltage analysis shows that sodium vacant layering takes place in the inner layer since it has a characteristic of Na content, and this phenomenon creates two-segment and solid-solution areas indicative in the voltage profiles.

2.1 Anode materials

Identification of appropriate electrode is important to tackle the trouble for the a hit improvement of a sodium-ion battery and the location in which analogy to Li-ion structures is the least applicable. Compared to lithium metallic anodes, gadgets primarily based totally on metal sodium have decrease theoretical electricity densities because of the decrease specific capacity (1166 mAh g^{-1}) and better widespread discount capability of Na. The excessive reactivity of metal sodium with the natural electrolyte solvents and dendrite formation all through Na metallic deposition are even extra tricky than with Li metallic anodes, whilst the low melting factor of Na (98°C) gives a significant protection threat in gadgets designed to be used at ambient temperatures the usage of a Na metallic electrode. Hence, it's far important to apply a system, that is, one in which Na ions are recycled to and fro from host electrodes in a 'rocking chair'. The effectively avoids using dangerously reactive Na metallic. Unfortunately, it's far very difficult at this early juncture withinside the f field to make complete cells, and, instead, maximum research have most effective explored the electrochemical overall performance of recent electrodes and substances used with Na metallic in 1/2 of cells.

a. Carbon Based Anode materials

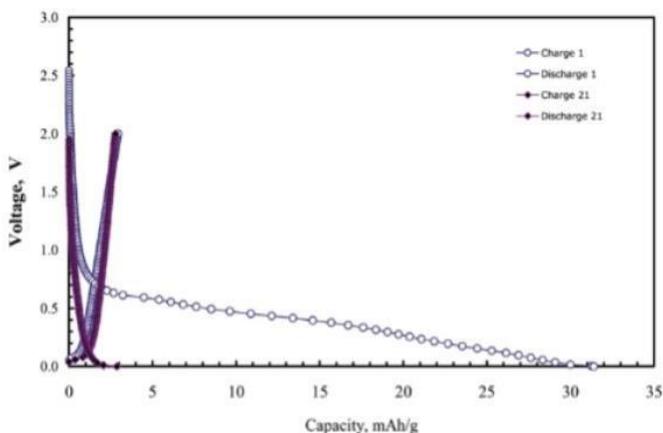


Figure 3. Na/C (graphite) cell showing lack of electrochemical activity.

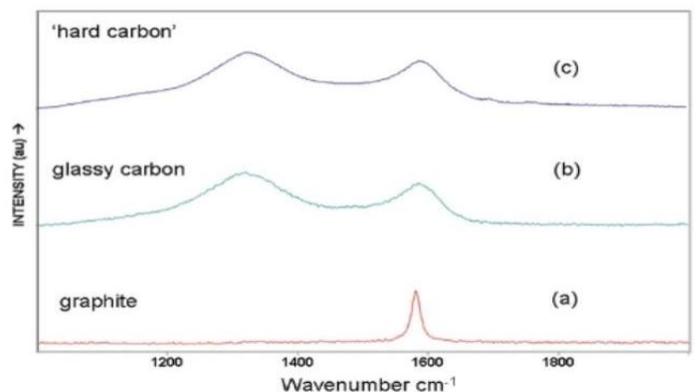


Figure 4. Raman spectra of (a) graphite, (b) glassy carbon, and (c) the 'hard carbon' used in the full cell study

Graphite, generally used as an anode in lithium-ion batteries, does not significantly intercalate sodium and is electable, as shown by the low and irreversible capacitance of Na/C (graphite) batteries.) in (Figure 3)[30]. Various other non-graphite anodes consisting mostly of different carbon materials have been shown to be able to insert Na, such as petroleum coke, carbon black, highly radical carbon fibers, and polymers. Hard carbon, that is, a general carbon material synthesized at high temperatures ($\sim 1000\text{ }^{\circ}\text{C}$, inert atmosphere) from carbon-based precursors has been more widely modeled, characteristic, and heated in Na-ion battery. These graphite-free but graphene-containing carbon materials are considered the “first generation” anode of choice for Na ion systems. Raman spectra of different atoms are shown in Fig 4. It is clear that graphite (spot a) has a strong and narrow band (symmetry $-C = C-$ elongated) at 1580 cm^{-1} , while the hard carbon material (trace c) resembles the Raman spectrum of vitreous carbon (trace b) carries an additional peak at 1350 cm^{-1} which is allowed by the increased disorder. Glass carbon contains a quadratic conglomerate of densely packed carbon particles.

The voltage profile for non-graphite carbon exhibits two distinct characteristics: a steep region below 1 V followed by a low voltage alternating reaction region below 100 mV with a total first discharge capacity of 300 mAh g^{-1} .

a. Metal Oxide Anode Materials

They are mainly early transition metal oxides, and the sodium insertion potential of most of them is too high to be of any practical use. With two highly stable alternating electrodes, it is possible to extend the cycle of Na ion batteries without losing capacity, as shown in thus demonstrating the viability of Na ion batteries as energy storage

devices. Metal oxide conversion reactions have been shown to be useful for Na ion anodes[31]. A Subsequent EXAFS studies demonstrated that the conversion reaction to form sodium oxide (Na_2O) was the primary reaction because the NiCo_2O This compound was also collected in full plots with an excess of Na 0.7 CoO_2 ; An improvement in the reversibility of the anode material has been observed, which is an important reminder in shielding materials for Na ion batteries: metallic sodium behaves rather poorly as an anti-electrode[31], this case, metal oxide reduction is followed by alloying (to form Na_3Sb) and thus a very high reversibility of 800 mAh g^{-1} has been demonstrated for more than 20 cycles.

b. Intermetallic Anode Materials

Carbon helps electrode conductivity and mechanical stability while Sn and Sb constitute a single SnSb phase that provides very high capabilities related to alloy reactions[32], 100% occur to individual metals, but SnSb / C nanocomposite can negotiate change in volume. In the proposed mechanism, the single-stage reaction of Na with SnSb occurs first to give Na_3Sb and Sn. The experimental possibility corresponds to the expected theoretical value for the Sn:Sb molar ratio of 1:1, demonstrating that the two metals participate in the same Na alloying reaction.

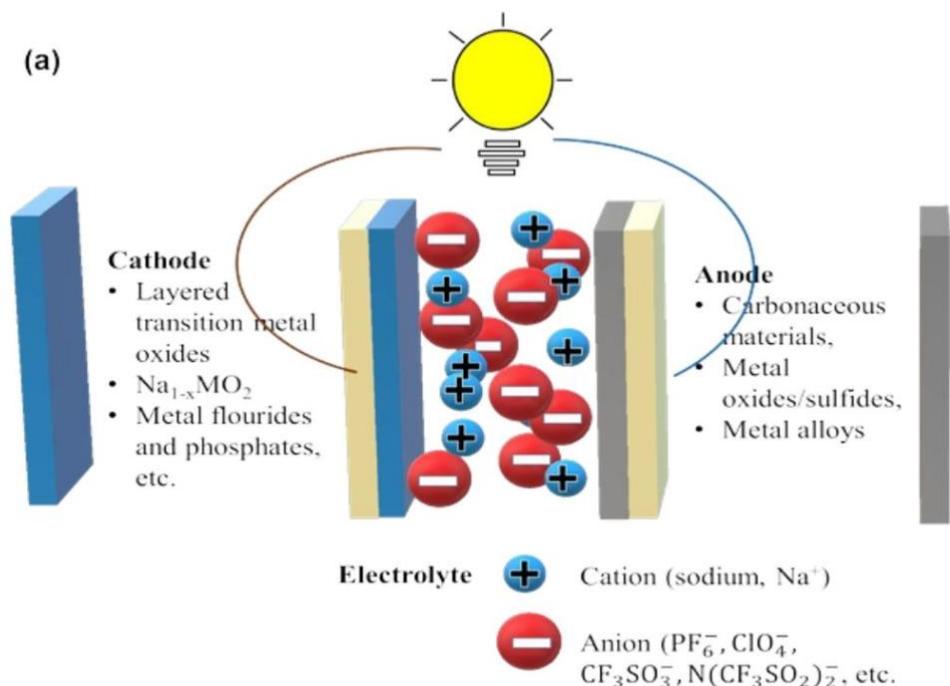
c. Electrolytes for Na-ion batteries

The electrolyte is an important component that controls the chemistry between the two electrodes and affects the electrochemical performance of the battery. It is an ionic conductive medium and an electronic insulator sandwiched between two electrodes. It acts as a medium of charge transfer between the anode and cathode. Many different types of organic liquid electrolytes are used commercially in energy storage devices, but they suffer from problems associated with

these liquid phase electrolytes, such as leakage, corrosion. at the electrode/electrolyte interface, volatile, flammable and superheated. To address these problems, various types of solid electrolytes have been investigated, along with alternatives such as crystalline inorganic electrolytes, glass electrolytes, polymer-based electrolytes, and systems. hybrid electrolyte[1].

The discovery of suitable liquid electrolytes along with advances in anodes will also be essential and provide excellent research opportunities. The most common electrolytic formulations for sodium batteries use NaPF_6 or NaClO as salts in carbonate ester solvents, especially propylene carbonate. Unfortunately, as mentioned earlier, the metal sodium anodes continuously corrode in the presence of most commonly used organic electrolytes, rather than forming a stable solid electrolyte. determination (SEI) between phases. Highly reducing sodium intercalated compounds for use as anodes may also require suitable SEIs to enable stable cycling in the cell, similar to those formed on the lithium graphite electrode in Li-ion system. Typical reduction products are impurities such as sodium propyl carbonate that are produced on the surface of the Na anode in reaction with PC, the most commonly used solvent in Na batteries. This species, in turn, can be oxidized at the cathode opposite the peak of the charge, thereby limiting capacity utilization and causing Coulomb inefficiency. The formulations and conditions required for proper SEI training will need to be co-developed with the anode material to ensure success in this field. For example, fluoroethylene carbonate (FEC) was recently observed to form a passivation film (reduced by 0.7 V) on the anodes of the natural metal carbon and sodium, thereby stabilizing the electrodes against side reactions with solvents other additives.

For example, those used in Li ion batteries such as vinylidene carbonate (VC), ethylene sulfite (ES) and trans difluoroethylene carbonate (DFEC) are not effective, but an improvement in cycle was



observed for FEC at 10 vol.% for the carbon anode. concluded, based on XPS and TOFSIMS data, that the SEI film on hard carbon is mostly inorganic salts and contains precipitates such as NaF on the surface (when NaPF_6 is used as the salt electrolyte).

2.2.2 Conclusion

Na ion-based electrochemical energy storage is an additional alternative to Li ion-based systems. The main advantage that can be argued with non-aqueous Na ion chemistry is the lower material cost compared with Li-based systems, although the actual utility of commercial Na ion implementation depends on the Li market. . some new materials and in some cases the same performance as the first Li ion technology. With improvements made in cell design and electrode engineering as part of Li ion battery advancements, it may be worthwhile to re-examine older Na electrode materials for their performance in cells.

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