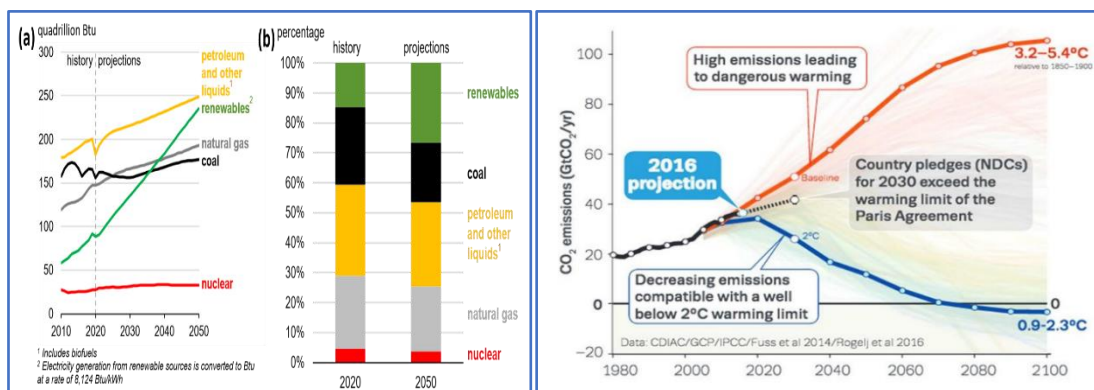


## 1.1 Fossil Fuel, Environment and Energy Security

### 1.1.1 Global Warming and Energy Security

#### 1.1.1.1 General Background

The tremendous rise in the world's energy consumption over the past few years has been correlated with worldwide economic growth. According to McKinsey global energy perspective 2022, due to growing living standards and electrification needs, power consumption is projected to triple by 2050 (500 million TJ). 3-4% annual demand growth rate in electricity is projected from 2010 to 2050 (*Global Energy Perspective 2022*, 2022) figure 1.1. It is expected to meet 80–90% of the total energy demand from renewable energy sources (RES) by 2050. The RES share is anticipated to increase from 29% to 60% in the next 15 years under further acceleration. Till 2022 the primary fuel in the world is still coal, followed by natural gas, oil, and other fossil fuels. Nuclear energy is also a clean alternative to nonconventional energy, but transportation and storage of nuclear waste pose a severe environmental risk.



**Figure 1.1** Primary energy consumption by energy source in (a) actual figure (b) in percentage. (2010-2050) (left) (*Global Energy Perspective 2022*, 2022) Projection plot of average temperature rise and CO<sub>2</sub> emission from 1980 to 2100 (right) (Oka, 2019)

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Since the 20<sup>th</sup> century, a major concern of pollutant gas emission and the greenhouse effect have been observed by the emission of gases like CO, and CH<sub>4</sub> by the burning of fossil fuel burning, transportation based on oil, heating, and power, are the primary source of the greenhouse effect. Growing climate change concerns have raised the issue of carbon footprint in the environment COP26 is planning to restructure the energy input method and effort, cut emissions to half by 2030, and achieve a net zero goal by 2050. In the meantime, the energy crisis has been brought on by overusing fossil fuel resources (Peter, 2018; Qian et al., 2013; Song et al., 2014; Y. Zhu et al., 2015). Thus, the focus is to develop new sustainable energy sources like solar, wind, and tidal energy; these sources have weather limitations and suffer from an energy storage system. Thus, we need to integrate these energy sources from integrated grid energy storage systems (*Abeywardana et al., 2015; H. Chen et al., 2009; Investigation of Solar Water Heating System with Phase Change Materials, n.d.; G. Wang et al., n.d.*).

### **1.1.1.2 Global Warming and Climate Change**

21<sup>st</sup> century has a big challenge of global warming and climate change. Global warming (average rise in the earth's atmosphere temperature) impacts the earth's living atmosphere. It is mainly caused due to the trapping of sunlight and solar radiation also the returning heat from the earth's surface by the pollutant gases like CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>2</sub>, and other fluorinated gases; their effect is known as the greenhouse effect. It is observed that the average global temperature rises of 0.18°C per decade (Amanda MacMillan Jeff Turrentine, 2021). Thus, in response to minimizing the risk of global warming, we need to reduce carbon emissions by as much as 40% by 2030 (Fiona Harvey, 2014) if we want to minimize climate change impact. The consequences of global warming are being felt everywhere. The major global event includes heavy

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rainfall in Kerala, nearly no rainfall in monsoon time in northern India, five wave of rainfall in Pakistan etc. Extreme heat waves have killed tens of thousands of people worldwide in recent years. Additionally, As long as fossil fuel consumption continues at its current rate, sea levels will rise several meters during the next 50 to 150 years, causing havoc on coastal towns all over the world. Between 1990 and 2012, the overall Greenhouse gas (GHG) emissions of EEA members varied, with greenhouse gas emissions falling by 14% in 33 EEA countries (*Why Did Greenhouse Gas Emissions Decrease in the EU between 1990 and 2012?*, 2014). In figure 1.1 (right), an obvious exponential curve can be seen going all the way back to the 1980s on a graph that shows carbon emissions by humanity into the atmosphere. If we take a deeper look over the past ten years, we'll see some neglected yet incredibly disturbing facts: On a worldwide basis, all of the scientific research and clean technology has been completely ineffective. Fossil fuels have a number of negative environmental effects, such as air pollution, global warming, worsening air quality and climate change.

### **1.1.1.3 Energy Security**

The term energy security expresses a continuous supply of energy essential to run the economy. Economic growth and energy consumption are interdependent. So, a stable energy supply is crucial for the political world and a challenge like technical and financial for both developed and developing nations. Prolonged disruptions would cause serious problems for most societies' ability to function economically and fundamentally. More than 90% of our country's energy need is fulfilled by conventional energy sources like coal, petroleum etc. (*India Energy Outlook 2021*, n.d.). So uneven distribution of conventional energy sources and the point to be noted here is we are one of the world's largest crude oil and coal importers. So, geopolitical interference impacts

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our energy security even if we are not directly or indirectly involved in the conflict. So, we need to shift our attention towards sustainable renewable energy sources for our energy needs and energy security because renewable energy sources are evenly present through-out the globe. Energy import reduction, diversification of supply portfolio, less sensitivity of the economy to price volatility, and energy security are all benefits of renewable energy. The use of renewable energy can also contribute to improving the dependability of energy services in areas that usually lack appropriate grid access. By utilizing a range of energy sources, sound management, and well-designed systems, energy security can be improved.

## **1.2 Renewable Energy Potential and Applicability**

### **1.2.1 Renewable Energy and its Challenges**

Global warming is mainly caused by carbon emissions. To minimize its impact and motivate the using of renewable energy, numerous initiatives have been made. However, there are certain challenges Infront of us adopting this technology are high installation costs. Lack of infrastructure, power storage system and lack of government support and policies are major hurdles in implementation of renewable energy.

### **1.2.2 Coupling Renewable Energy with Energy Storage System**

The interactive inverter supplies the main service panel with the dc power that the PV modules generate when the sun shines. The interactive inverter will shut down during a power loss and "interact" with the grid to send any excess electricity to the utility. This stops the PV modules from generating electricity that might activate downed power lines.

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There is a ~7% of voltage fluctuation limit that which power grid system can tolerate, which has already been achieved by direct supply of PV system, but for further supply of direct power from the PV, we necessarily need to connect the solar grid system to the battery storage system. So here point to be noted is that to utilize the full potential of the renewable solar energy system, we need to couple our solar system with the big battery storage system to achieve our energy need goal from the renewable energy sources.

### **1.2.3 Classification of Energy Storage**

**1.2.3.1 Grid Energy Storage:** Large-scale grid energy storage is accomplished via grid energy storage techniques. Electrical energy is stored during periods of high supply and low cost (power sources such as renewable electricity from wind, tidal, and solar power) or low demand and is then released back into the grid during periods of low supply and high cost of electricity. The deployed grid-scale battery storage capacity increases 44-fold to 680 GW in the Net Zero Scenario between 2021 and 2030. Up from 6 GW in 2021, about 140 GW of capacity will be created in just 2030. Annual additions must increase dramatically, reaching an average of over 80 GW per year over the years 2022–2030, to stay on pace with the Net Zero Scenario (*Grid-Scale Storage, 2022*). In addition to lithium-ion batteries, flow batteries may prove to be a game-changing innovation in stationary storage because they exhibit no performance deterioration for 25 to 30 years and can be scaled to meet varying levels of energy storage with a little upfront cost. With a capacity of 100 MW for 4 hour (400 MWh), the largest Vanadium redox flow battery in the world was put into service in China in July 2022. Redox flow batteries (RFB) are Electrochemical energy storage devices where energy is stored in liquid electrolyte solutions which flow through electrochemical cells during charge/discharge figure 1.2.



**Figure 1.2** Schematic of redox flow battery for grid energy storage system (left) Portable electronics employing Li-ion battery storage technology (middle) Schematic of battery pack in electric vehicles (right) (figure taken from open internet source)

### 1.2.3.2 Portable Electronic Energy Storage

Lithium-ion battery dominance in the portable electronic energy storage market for the last three decades because of high gravimetric energy compared to other storage systems. LIB is employed in the majority of portable consumer devices (figure 1.2 middle), including cell Cameras, laptops, and cell phones. In the past 15 years, LIBs for the portable electronics segment experienced a volumetric energy density rise of two- to three-fold. However, demand anticipated ~20% annual growth, whilst energy density is estimated to increase by ~10% annually (Hui (Claire) Xiong, 2018). There is a need for the replacement of complete conventional energy from bikes to Aeroplanes in the transportation sector. So, all eyes are on high-energy-density LIB from the aviation sector.

### 1.2.3.3 Electric Vehicles (EV's):

Increasing fuel prices and climate change have made a more sustainable option necessary. LIB a more cost-effective and environmentally responsible choice. Recent forecasts suggest that more than half of passenger vehicles sold by 2035 will be electric vehicles. They are not only cost-effective in the long run but also environmentally friendly. Coming to the design of the battery, the battery pack in electric vehicles

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consists of thousands of cells managed by charging and discharging. Battery pack comes in cylindrical, prismatic, and pouch cells arranged into the module and assembled into the pack, and these packs are glued together (figure 1.2 right). The need to reduce the quantity of metals mined for EV batteries is the first hurdle. A single-car lithium-ion battery pack (NMC532) contains about 35 kg of nickel, 20 kg of manganese, 14 kg of cobalt, and 8 kg of lithium (23. *Battery Challenge Nature*, n.d.).

### **1.3 Energy Storage: Rechargeable Battery**

#### **1.3.1 Historical Background**

Initial development in energy storage by Leyden Jar in 1745 in the Netherland. Ewald George von Kleist experiments with cells in a jar and arranges in series to make a battery. An Italian physicist Volta created the first liquid electrolyte battery in 1800, using alternatively arranged zinc and copper discs separated by cardboard and submerged in salt water. French physicist Gaston Plante invented the rechargeable lead-sulfuric acid battery in 1859 (Kurzweil, 2010). Jungner discovered the Ni-Cd battery in 1899 (Eguro, 2014). Na-S batteries with ceramic electrolyte ( $\beta$ -alumina) operated at high temperatures (300 °C) were developed by Ford Motors researchers in the 1960s (Paul Breeze, 2019). In the 1970s, Li-ion was the first investigation for energy storage applications.  $\text{TiS}_2$  was initially proposed by Whittingham for electrochemical lithium insertion and application in energy storage devices. In 1980 Pro. J.B Goodenough developed layered oxide for  $\text{LiCoO}_2$ , used as a positive electrode material for lithium storage. Meanwhile,  $\text{Na}_x\text{CoO}_2$ , is also investigated as a Sodium-ion battery cathode. Graphite anode invention by Rachid Yazami in 1982 and a complete rechargeable LIB prototype by Asahi Chemical, Japan, in 1991 effort help to commercialize LIB by Sony for portable electronics.

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### **1.3.2 Introduction and challenges of Li-ion Battery**

Basic Li-ion cells are joined in parallel or series to enhance voltage or in combination to boost current in a Li-ion battery. A module can incorporate several battery cells. A battery pack can intergrade many modules. For instance, a typical Tesla car's 85 kWh battery pack has 7104 cells (Matt Pressman, 2017). An electrolyte containing lithium-ions separates the cathode (positive electrode) with the anode (negative electrode) of a standard Li-ion cell. A separator, commonly used, is a microporous polymer membrane that separates the electrodes and permits the lithium-ions movement between the two electrodes through electrolyte and electron from the outer circuit. High cost, global abundance and geographical distribution of Li resources are major concern of Li ion battery over its future availability and uses. Thus, there is urgent need of its alternative.

### **1.3.4 Na-ion battery (NIB) as an Alternative to Li-ion Battery (LIB)**

Keeping in mind the issue of raw material cost, safety and geopolitical interference in Li supply, we need to look into the LIB alternative. Na just comes below Li in the periodic table. Size of Na (0.102 nm) is comparatively bigger than Li (0.076 nm), and electrochemical potential (-2.7 V vs SHE) is nearly comparable to Li (-3.04 V vs. SHE). Huge presence in earth crust (x 1400 time of Li) availability (Yabuuchi, Kubota, et al., 2014a) these factors make Na as a suitable candidate for Li alternative. The current collector used at the anode side in NIB (Aluminium) is cheaper than the Cu used in LIB; also, Aluminium does not form an alloy with sodium, while Al forms an alloy with Li in LIB. The CO<sub>2</sub> signature of the Al is less than the Cu. Due to the high softness of Al, machinability is easy, and dendrite formation might be more effectively prevented than in the case of Li. Another important advantage of NIB is the transport



and charge transfer property of sodium ions in liquid or polymer electrolytes is easier than the Li due to the lower solvation enthalpy.

**Table 1.1:** Comparison of some alkali metals on basis of earth crust abundance, effective ionic radii, and standard potential. (Shannon, 1976)

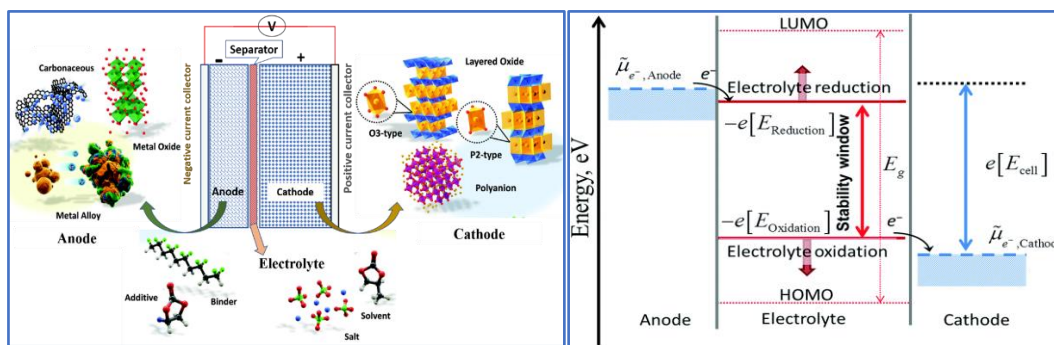
<b>Element</b>	<b>Abundance</b>	<b>Ionic size (nm)</b>	<b>Standard Potential(V) vs. SHE</b>
<b>Li</b>	0.002 %	0.076	-3.040
<b>Na</b>	2.8 %	0.102	-2.713
<b>K</b>	2.6 %	0.138	-2.924
<b>Mg</b>	2.1 %	0.072	-2.356
<b>Ca</b>	3.6 %	0.100	-2.840
<b>Zn</b>	0.007 %	0.074	-0.763
<b>Al</b>	8.1 %	0.054	-1.676

## **1.4 Sodium-ion Battery**

### **1.4.1 Introduction**

Room temperature Non-aqueous was first studied in the 1980s and had rapid revival to date. Today companies like Faradion, AMTE power, and HiNa battery are the major manufacturer of sodium-ion batteries. NIB high a performance, safe, and cost-effective battery solution for key applications, such as transportation, storage, backup power, and energy in remote locations. It Provides lithium-ion performance at lead-acid prices. Sodium-ion battery employs the rocking chair mechanism where sodium-ion moves from cathode to anode and vice versa through the ion-conducting electrolyte. Battery

technology and storage mechanism are very similar to LIB. However same technology as LIB can't be applied to NIB because of size difference ( $\text{Na}^+$  ion 0.076 nm and  $\text{Li}^+$  ion 0.102 nm), standard electrode potential ( $\text{Na}$  -2.71 V vs. SHE and  $\text{Li}$  -3.04 V vs. SHE) also, the molecular weight of sodium is higher than the  $\text{Li}$  ( $\text{Na}$  23 g/mol and  $\text{Li}$  6.9 g/mol) means theoretically gravimetric capacity of  $\text{Na}$  is less than the  $\text{Li}$  (1168 mAh/g and 3884 mAh/g). Thus, due to the enormous demand for the energy storage system, sodium-ion battery has huge potential to establish itself as a LIB storage alternative.



**Figure 1.3** Graphical design of NIB with the component (left) (Hwang et al., 2017). Schematic potential limit for cathode and anode, stability window of electrolyte and HOMO, LUMO energy level (right) (Peljo & Girault, 2018)

## 1.4.2 Literature Review: Sodium-ion Battery

### Material Selection

The energy density of the Na-ion battery is strongly dependent on the average working voltage and specific capacity. Therefore, to design a high energy density battery needs the sensible design of electrodes. The selection of electrodes depends on the electrolyte electrochemical potential window. The cell potential is the difference between the electrochemical potential of the cathode and anode. The working voltage of cell is

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dependent on the electrolyte potential window, which is the difference between the Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Both electrodes are electronically conducting; an anode electrochemical potential ( $\mu_a$ ) higher than the electrolyte LUMO will reduce the electrolyte unless the passivation layer creates an electron transfer barrier from the anode to the electrolyte. Similarly, A cathode with an electrochemical potential ( $\mu_c$ ) below the HOMO will oxidize the electrolyte unless a passivation layer blocks electron transfer from the electrolyte HOMO to the cathode. Thus, for a thermodynamically stable cell electrode, electrochemical potential should be within the electrolyte window. The electrochemical potential of electrodes is shown in figure 1.3(right).

The open circuit potential of the cell is represented as

$$eV_{oc} = \mu_a - \mu_c \leq E_g$$

where  $e$  is electron charge magnitude. A passivating layer at the electrode-electrolyte interface stabilizes the gives kinetic stability to higher  $V_{oc}$ .

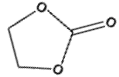
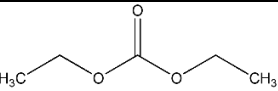
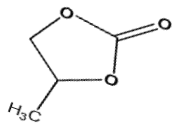
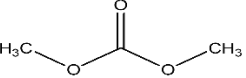
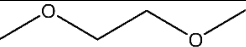
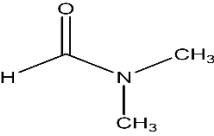
## **Electrolyte**

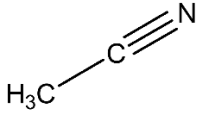
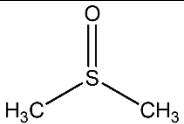
Electrolytes play a crucial role in battery, providing  $\text{Na}^+$  ion conduction path and acting as ion conduction medium between cathode and anode and preventing self-discharge. The electrolyte should support all Faradaic activities taking place at the electrodes throughout cell operation. This implies that the electrolyte should have a broad electrochemical stability window in order to prevent any significant electrolyte degradation. The electrolyte is composed of salt in a high-dielectric solvent, which easily dissociates the salt ion. To functionalize, an electrolyte additive like FEC (fluoroethylene carbonate) is added, which modifies the SEI (Solid electrolyte

interphase). Electrolyte for a sodium-ion battery can be classified into four categories i) Aqueous electrolyte in which sodium-containing salt is dissolved in water ii) Nonaqueous electrolyte where sodium-containing salt (table 3) are dissolved in non-aqueous solvent (table 2). iii) ionic liquid-based electrolyte where organic salt is doped with sodium salt equivalent iv) polymer gel electrolyte v) ceramic electrolyte. We are here primarily discussing non-aqueous liquid electrolytes due to their high ionic conductivity. The most commonly used electrolyte is 1M NaPF<sub>6</sub> in EC: DEC: PC.

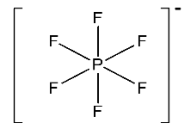
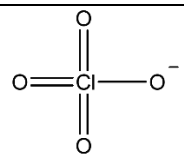
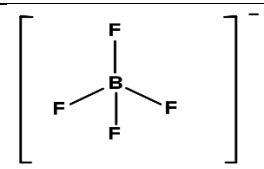
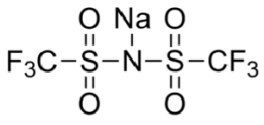
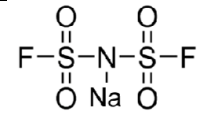
Other salt and solvent used for the sodium-ion battery is tabulated below

**Table 1.2** Properties of commonly used solvent/co-solvent for sodium-ion battery. (Tian et al., 2022)

Solvent/ Cosolvent	Chemical structure	T <sub>m</sub> (°C)	T <sub>b</sub> (°C)	T <sub>f</sub> (°C)	η (cP)	e/ 25°C	E <sub>Lumo</sub> (eV)
EC		36.4	248	160	1.9 (40°C)	89.78	1.175
DEC		-74.3	126	31	0.75	2.8	1.288
PC		48.8	242	132	2.53	64.92	1.235
DMC		4.6	91	18	0.59 (20°C)	3.1	1.054
DME		-58	84	0	0.46	7.2	-
DMF		-60.4	153	67	0.8	37	-

<b>ACN</b>		-44	81.6	2	0.35	38	-
<b>DMSO</b>		18.4	189	95	1.99	46.7	-

**Table 1.3** Commonly used salt for sodium-ion battery with property (Tian et al., 2022).

<b>Salt</b>	<b>Anion Chemical structure</b>	<b>T<sub>m</sub> (°C)</b> <b>Na(Li)</b>	<b>Al corrosion</b>	<b>In 1M solution (mScm<sup>-1</sup>) [solvent]</b>	<b>Anodic stability V vs.(Na/Na<sup>+</sup>)</b>
<b>NaPF<sub>6</sub></b>		Dec 300 (dec)	No	7.9 (PC) 6.8(EC:DMC)	5
<b>NaClO<sub>4</sub></b>		468 (236)	No	6.4 (PC) 8 (EC:PC) 5 (EC:DMC)	4.7
<b>NaBF<sub>4</sub></b>		384 (293)	No	-	5
<b>NaTFSI</b>		257 (234)	High	6.2 (PC)	Limited to 3.4V by Al dissolution, but 5V with 5% NaPF <sub>6</sub>
<b>NaFSI</b>		118 (130)	High	0	Limited to 3.4V by Al dissolution, but 5V with 5% NaPF <sub>6</sub>

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Thus, for an efficient battery, electrolytes should have i) Excellent ionic conductivity, ii) inert towards cell component, iii) a Large potential window iv) a large thermal stability window.

### **Anode**

Research in anode has achieved high specific capacity as well as low potential in spite of that dendrite formation and safety concerns prevent its use as a negative electrode for sodium-ion batteries. Therefore, need for a safer and more efficient anode for sodium-ion batteries. Different type of anode material is used NIB, including carbonaceous, Alloying type, conversion type, and intercalation type.

### **Cathode**

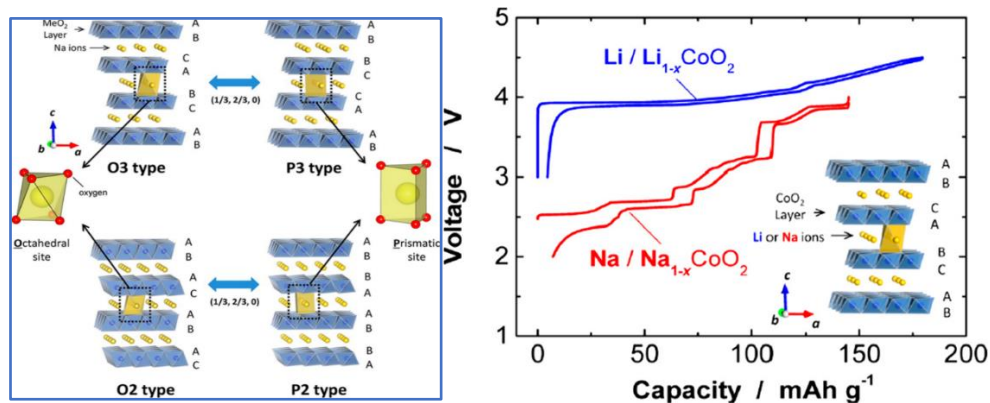
Cathodes are the most voluminous part of the cell; they affect the overall capacity, voltage, and power density of the cell. They act as intercalation hosts for sodium. For a material for good cathode, it should be electronically conducting, have a high diffusion coefficient for Na and high voltage with respect to the Na, and be low cost and high safety. A set of materials has been studied for sodium-ion battery cathode(M. Chen et al., 2019; P. F. Wang et al., 2018).

### **1.4.3 Challenges with Conventional Sodium-ion Battery**

Although layered transition metal oxides are excellent possibilities for high-capacity cathode materials for NIBs, electrode materials have three significant limitations are:

## Phase Transition

There are several oxygen layers stacking sequential changes taking place during charge-discharge in P2 and O3 phases. During de-Sodiation P2 to O3 phase transition takes place due to the gliding ( $60^\circ$ ) of the  $\text{TMO}_6$  layer resulting in contraction in the crystal structure and a decrease in interlayer spacing. Since big  $\text{Na}^+$  in the P2-type phase stabilizes large prismatic sites energetically, which causes  $\text{TMO}_2$  slabs to glide (move) to form octahedral sites after  $\text{Na}^+$  extraction with AB AC AB oxygen stacking (Tournadre et al., 2004). In general, bigger  $\text{Na}^+$  ions coupled with charge ordering and the ordering arrangement between  $\text{Na}^+$  and vacancies at different Na contents cause layered  $\text{Na}_x\text{TMO}_2$  to exhibit more complex phase transitions than its Li analogs after the removal of Na ions from alkali-ion layers. Improving the electrochemical performance of layered oxides in NIBs requires preventing or decreasing these irreversible phase transitions because they frequently result in structural collapse and a rapid capacity reduction.



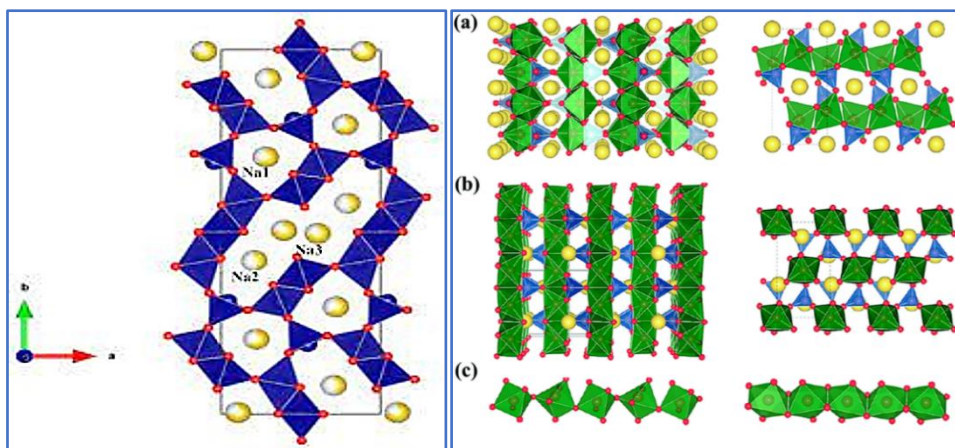
**Figure 1.4** Schematic of Phase changes in layered sodium Transition metal oxide (Yabuuchi, Kubota, et al., 2014b), Phase change in layered cathode  $\text{NaCoO}_2$  for sodium-ion battery (Abraham, 2020a)

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## 1.5 Polyanionic Cathode for Sodium-ion Battery

### 1.5.1 Introduction

In layered cathode material, structural stability is a big issue so here we are trying to design a material with a large framework and tunnel for easy sodium-ion migration. A bigger anionic network is built up ( $\text{XO}_4$ ) tetrahedra and  $\text{MO}_6$  octahedra, where  $\text{X} = \text{S}, \text{P}, \text{Si}, \text{Mo}$  etc. Here transition metal oxide octahedra ( $\text{MO}_6$ ) or square pyramid  $\text{MO}_5$  and anion tetrahedra ( $\text{XO}_4$ )<sup>n-</sup> connected in the edge-sharing, creating an S-shaped tunnel[figure 1.5(left)]. The sodium ions are primarily driven to diffuse along the c direction by this special tunnel shape.  $\text{Na}_{0.44}\text{MnO}_2$ , a combination with tunnel-like properties, was first presented by Hagemuller's group in 1971 (Cox et al., 1971).



**Figure 1.5** Sodium-ion movement in tunneled polyanion structure (left) (Ferrara et al., 2018), Schematic of  $\text{NaFePO}_4$  (a) Olivine (b) Maricite (c) Corner sharing and edge-sharing among neighboring  $\text{FeO}_6$  and  $\text{PO}_4$  (right). (Galceran et al., 2014; Saracibar et al., 2016)

### 1.5.2 Phosphates

Commercialization of  $\text{LiFePO}_4$  inspired by its analog  $\text{NaFePO}_4$ , it is found to be in two phases, Olivine and Maricite (Avdeev et al., 2013; Moreau et al., 2010). In the Olivine phase,  $\text{FeO}_6$  and  $\text{PO}_4$  are connected to each other in the corner-sharing fashion and



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building 1D tunnel structure for sodium migration along the b axis. In contrast, in the case of Maricite, neighboring  $\text{FeO}_6$  units are edge shared and then connected with  $\text{PO}_4$  by corner sharing manner since there is no diffusion channel in Maricite (figure 1.5 (right)) so it is electrochemically inactive. The Cabanas group develops the olivine  $\text{NaFePO}_4$  reaction mechanism and claims 17.58% volumetric change between the two end members of the system and formation of the intermediate phase  $\text{Na}_{2/3}\text{FePO}_4$  (from  $\text{NaFePO}_4$  to  $\text{FePO}_4$ )(Galceran et al., 2014; Saracibar et al., 2016)

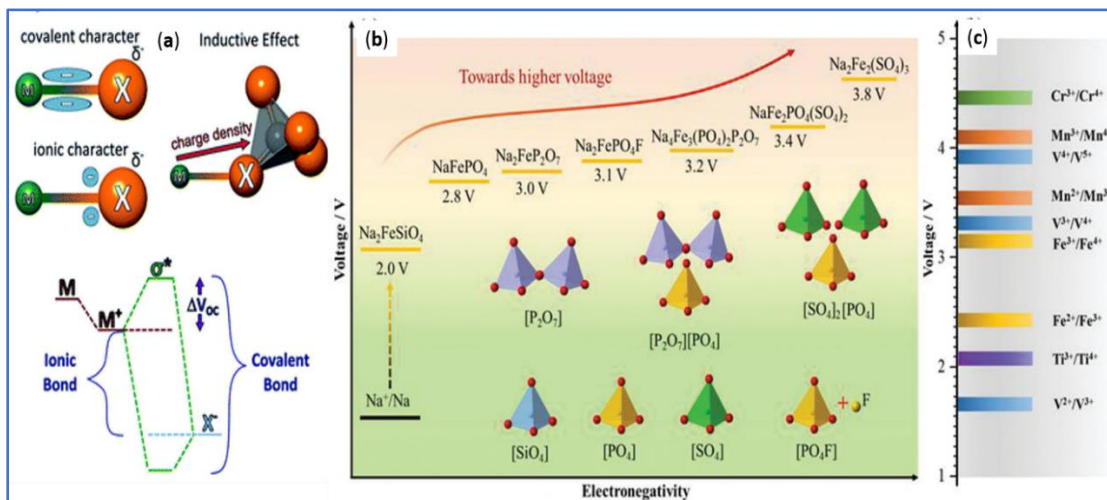
### 1.5.3 NASICON

Natrium superionic conductivity (NASICON) is the class of structurally stable material with generalized formula  $\text{A}_x\text{M}_2(\text{XO}_4)_3$  ( $1 \leq x \leq 4$ ) where A is alkali metal (Na, Li, K, Rb, Mg, Ca etc.) and M is the transition metal (Fe, Cr, Mn, Co, Ni etc.), X is polyanion (S, P, Si, B). Here  $\text{MO}_6$  octahedra are connected by corner sharing with  $\text{XO}_4$  tetrahedra making a tunnel skeleton for sodium-ion migration. NASICONs are well known for their excellent structural stability and ionic conductivity. The first NASICON material,  $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$  ( $0 < x < 3$ ), was described as a solid-state electrolyte in the 1960s by Goodenough et al(Goodenough et al., 1976). This structure allows for the replacement and tuning of both the cation M and anion X, providing excellent material engineering flexibility(S. Chen et al., 2017; Jian et al., 2017a).

## 1.6 Materials Optimization and Design

First is the material instability is the major concern for layered material for sodium-ion batteries. So, designing a material with a framework skeleton which provides a stable structure on sodium intercalation. The second challenge is to increase the Energy density of the battery since energy density is a product of specific energy and

electrochemical potential of the electrode. So, we are here designing a high-potential window cathode for achieving a high energy density battery. We consider  $AM_2(XO_4)_3$  a polyanionic NASICON where A is an alkali metal like Li, Na, K etc., and M is a transition metal like Fe, Ni, Co, Mn etc. X is S, P, B etc.  $Fe_2O_3$  cathode provides the cell voltage  $<2.0$  V,  $Fe_2(MoO_4)_3 <3.0$  V,  $Fe_2(WO_4)_3 <3.0$  V,  $Fe_2(SO_4)_3 <3.6$  V in all these cases, iron is in same oxidation state and attachment of polyanion playing a crucial role in shifting up of redox energy by altering the Fe-O bond characteristics. Here X-O bond plays an important role in altering the ionic character of the M-O bond through the **inductive effect**. Strong X-O bonding in polyanion-type compounds can bring about ionicity in M-O bonding, and the latter's weaker ionic bonding lengthens the gap between its antibonding orbitals relative to the Na/Na<sup>+</sup> redox pair, resulting in a larger redox potential.



**Figure 1.6** Schematic description of (a) inductive effect in polyanion. (b) the redox potential of different Fe-based polyanions (c) the redox potential of different transition metals (Niu et al., 2017; Niu et al., 2019).

Additionally, the strong X–O covalent connections significantly increase O's stability in the lattice, enhancing the materials' safety and making them more appropriate for

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rechargeable secondary batteries. Thus, I have started work with mixed Iron polyanion  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  NASICON to achieve higher redox potential by following the path of figure 1.16b for better structural stability and enhanced electron transfer.

## **1.7 Target of Na-ion Battery**

The global battery market is expected to grow at a compounded annual growth rate of 14.1% from 2020 to 2027 to reach USD 310.87 billion by 2027. The market growth is attributed to the high demand for automotive applications (*Battery Market Size, Share & Trends Analysis Report*, 2019), and the global sodium-ion battery market was valued at USD 1025 million in 2021 and is estimated to reach an expected value of USD 2665 million by 2030, growing at a CAGR of 11.2% during the forecast period (2022 – 2030) (*Sodium-Ion Battery Market*, 2022). Sodium-ion battery has set their footprint across the globe as a large-scale and low-cost alternative for lithium-ion batteries. Increased demand for electric vehicles is the primary driver of the Sodium-ion Battery Market. In recent years, there has been a significant drive to electrify transport to lower carbon emissions from fuel use. Fuel expenses account for around 30% of telecom tower running costs. Thus, companies are actively searching for energy-efficient alternatives. The telecom sector is being affected by rising fuel prices. Smart grid relies on reliable power, and sodium-ion batteries can be largely used to meet grid energy storage requirements. Current R&D in battery technology is growing rapidly to accommodate the exponential demand of energy storage. Alleviating pressure on lithium reserve is the primary moto of lithium alternative battery research.