



# Group 14 elements (Si, Ge, Sn) based anodes for Lithium Ion Battery: An Overview

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**Abstract**— Lithium-ion batteries have become the most prominent alternative energy sources. But to serve the need of portable devices and electric vehicles, immense efforts are required to be made to provide high energy density with low cost and long cycle life. Group 14 elements i.e. Si, Ge, Sn anode materials are regarded as the most promising alternatives to graphite to enhance the capacity of LIBs as a result of their high gravimetric and volumetric capacities, environment friendliness and natural abundant reserves. However effective practical implementation of Si/Ge/Sn based anodes LIBs is hampered by the drastic volume expansion during lithiation and delithiation accompanied by the formation of unstable Solid Electrolyte Interface (SEI) layer leading to loss in coulombic efficiency and capacity fading. In the last two decades, tremendous research has been taken place in order to overcome these issues. Among them, the most interesting approach includes preparing the nanostructure materials. But this technique is not very cost effective and moreover, Si/Ge/Sn nanostructure materials have been encountered with low coulombic efficiency. The other effective technique is to prepare the composite anodes using conductive additives. This review focuses on the present challenges and strategies for improving the group 14 elements (Si, Ge, Sn) based anodes for highly efficient Lithium-Ion Batteries.

**Keywords**— Lithium-ion battery, high-capacity anodes, Solid Electrolyte Interface, All-solid-state batteries; 14 group elements

## I. INTRODUCTION

At present, up to 80% of the energy demands are fulfilled by fossil fuels. This huge consumption is not only depleting the fossil fuels at a very fast rate but also leading to high CO<sub>2</sub> emission causing various issues like

environmental pollution, global warming & climate change, respiratory diseases etc [1]. Thus, to achieve country's goal of low carbon future, it is necessary to produce clean, safe and sustainable form of energy. Energy from natural renewable energy resources like solar energy, wind energy can be the solution, but these suffers from various limitations. One of the major issues with these renewable energies is their dependency on daily or seasonal weather fluctuations hence they are not efficient to provide continuous flow of energy and requires a lot of space. To bridge this gap of demand and supply, an efficient storage media is necessary. Among various energy storage devices, Li-ion battery is one of the best solutions to reduce the dependency on fossil fuels without high infrastructure expenses. The first lithium-ion battery was commercialized in 1991 by Sony. From the last few decades, there has been vast growth in lithium-ion battery related industry. From portable devices, mobile phones, laptops to transportation EVs and HEVs, there is rapidly increasing demand of Lithium-ion battery. High energy density, self-discharge, low maintenance, higher cell voltage, no memory effect, longevity, lighter mass, all these characteristics make lithium-ion batteries a versatile device and best choice over other rechargeable batteries like lead-acid battery, Ni-Cd battery, Nickel metal hydride battery [2]. The major elements of battery are cathode, anode, electrolyte on which the overall performance and the characteristic of battery depends. Most of the commercialized lithium-ion batteries consist of lithium metal oxide as cathode and graphite as anode having theoretical gravimetric capacity of 372 mAh/g and volumetric capacity of 756mAh/cm<sup>3</sup> with respect to graphite anode [3]. The electrochemical process taking place in lithium-ion battery is due to the movement of Li-ions between anode and cathode. During charging, Li-ions from cathode moves towards the anode through the electrolyte. In the case of graphite anode, all the Li-ions get intercalated within the

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layers of graphite. Once all the Li-ions reach the anode structure to saturate it, the cell is said to be fully charged. During discharging, all the Li-ion moves in reverse direction and reaches the cathode. Thus, current flows from cathode to anode in the outer circuit. The electrolyte acts as ionic conductor providing the path for the flow of Li-ions within the cell and obstructing the flow of electrons. During both the process, electrons flow through outer circuitry [3].

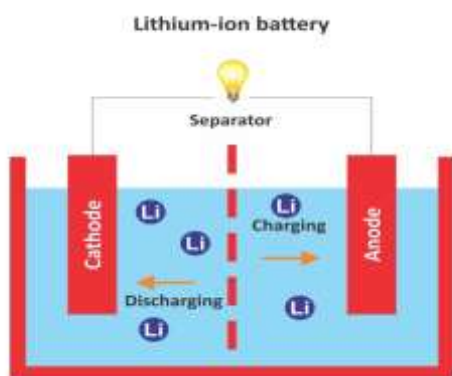


Fig .1 Lithium Ion Battery working.

Despite having a wide application, a variety of challenges and opportunities still needs to be rectified to make LIBs worthy to meet the present-day energy demands. One of the biggest challenges that need to be accomplished is the low energy storage capacity. For enhancing the overall performance of LIBs, anode materials play a very vital role [3,4] as anode materials are responsible for storing Li ion within their structure during charging. The fully lithiated state of graphite anode is  $\text{LiC}_6$ . Hence six (6) carbon atoms are utilized to hold only one Li ion, which is too low to meet up the present high energy demands. Thus, to achieve the objective of higher specific capacity especially in case of EVs, large number of cells are required, which not only increases the size, makes the device bulky, but also the cost of device is augmented. This dependence loop of cost, size, total mass of the device urges for the development of anode materials with higher energy and power density, low cost, safe and environmentally friendly features. Thus, in improving the capacity of battery, intrinsic characteristics, and morphology of anode materials both play significant role. Among numerous types of anode materials, Group 14 elements Silicon (Si), Germanium (Ge), Tin (Sn) are considered as the most promising anode materials having gravimetric capacities in the range 1000- 4000 mAh/g [4].

## II. OPPORTUNITIES WITH GROUP 14 ELEMENTS

Due to low specific capacity of graphite anodes, LIB technology still cries for great research to improve its overall performance. From the last few years, group 14 elements particularly Silicon (Si), germanium (Ge), Tin (Sn) has gained the attention of researchers because of

their high theoretical specific capacities 4200 mAh/g [4,5], 1625 mAh/g [6], 994 mAh/g [7] corresponding to the fully lithiated phase  $\text{Li}_{22}\text{Si}_5$ ,  $\text{Li}_{22}\text{Ge}_5$ ,  $\text{Li}_{22}\text{Sn}_5$  respectively [4-7]. Thereby having the capacity of storing 4.4 Li ions per atom, whereas for graphite the capacity is limited to 372 mAh/g corresponding to fully lithiated state  $\text{LiC}_6$ . Moreover, for graphite, lithiation voltage is  $<0.1\text{V}$  whereas in case of Si, Ge, Sn it is quite high  $\sim 0.2\text{V}$  [4]. This higher value affects the electrochemical performance by avoiding electrodeposition of lithium on anode and also enhance the safety performance of LIBs. Besides these advantages, there are certain qualities of Si, Ge, Sn which makes them outstanding anode material over other discovered anode materials like (i) silicon is the second most abundant element on earth ( $\sim 27.7\%$ ), (ii) Ge and Sn have high electrical conductivities, (iii) all the three materials are environmentally friendly in nature [4]. Thus, replacement of graphite with Si, Ge, and Sn will definitely result in high energy density, safe and lighter batteries..

## III. CHALLENGES WITH GROUP 14 ELEMENTS

The group 14 elements (Si, Ge, Sn) have great advantages over other elements as discussed in previous section but on the other hand, these materials suffer from certain challenges which inhibit their commercialization. The interaction of Li-ion with these elements is based on alloy mechanism instead of intercalation that occurs in graphite anodes forming  $\text{Li}_x\text{M}$  type compounds ( $\text{M} = \text{Si, Ge, Sn}$  and  $x > 1$ ). In addition, the alloying mechanism is more complicated and time consuming in contrast to intercalation [8]. As a result of alloy reaction these materials suffers from huge volume expansion due to intake of large amount of Li. All the three elements Si, Ge, Sn have been reported to undergo volume change of approximately 400%, 270%, 257% respectively during lithiation and delithiation, resulting in cracks and even pulverization of particles [9].



Fig.2 volume expansion

Some of the major issues that occurs due to volume expansion are-

- i) Because of the violent volume change during the cyclic process, the electrical contact between the anode and current collector is disconnected and these isolated domains are unable to contribute in enhancing the battery capacity [4].
- ii) The Solid Electrolyte Interface (SEI) layer formed during the initial charge- discharge cycle as a result of reaction between electrolyte and active material. This layer acts as a barrier between electrolyte and anode, also preventing the decomposition of electrolyte. Due to violent expansion the SEI layer breaks and aids the recurrent

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formation of new SEI layer, which not only consumes large number of Li-ions but also makes the layer thicker, increasing the resistance in ionic conduction. It also leads to reduced coulombic efficiency [4]. Hence, the instability of SEI layer at the interface between anode material (Si, Ge, Sn) and electrolyte is another cause which hampered the commercialization of these materials

#### IV. STRATEGIES TO OVERCOME THE CHALLENGES

Various approaches have been made in the last few years in order to maintain the structural integrity of Si, Ge and Sn electrodes and also to stabilize the electrode-electrolyte interface. The most constructive approaches include:

- 1) Reducing the particle size to nanometer range and
- 2) Preparing composite anodes using conductive additives.

Remarkable advancement has been achieved by advancement in nanotechnology and composites materials in extending the cycle life and improving the rate performance of next generation LIBs.

##### **Nanostructured Si, Ge, Sn anodes**

The size of the particles plays significant role in improving the electrochemical performance of Lithium-Ion Battery. Decreasing the size to nano scale increases the surface to volume ratio which helps in reducing the mechanical stress arising from volume expansion. Also, the distance for electron transfer and Li-ion diffusion is shortened thus permitting the rapid lithiation / delithiation [10], thereby improving electrochemical stability, rate capability, cycle life.

E. V. Astrova and co-workers prepared the nanostructured single crystal silicon anode using photolithography, electrochemical anodization, and subsequent anisotropic shaping. The authors reported that nanostructured anodes with 300-nm-thick walls, were able to retain a constant discharge capacity and Coulombic efficiency close to 100% for more than 1000 cycles at 0.36 C [11]. Ge and co-workers synthesized silicon nanowires as anode by direct etching of boron doped silicon wafer. This anode was reported with high electrochemical performance and long cycle life with capacity retention of 2000 mAh/g at 18 A/g after 250 cycles [12]. A binder free nanostructure germanium anode prepared by S. Fugattini et al. was reported with 95% capacity retention at 1C and 450 mAh/g at 60C [13]. The nanowired anodes of germanium oxide with diameter 20-40 nm and length ~0.5µm showed great features with specific capacity of 1300 mAh/g at 1C and 4C at room temperature and at low temperature capacity of 255 mAh/g at -50°C [14]. Zhang et al. reported the monolithic Ge microcubes as anodes of nanoscale blocks shows improved high initial coulombic efficiency of 91.8% and 80% for half cells and full cells respectively [15]. The SnSb nanostructured electrode prepared by Walter et al. exhibit initial coulombic efficiency of 63-70% over 100 cycles. Also, when paired

with LiCoO<sub>2</sub> cathode showed the energy density of 340 Wh/ kg and a capacity retention up to 60 cycles [16].

It has been reported that although nanosized Si, Ge and Sn based anodes are able to mitigate pulverization issues, but the volume expansion still exists, as a result of which, SEI layer still demolishes and continuously reforms, hence reducing coulombic efficiency [4,10]. Also, this technique is costly which constraints the wide commercialization of nanostructure group 14 (Si, Ge, Sn) element-based anodes for Lithium-Ion battery. To overcome the shortcomings of nanosized anodes, another constructive approach is the preparation of composites using carbon additives.

##### **Si, Ge, Sn based composites anodes**

Preparing composite anodes using carbon additives (carbon nanowires, graphite etc.) and group 14 materials (Si, Ge, Sn) have been proved to exhibit effective improvement in electrochemical performance because of its softness, high electrical conductivity, good mechanical strength, ability to store lithium and little volume expansion. The carbon additive coating on the surface averts the head on exposure of anode material to the electrolyte, hence stabilizing the SEI layer and enhancing the coulombic efficiency [4]. Thus, for commercialization of these high-capacity group 14 element-based anodes preparing their composites with carbon additives is effective technique. Though, there is need for sound research to be done in this respect to meet up the future energy demands with highly efficient Lithium-Ion Battery using Si, Ge, Sn based anodes.

Wang et al. analyzed the behaviour of monodisperse Si-C nanocomposite spheres. The study reveals that monodisperse spherical nature alleviate the fracture in the anode material and carbon coating prevents the Si atom to directly interact with electrolyte, thereby maintaining stable solid electrolyte interface and also improves the coulombic efficiency. The prepared electrode showed a high reversible capacity of 3207 mAh/g with capacity retention of 85% for 100 cycles [17]. The performance of composite anodes using nanoporous Si particles, Li<sub>3</sub>PS<sub>4</sub> solid electrolyte and acetylene black (AB) was examined by Ryoto Okuno and co-workers, the results shows that charge capacity increases with increasing the content of carbon additive from 2700 mAh/g – 3015 mAh/g and new conduction paths are created by adding carbon additive [18]. A wide range of literature suggests the high feasibility of Ge/C nano composites based full cell. Li et al. fabricated a C-Ge composite anode [19]. Carbon coating provides a large surface area and mitigates the massive volume change. This electrode had shown high conductivity and good structural stability [19]. Recently, Zhang et al. fabricated a three-dimensional (3D) germanium/carbon porous composite anode. The in-situ X-ray diffraction and electrochemical dilatometry exhibit the carbon matrix and provide a high reversible lithiation and delithiation, resulting in low volume expansion and high stability [20].

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Sn has high electrical conductivity and is less brittle than Si [6]. Liu et al. [21] prepared a carbon-coated 3D Sn scaffold with interconnected pore structures. This 3D sphere-caged Sn/C composite increased the surface area for active material loading and reduced the stress due to electrode expansion. The composite electrode showed an initial coulombic efficiency of 78.8% and a volumetric capacity of  $\approx 1700 \text{ mAh cm}^{-3}$  over 200 cycles at 0.5 C. Moreover, the Sn/C anode of thickness  $\approx 100 \mu\text{m}$  showed good capacity retention. The Sn/C anode was further tested in a full cell with  $\text{LiMn}_2\text{O}_4$  as cathode. Even after 100 cycles, the Sn/C anode retained a volumetric capacity of  $\approx 1020 \text{ mAh cm}^{-3}$  at 0.5 C, showing that it may have an amazing electrochemical performance in practical full-cell Lithium-ion battery.

## V. CONCLUSIONS

Group-14 elements (Si, Ge, Sn) have emerged as the most promising alternatives of existing anodes for highly efficient LIBs because of very high capacities as compared to another element. From earlier times, great efforts have been made to develop high energy density, low cost, environmentally friendly LIBs using Si, Ge, Sn as anodes. Besides having various advantages, these materials suffer from drastic issues also i.e. volume expansion during lithiation / delithiation which leads to unstable Solid Electrolyte Interface (SEI) layer and low columbic efficiency, thereby inhibiting the commercialization of Si, Ge, Sn based anodes for LIBs. Though a lot of research has been done but still the practical application of these high-capacity materials based anodes is hindered because of low columbic efficiency and low capacity retention after long cycles. To mitigate these issues forming composite anodes using carbon additives can be effective in alleviating the volume expansion and also for improving the electrochemical performance. This is constructive and promising approach for improving the energy density of Lithium-ion Battery making them more economical and advantageous for large scale utilization.

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