A Review of Metal Silicides for Lithium-Ion Battery Anode Application

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Abstract

Lithium batteries (LIBs) with low capacity graphite anode ($\sim 372 \text{ mAh g}^{-1}$) cannot meet the ever-growing demand for new energy electric vehicles and renewable energy storage. It is essential to replace graphite anode with higher capacity anode materials for high-energy density LIBs. Silicon (Si) is well known to be a possible alternative for graphite anode due to its highest capacity ($\sim 4200 \text{ mAh g}^{-1}$). Unfortunately, large volume change during lithiation and delithiation has prevented the Si anode from being commercialized. Metal silicides are a promising type of anode materials which can improve cycling stability via the accommodation of volume change by dispersing Si in the metal inactive/active matrix, while maintain greater capacity than graphite. Here, we present a classification of Si alloying with metals in periodic table of elements, review the available literature on metal silicide anodes to outline the progress in improving and understanding the electrochemical performance of various metal silicides, analyze the challenges that remain in using metal silicides, and offer perspectives regarding their future research and development as anode materials for commercial LIBs application.

Keywords Li-ion battery · Metal silicides · Anode materials · Electrochemical performance

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1 Introduction

Lithium-ion secondary batteries, with high energy density (per weight and volume), and the ability to deliver high power output, have dominated the power source field for portable electronic devices [1–6]. However, current lithium battery technology cannot satisfy the increasingly demanding energy and power requirements of electric vehicles and power storage for certain renewable energy sources such as solar and wind energy. Thus, the development of batteries with high gravimetric and volumetric energy and power density has stimulated intense research interest in recent years. Many efforts have been made in exploring various battery anode/cathode materials, electrolyte, and separators [7–11]. One particular focus area is the development of new anode materials, with substantially higher energy densities, to replace currently existing graphite anodes which cannot fulfill the higher storage capacity requirements [9]. In this context, Si offers a theoretical maximum specific capacity of about 4200 mAh g^{-1} which is over tenfold greater than that of graphite (370 mAh g^{-1}) [12]. In addition to its outstanding capacity, Si is the second most abundant element in the Earth's crust with a global production of

over 7 million tonnes in 2012 [US geological survey]. Due to these attributions, much attention has been given to using Si as Li-ion battery anode material.

The use of pure silicon as an anode material in lithium-ion batteries has been limited by its high electrical resistivity, low diffusion coefficient of Li^+ within the Si structure, and most significantly, the large volume change during the alloying/de-alloying processes which ultimately leads to fatigue and degradation of the electrode [13–15]. The large volume change can be attributed to the formation of a series of Si-Li compounds according to the basic reaction: $x\text{Li} + \text{Si} \leftrightarrow \text{Li}_x\text{Si}$ ($x = 1.71, 3.25$ or 4.4). With increasing Li insertion in the host lattice, the volume per Si atom in the unit cell for each compound increases progressively. For example, the volume per Si atom in cubic $\text{Li}_{22}\text{Si}_5$ ($\text{Li}_{4.4}\text{Si}$) structure is 0.0824 nm^3 , four times higher than that of the parent Si atom (0.020 nm^3), which means a volume expansion 310% of the Si lattice takes place [12]. This large volume change during lithiation causes high internal stress, electrode pulverization, and subsequent loss of electrical contact between the active material and current collector, resulting in poor reversibility and rapid capacity fade [9]. Clearly, these issues are detrimental to the use of silicon in batteries where commercial market forces require long cycle lifetimes in the range of several thousand cycles.

In order to improve the performance of Si anodes (i.e., stabilization of high capacity and increased cycle lifetimes), several approaches have been developed to alleviate the detrimental effect of large volume change generated during the alloying/de-alloying processes. These approaches include: (a) particle size reduction to nanometer scale [16]; (b) Si/C nanocomposite structures [17]; (c) high porosity structures; (d) alternative binders [18]; and (e) metal-Si intermetallic compounds. This manuscript will focus on the applications of metal-Si intermetallic compounds (i.e., metal silicides) as an approach to obtain better capacity retention and cycle life.

Metal silicides are widely used in silicon integrated circuits as contacts and interconnections. In addition to microelectronics application, metal silicides are also important for other applications such as thermoelectric devices and jet engines. Of all these applications, we are particularly interested in the application of silicides in lithium-ion batteries.

This paper reviews the available literature on metal silicide anode materials published from the first use in 1999 [19], explores some of the recent development regarding to their synthesis and microstructural characterization/electrochemical performance in order to assess the viability of this type of material as a replacement for graphite in Li-ion batteries, and gives a general outlook for the application of metal silicides in LIBs. After analyzing the literature data, the challenges and future research directions/

PERIODIC TABLE OF ELEMENTS

Fig. 1 Metal elements used for the formation of silicides in the M-Si system

Table 1 Typical silicides of elements in metal groups

Elements	Group	Product
Li	I	$\text{Li}_{22}\text{Si}_5$ $\text{Li}_{13}\text{Si}_4$ Li_7Si_3 $\text{Li}_{12}\text{Si}_7$ LiSi
Ca	II	Ca_2Si Ca_5Si_3 CaSi CaSi_2
Mg	II	Mg_2Si
Ti	III	Ti_3Si Ti_5Si_4 TiSi TiSi_2
Co	III	Co_2Si CoSi Co_2Si_3 CoSi_2
Fe	III	Fe_3Si Fe_5Si_3 FeSi FeSi_2
Mn	III	Mn_3Si Mn_5Si_2 MnSi MnSi_2
Ni	III	Ni_2Si Ni_3Si_2 NiSi NiSi_2
Cr	III	Cr_3Si Cr_5Si_3 CrSi CrSi_2
Cu	III	Cu_3Si $\text{Cu}_{15}\text{Si}_4$ Cu_5Si
Ag	III	$\text{Ag} + \text{Si}$
Al	IV	$\text{Al} + \text{Si}$
Sn	IV	$\text{Sn} + \text{Si}$
Ge	IV	$\text{Ge}_{1-x}\text{Si}_x$ ($x = 0-1$ at%)

perspectives in the development of metal-silicide anodes are also indicated in this review.

2 Types of Metal Silicides and Their Effects on Electrochemical Properties

Metals (Ms) can be divided into four groups, as shown in the periodic table (Fig. 1). These are alkali metals (Group-I), alkaline earth metals (Group-II), transition metals (Group-III), and other metal elements (Group-IV). Metals in Groups I-III react with silicon to form one or more silicides except for Be, Zn, Ag, Cd, Au, and Hg. Metals in Group-IV do not react with silicon to form silicides, but they can form either a two phase ($\text{M} + \text{Si}$) structure such as Al-Si , Ag-Si , and Sn-Si or solid solution like Si-Ge system. Typical metal silicide products are listed in Table 1.

Metal silicides are classified into two types in this work, according to lithium inactive/active metals. One is Mi_xSi_y where Mi represents an inactive metal element such

as Ti (which does not form Li-containing compounds). The other is Ma_xSi_y , where Ma represents an active metal element such as Mg (which does form Li-containing compounds). Members of the Mi_xSi_y compound family can be used as anodes by virtue of the following reversible reaction [20, 21]:

In this context, the Mi plays a buffering role but does not actively participate in compound formation with the Li atoms, whereas in the case of Ma_xSi_y , the reversible reaction is shown in Eq. 2 [22, 23]:

For this scenario, both the Si and Ma are required for reaction with the Li cations. Formation of lithiated phase compounds occurs at different voltages, and thus, one component can act as a buffer for the other one. In these electrochemical reactions, the original anode materials can be converted into a Li–Si compound and a second displaced phase. The displaced phase, existing in the form of either pure metal or compound, can serve as a buffering matrix reducing the effect of the lithiated phase volume expansion during repeated cycling tests.

2.1 Binary Metal Silicides

Of all metal silicides, binary metal silicides drew the first attention on improving the electrochemical performance of silicon in lithium batteries. This section sorts out and discusses electrochemical performance of active and inactive binary metal silicide anodes reported so far.

2.1.1 Active Metal-Containing Ma_xSi_y

2.1.1.1 Mg–Si Magnesium and silicon are both naturally abundant, lightweight and inexpensive, and lithium can be inserted into Mg and Si at room temperature, which are desirable features for a battery material [24]. It has been reported that magnesium silicide possesses a highly specific capacity of 1370 mAh g^{-1} at 10 mA g^{-1} , equal to 3.9 Li per Mg_2Si . However, experimental testing showed that the capacity faded rapidly to less than 100 mAh g^{-1} after 10 cycles at 30 mA g^{-1} [19]. To understand the capacity fade, some reaction mechanisms were proposed by Roberts et al. [22]. During lithiation, the insertion of Li into Mg_2Si occurs first, and Li_2MgSi with a cubic fluorite type structure is then formed along with the extraction of Mg from Mg_2Si . Li_2MgSi is then converted to Li–Mg and Li–Si alloys at low current densities and low potentials during the lithiation process [22, 25]. The presence of Li–Mg and Mg phases

at the end of extraction was confirmed through X-ray diffraction (XRD) data analysis [19]. These irreversible reactions are attributed to the capacity fade, since lithium is then bound up inside the anode and thus not available for battery reactions. Moreover, Li insertion into the remaining Mg phase results in volume change, aggravating the cracking and disintegration of electrodes.

Further to the above issues, Mg is very chemically active and easily oxidized during mechanical alloying or processing to form the MgSi starting material. This oxide layer can decrease the electrochemical performance of the final Mg_2Si alloy. In order to overcome this issue, high purity nanocrystalline Mg_2Si was obtained by hydrogen-driven chemical reaction [26]. Mg_2Si synthesized using this methodology exhibited an improved Li-ion storage ability because of its recorded initial capacity of 1095 mAh g^{-1} at 100 mA g^{-1} current density, and the discharge capacity remained stable at 406 mAh g^{-1} after 60 cycles. A metathesis reaction route to obtain fine Mg_2Si particles was reported by Itahara et al. [27]. It is well known that Mg_2Si easily suffers from oxidation, so the effect of oxidation on the electrochemical performance of Mg_2Si was also investigated [27]. As shown in Fig. 2, the initial discharge capacity of oxygen-free fine Mg_2Si particles C-1 (C-2) was 740 (about 480) mAh g^{-1} at 100 mA g^{-1} , and the reversible capacity is still more than 300 (less than 200) mAh g^{-1} after 100 cycles. The studies by Itahara et al. verified that oxidation of the Mg_2Si would be disadvantageous to the specific capacity and cycling stability.

Although Mg_2Si has a satisfactory capacity, it decays sharply at the beginning of cycles, which seriously affects the electrochemical performance. Tamirat et al. [28] have designed and synthesized carbon-coated Mg_2Si nanoparticles by mechanically activated annealing and thermal vapor deposition which focused to enhance its cyclic stability. As shown in Fig. 3, the specific discharge/charge capacity of pure Mg_2Si was $1390/744 \text{ mAh g}^{-1}$ (the initial coulomb efficiency was 53.53%) and vanished about 15th cycle. The reasons for this phenomenon are due to the volume expansion of Mg_2Si during the intercalation/deintercalation, the irreversible decomposition of Mg_2Si and the partially irreversible Li–Mg alloy [29]. Meanwhile, the carbon-coated Mg_2Si -active materials, which increase the conductivity and electronic contact, show excellent cycling performance and rate performance (Fig. 3b, c). The initial cycle discharge/charge capacities of $1199/726 \text{ mAh g}^{-1}$ (with coulomb efficiency 60.55%) were maintained to $470.9/470.1 \text{ mAh g}^{-1}$ in the 500th cycle. Furthermore, the anode material shows 380 mAh g^{-1} at a 2 A g^{-1} current density.

2.1.1.2 Si–Ge Germanium (Ge) is a semiconductor with relative high electrical conductivity, and moreover, the

Fig. 2 **a** IR spectra for samples C-1 and C-2 measured in air with the attenuated total reflectance (ATR) method. **b** Discharge capacity for samples C-1 and C-2 over 100 cycles evaluated at a constant current of 100 mA g^{-1} with a voltage window of 0.02–1.5 V (vs. Li/Li^+). The commercial sample is an Mg_2Si reagent powder with particle diameters less than $53 \mu\text{m}$ [27]

Fig. 3 **a** Cycling performance of Pure Mg_2Si . **b** Rate performance of carbon-coated Mg_2Si electrode at different current density. **c** Cycling performance of carbon-coated Mg_2Si with its corresponding coulombic efficiency measured at 100 mA g^{-1} [28]

diffusivity of Li in Ge at room temperature is about 400 times higher than that in silicon. Therefore, Si-Ge composites have been researched as high-performance anode materials for lithium-ion batteries. Duveau et al. prepared $\text{Ge}_x\text{Si}_{1-x}$ by mechanosynthesis, all the active material increase the capacity compared with Ge. And all the synthesized $\text{Ge}_x\text{Si}_{1-x}$ electrode materials showed excellent cycling performance and rate performance compared to pure Si electrodes [30]. However, the volume expansion still exists due to the increase in silicon content. To solve this issue, nanostructured metal silicides such as nanotube, nanowires, core-shell nanoparticles, and hollow mesoporous have been studied. Song et al. [31] reported a nanotube heterostructure array, as shown in Fig. 4a, b, with a high-capacity Si inner layer and a highly conductive Ge outer layer produced by chemical vapor deposition (CVD). The Si/Ge composite nanotube array electrode exhibits higher initial specific capacity and coulombic efficiency (88.5%) than those of previously reported pure Ge electrodes, and displayed good retention of capacity (85% after 50 cycles) and twice the capacity at a 3 C rate compared to the Si electrode in spite

of a reduced initial capacity (Fig. 3c, d). These outstanding electrochemical performances are due to the reduced maximum hoop strain, enhanced electric conductivity, and accelerated Li diffusion of this Si/Ge composite electrode. Using the volume expansion characteristics of Si/Ge anode materials during the lithiation and delithiation, Stokes et al. [32, 33] reported an axial Si-Ge heterostructure nanowires. The heterostructure nanowires were prepared by two steps. First, synthesize a nanowire through an injection of phenyl silane onto an evaporated layer of Sn on stainless steel. Then, triphenylgermane was injected to yield axial heterostructures (Fig. 4f). During the charge and discharge process, the heterostructure nanowires can form a porous network of uniform $\text{Si}_{1-x}\text{Ge}_x$ compounds. Owing to this special process, $\text{Si}_{1-x}\text{Ge}_x$ composite anode exhibits high initial capacities of 1644 mAh g^{-1} , excellent capacity retention of 71.8% after 400 cycles and high power rate of 600 mAh g^{-1} at 10C (Fig. 4e).

Si/Ge porous nanorod arrays utilizing ZnO nanorod arrays as a sacrificial template and co-sputtering method have also been investigated as an anode material for

Fig. 4 **a** SEM images of a vertically aligned Si/Ge nanotube array on a stainless steel substrate. **b** Magnification TEM images of a single Si/Ge nanotube. Inset of **b** shows selective area electron diffraction pattern. **c** Cycle performances. **d** Rate capabilities of Si nanotube and Si/Ge nanotube array electrodes at various C rates [31]. **e** Charge and discharge capacities (mAh g^{-1}) of Si-Ge heterostructure nanowires demonstrated at different current rates. **f** Overview of the synthetic protocol used to prepare Sn-seeded Si-Ge hNWs directly from current collectors and the changes in morphology due to repeated cycling with Li from segmented crystalline structures to an amorphous alloyed network after 50 cycles [33]

lithium-ion batteries [34]. This type of anode showed enhanced performance (about 1000 mAh g⁻¹ after 100 cycles) over bare Si porous nanorod arrays (nearly 600 mAh g⁻¹ after 100 cycles) because of good contact between the porous nanorod arrays and the current collector. The greatly improved conductivity and lithium-ion diffusivity in SiGe layer caused by addition of Ge may be responsible for the enhanced performance. However, the SiGe porous nanorod arrays show a first Coulombic efficiency of 31.8%, which is significantly lower than the data of Si/Ge double-layered nanotube arrays (88.5%). This could be due to the formation of a substantial solid electrolyte interphase (SEI) and other side reactions, since co-sputtering process may suffer from more oxidation compared to CVD method [34].

2.1.1.3 Ca-Si According to the research of Netz et al. [35], CaSi₂ was reported to show a high reversible capacity, corresponding to 1.15 Li mol⁻¹. Based on the predicted Ca-Si-Li room-temperature phase diagram, the reaction mechanism was proposed for the Li insertion in a CaSi₂ anode as follows [23]:

A charge capacity above 1500 mAh g⁻¹ was exhibited when cycling over a wide voltage window of 0.005–1.5 V, which was reduced to 310 mAh g⁻¹ after 10 cycles [23]. Beyond mechanical cracking during Li insertion/extraction, lower melting temperatures, high ductility and elastic modulus of Ca-Si alloy matrices were regarded as the other reason for its poor cycle life. Under the stated test conditions, the material cannot tolerate large volume changes and consequently severe capacity fade during initial cycling is observed.

2.1.1.4 Si-Ag Lithium insertion in SiAg powders produced by mechanical alloying has also been investigated [36]. The results of X-ray diffraction (XRD) and scanning electron microscopy (SEM) showed that nanoscaled Si particles were uniformly dispersed in a ductile Ag matrix, but a stable capacity of only 280 mAh g⁻¹ was obtained [36]. The poor cycling was due to the anode pulverization which was caused during the Li-insertion volume change. This result means that the addition of Ag cannot accommodate the large volume changes of the Si. Other SiAg anodes prepared by electroless deposition of Ag particles on commercial Si powder were also characterized by SEM, XRD, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), liquid solid chromatography (LSC) and electrochemical impedance spectroscopy (EIS) [37]. An improved performance of this AgSi anode was attributed to formation of an SEI film, which was believed to keep binding to the Si particles during

lithium insertion and thereby ensuring good electric contact between particles as well as reducing fragmentation through the volume expansion process [37]. Similarly, the effect of thin alumina deposits on top of Si-based nanowires has been studied. A thin alumina deposit can act as a substitute for the SEI, preventing electrolyte decomposition and prolonging the lifetime of the anode [38].

2.1.1.5 Si-Sn Among metal silicide anode materials, the Si/Sn binary system is considered to be one of the potential silicides because Sn as active matrix has high theoretical capacity of about 993 mAh g⁻¹ for Li_{4.4}Sn, and Sn also shows excellent conductivity of 9.2×10^4 S cm⁻¹ at 20 °C which is much higher than Si. However, the Si and Sn interact with Li⁺ to form alloys instead of intercalating which gives rise to serious volume expansion during the reversible cycling reactions [39, 40]. In order to alleviate alloying-induced volume expansion, several strategies were reported such as designing the Si-Sn nanocomposites [41, 42] thin film [43, 44] and Si/Sn/C composite [45] with the aim to improve their electrochemical performance. Xiao et al. [42] have demonstrated that the Si and Sn are incompatible, and the existence of Sn can improve the conductivity and absorb the elastic strain energy to prevent crack growth. Zhong et al. [46] added Sn nanoparticles to the silicon-based anode which can reduce the active material surface area while maintaining its nanostructure. Therefore, the as-prepared nanocomposite showed the specific capacity of 1500 mAh g⁻¹ and preferable initial Coulomb efficiency of 81% and maintained the capacity of 110 mAh g⁻¹ after 100 cycles. In order to achieve homogeneous mixing between Si and Sn, Yao et al. [39] synthesized Si-Sn nanocomposites by chemical reduction. The prepared Si-Sn sample exhibited a discharge capacity of 2245 mAh g⁻¹ with the initial Coulombic efficiency of 61.5% and exhibited excellent cycling stability with a reversible capacity of 700 mAh g⁻¹ after 200 cycles. Moreover, a hierarchical microporous Si/Sn composite was reported by Hao et al. [47]. The pores-containing Si₈₅Sn₁₅ showed a 1600 mAh g⁻¹ after 70 cycles, even at a current density of up to 3000 mA g⁻¹. Due to the special hierarchical microporous structure, the diffusion distance of Li⁺ can be shortened and the void space can serve as additional buffer for the electrode materials during the cycling. In addition, the diffusion rate was increased owing to the existence of Sn.

2.1.1.6 Other Ma_xSi_y Other active metals, such as Al [48], Zn [49], were investigated as quite important alloy components in the recent literature. Zhang et al. [50] prepared multilayer Si/Al film with 3D nanostructure which exhibited the capacity as high as 1015 mAh g⁻¹ after 120 cycles at a current density of 4.1 A g⁻¹. This work provided a new idea for the development of Al/Si anode. Tahmasebi

et al. [51] synthesized Al–Si thin film and found that the multiple thin film had quite stable structure, providing a long-term cycling stability. Transition metals (Cr, Fe, Mn, Ni, etc.) were generally used in the Al–Si alloy to stabilize the amorphous structure and improve the electrochemical performance [52]. Furthermore, Zn was introduced into the Si anode to improve the cycle stability and rate capability by virtue of their similar atomic sizes, bonding characteristics and electronegativity [53].

2.1.2 Inactive Metal-Containing M_xSi_y

2.1.2.1 Ni–Si

Nickel is a typical inactive metal which does not react with Li^+ at room temperature [54, 55]. However, Ni can react with Si to form metal silicide compounds. These compounds can then be used for the intercalation of Li^+ cations. Reaction mechanisms for this reaction have been proposed for the Li insertion and extraction in the Ni–Si alloy anode [20, 21]:

In the proposed mechanisms, the theoretical specific capacity for NiSi is 1360 mAh g^{-1} if all the Si reacts with Li to form $\text{Li}_{4.4}\text{Si}$. It was believed that the element Ni formed during initial charge would act as buffering matrix to suppress the Si volume change [20]. Mechanical milling was firstly attempted to form Ni–Si alloy anodes, and a homogenous NiSi phase was obtained. Although a high lithium storage capacity of 1180 mAh g^{-1} has been

achieved in the initial discharge, the capacity faded rapidly, rendering the electrode unsuitable for batteries application [20]. A solution to this was proposed where a Si-rich Ni–Si composite consisting of Si and Si_2Ni was prepared by hydrogen plasma–metal reaction. For this Si–Ni alloy, the Si-rich structure resulted in its high lithium storage capacity of 1304 mAh g^{-1} , and the slower fading rate compared with pure Si anode could be attributed to the buffering of inert Si_2Ni matrix [56]. Other than these structures of Si dispersed in inactive NiSi_x matrices, a Ni–Si composite in which Si nanoparticles are welded onto surfaces of metal particles by forming intermetallic interphases through a rapid heat treatment have also been researched [57]. The Si/Ni composite synthesized at 900 °C delivered a capacity of 498 mAh g^{-1} at a current density of 233 mA g^{-1} and 73.7% of the capacity remained by the 100th cycle [37]. For this Ni–Si composite, the interparticle spacing could effectively accommodate the volume expansion of Si, leading to improved cycling performance. Moreover, the electrochemically inactive intermetallic interphases in this composite serve as a special “glue” to prevent Si from losing electrical contact with binders and conductors. This synthesis concept can be employed to synthesize a variety of Si/metal composites, where the Si could be powders, wires, or films while the metal could be particles, wires, or foil-like substrates such as stainless steel.

In order to further improve the performance of Ni–Si composite, various nanostructured Ni–Si composites were synthesized using CVD [58–60]. Figure 5a illustrated a typical growth procedure of the Si– NiSi_x nanocomposites

Fig. 5 **a** The schematic illustration for the growth process of the Si– NiSi_x nanocomposites. **b** TEM image of an individual a-Si/ NiSi_x nanowire. The inset shows a plan-view SEM image of a-Si/ NiSi_x grown on substrate. **c** HRTEM image of an individual a-Si/ NiSi_x nanowire at the core region and the corresponding electron diffraction pattern (inset). **d** The discharge capacity for the a-Si/ NiSi_x nanowire and the a-Si/c-Si nanowire, respectively. **e** The rate capability for the a-Si/ NiSi_x nanowire and the a-Si/c-Si nanowire, respectively [59]

by the CVD method [58]. According to the morphology characterization results in Fig. 5b, c, the Si-NiSi_x nanocomposites are uniform nanowires composited of amorphous Si (a-Si) shell and NiSi₂ core [58]. These a-Si/NiSi_x core-shell nanowires exhibited a highly reversible capacity of over 3000 mAh g⁻¹ even at a 2C rate, and almost 83% of the first discharge capacity was retained after the 50th cycle with high charge capacity above 3000 mAh g⁻¹ (Fig. 5d, e) [58]. Yang et al. [59] reported the Ni₃Si₂-supported Si (Ni₃Si₂-Si) nanowires with a high reversible capacity of ~1800 and ~1600 mAh g⁻¹ at a high current rate of 1C and 2C during 100 cycles, respectively. Subsequently, they synthesized the vertically ordered Ni₃Si₂/Si nanorod (NR) arrays on Ni foam, which showed good cycling performance and high capacity [60]. A high and steady discharge capacity of 2184 mAh g⁻¹ and 1900 mAh g⁻¹ can be achieved after 50 cycles at 1 C (4.2 A g⁻¹) and 2 C (8.4 A g⁻¹), respectively [60]. These greatly improved performances could be attributed to the lower resistivity of nickel silicides and maintenance of good contacts with the current collector, and relatively small volume expansion routes in the core-shell nanowires prepared by accurate CVD method.

In addition to the CVD method, template-assisted electrochemical deposition was employed to prepare three-dimensional Ni-Si nanocable arrays as high-performance anodes for lithium-ion batteries. The optimum composite nanocable array electrode achieves a high specific capacity of 1900 mAh g⁻¹ at 0.05 C [61]. The specific capacity remains at 1300 mAh g⁻¹ (88% of initial capacity) after 100 cycles at 0.5 C, suggesting good capacity retention ability. The high performance of the composite nanocable electrode is attributed to its excellent adhesion of the active material on the three-dimensional current collector and short ionic/electronic transport pathways during cycling. Wang et al. reported a three-dimensional (3D) anode comprising a Ni-coated Si microchannel plate (Si-MCP) as the matrix and active materials prepared by photo-assisted electrochemical etching and electroless deposition [62]. In this case, introduction of Ni coating turned out to have an obvious effect in improving the reversible capacity, but the number of cycles achieved is still not satisfactory for commercial battery applications.

2.1.2.2 Fe-Si The reaction mechanism of Fe in Fe-Si alloy anode is the same as Ni in Ni-Si:

After mechanically milling Fe with Si, the product contained FeSi and Si phases and had a large particle size [21]. Although FeSi and NiSi alloy anodes have shown similar initial reversible capacities, NiSi composite showed

better capacity retention compared to FeSi [21]. The poor cycle life of FeSi was due to the large particle size of the unalloyed Si, which resulted in a large overall volume change.

To improve the electrochemical performance of Fe-Si alloy, Fe-Si alloy powders were annealed at 1000 °C before milling [63]. From XRD analysis, the peaks of annealed alloys broaden with milling time and only α, β-FeSi₂ phase is detected [58]. It was hypothesized that the Si particles were embedded within the FeSi₂ phase which can act as a stable buffering matrix to minimize volume change. Taking Fe₂₇Si₇₃ alloy as an example, its discharge capacity can be stable at 150 mAh g⁻¹ [63]. However, Si-rich FeSi alloys (Fe₂₀Si₈₀) deliver large initial capacity, but the capacity degrades rapidly with cycling. Poor cycling performance was attributed to the small amount of FeSi₂ phase present in the anode, which could not completely cover all the Si particles [63]. In order to give full play to the advantages of initial coulomb efficiency and low cost of Fe-Si alloy, structure design is also used to further improve the energy density and cycle stability of active materials. He et al. [64] obtained a nanocrystal-FeSi-embedded Si/SiO_x (FSO) anode by mechanical milling and heat treatment with Fe-Si compounds which prepared by industry (Fig. 6a). The FSO anode exhibits excellent cycling stability with 84% capacity retention over 1000 cycles at 1 A g⁻¹ (Fig. 6b). This satisfactory electrochemical performance is mainly due to the SiO_x shell was obtained by the oxidation of Si and the formation of solid FeSi core during the heat treatment, which inhibits the volume expansion and electrolyte corrosion during the cycles.

Fig. 6 **a** The schematic drawing of the ball milling and the calcining process for the preparation of FSO anode materials. **b** Cycling property of the FSO-800 °C electrode [64]

2.1.2.3 Cu–Si Similar research was also conducted on CuSi alloy. Ball milling of Cu and Si powders produces Cu_5Si alloy integrated with unalloyed silicon, followed by heat treatment of the milled sample at 600 °C [65]. However, the cycle capacity was drastically cut probably due to deactivation of more active silicon by alloying with copper and coating with inert Cu_5Si alloy [65]. Unlike mechanically milled alloys, a Cu–Si composite alloy was formed by electroless deposition of Cu on Si powders. To increase adhesion between Cu and Si, Cu was deposited on etched Si, followed by annealing at 400 °C [66]. The Cu-coated Si powder showed higher electronic conductivity than the untreated material. However, its conductivity was reduced during annealing, which resulted in formation of resistive Cu_3Si alloys [66]. When charged–discharged between 0.0 and 2.0 V, the Cu-coated Si electrode showed an unsatisfactory cycle life because of Cu detachment from the Si surface after just a few cycles, as was observed by SEM analysis [66]. As a good model to solve this problem, Prieto et al. [67] reported the in situ doping of Si nanowires with Cu, which results in nanowires containing nanocrystalline inclusions of Cu_3Si and significantly

enhanced electrical conductivity. The electronic transport measurements conducted on single nanowires indicate that the electronic resistivity of the doped nanowires is several orders of magnitude lower than undoped Si. However, no galvanostatic cycling performance was reported for this anode [67]. Copper silicides can not only release the volume expansion in the process of charging and discharging, but also enhance the electronic conductivity. To further achieve high energy density, high power performance and excellent cycling stability, structural design is considered as a feasible approach. Song et al. [68] reported that highly connected hollow Si–Co alloy mixture nanotubes without any binder which can easily realize the volume expansion inward instead of outward. Because of the existence of nanowire structure, the Si–Co alloys serve a high specific capacity of 780 mAh g^{-1} , and high capacity retention performance of 88% after 1000 cycles. Song et al. [69] synthesized anti-pulverization and yet conductive Cu_3Si embedded Cu–Si NW hybrid anode by crossing-interconnected-hierarchical-hollow (Fig. 7). Upon the simple H_2 annealing, the CuO is reduced to Cu and Cu diffused into Si alloy. Owing to this special structure, on the one hand, it can increase the load

Fig. 7 Preparation process of the HCS NW structure grown overall on the copper foam substrate. A schematic illustration of the preparation of the HCS NW hybrid structure. **a** Copper foam. **b** and **c** Crossing CuO NWs grown on the CuO foam after thermal oxidation growth in atmosphere. **d** Interconnected CuO/a-Si core-shell NWs after coating the a-Si layer. **e** Sn-catalyzed Si NWs were grafted on the front and back plates of the CuO/a-Si core-shell NW foam, respectively, and finally obtained hierarchical nano-branched c-Si/CuO@a-Si core shell NW structures grown overall on the foam substrate in the PECVD system. **f** The hierarchical Cu–Si NW hybrid structure grown on the copper foam after a high temperature H_2 annealing process. **g** ALD-coated ultra-thin Al_2O_3 on the hierarchical Cu–Si NW structure, and the corresponding image enlarged for detail. **h** Schematic diagram and photographs of the front and back plates of the HCS hybrid structure. **i** Photographs of a water droplet and **j** an electrolyte droplet on the surface of the HCS NW hybrid structure. **k** Cycling rate performance of the HCS NW hybrid anode with a mass loading of 1.2 mg cm^{-2} . **l** Ultra-long-term cycling performance for ICS NT trunks (interconnected Cu–Si alloy nanotube trunks) at 20 A g^{-1} [69]

of Si and inhibit the volume expansion, on the other hand, it can improve the electronic conductivity and mechanical support. A high specific capacity of 560 mAh g^{-1} has been achieved after 6000 cycles at 20 A g^{-1} , with a satisfactory capacity retention rate of 70%.

2.1.2.4 Ti–Si As a new anode material for lithium-ion batteries, titanium silicide has drawn much attention since it is lightweight, highly electrically conductive, and thermally stable [70]. Titanium silicides have been prepared either by ball milling the melt-spun ribbons or by mechanically alloying a mixture of element powder. The influence of the milling time on the electrochemical performance of these anodes in lithium-ion batteries has been investigated [71]. By optimizing the milling time, the best reversible capacity of $\text{Ti}_{25}\text{Si}_{75}$ melt-spun powders of 450 mAh g^{-1} after 50 cycles can be achieved [71].

Zhou et al. [72–75] reported unique two-dimensional C49 titanium disilicide (TiSi_2 nanonet) grown on Ti foil in a CVD reactor with TiCl_4 and SiH_4 as the precursors. Studies of the reaction mechanism with Li^+ reveal that the properties of C49 TiSi_2 differ from ordinary TiSi_2 drastically. C49 TiSi_2 structure (TiSi_2 nanonet) is characterized by an orthorhombic unit cell where a Si-only layer appears every

few atomic layers of mixed Ti and Si, and the Si-only layers serve as the host for high capacity (about 600 mAh g^{-1}) (Fig. 8a) [72]. While ordinary TiSi_2 structures without Si-only layers, such as C54 TiSi_2 nanowires, exhibit low charge or discharge capacity ($< 100 \text{ mAh g}^{-1}$) (Fig. 8b) [72]. In order to stabilize TiSi_2 for improving performance and also rule out the possibility that the measured capacity is due to surface reactions, a thin ($< 5 \text{ nm}$) layer of oxide was coated on the surface of TiSi_2 for analysis (Fig. 8c) [73]. Concomitantly, the TiSi_2 nanonet can act as a good current collector because of its high surface area (ca. $100 \text{ m}^2 \text{ g}^{-1}$), highly conductivity ($\sim 105 \text{ S cm}^{-1}$), and mechanical strength [73]. To achieve this the Si nanoparticles (approximately 20 nm dia.) are directly grown on the TiSi_2 nanonets surfaces, synthesizing a unique heteronanostructure consisting of two-dimensional TiSi_2 nanonets and particulate Si coating as the anode material for Li^+ storage (Fig. 8d) [74]. At a charge/discharge rate of 8400 mA g^{-1} , specific capacities $> 1000 \text{ mAh g}^{-1}$ were measured. Only an average of 0.1% capacity fade per cycle was observed between the 20th and the 100th cycles (Fig. 8e) [74]. Similarly, a high-performance cathode is enabled by the $\text{TiSi}_2\text{--V}_2\text{O}_5$ combination [75].

Fig. 8 **a, b** The capacities of C49 TiSi_2 nanonets and ordinary C54 TiSi_2 nanowires at a current density of 1000 mA g^{-1} , respectively. Insets: corresponding SEM pictures of the nanonets and nanowires, respectively. **c** Charge capacity and Coulombic efficiency of TiSi_2 nanonets with oxide coating at a rate of 2000 mA g^{-1} . Potential range: 1.0–0.01 V. Inset: Schematic and TEM images for clearly understand of TiSi_2 nanonets with oxide coating. **d** A TEM picture manifesting the particulate nature of the Si coating on TiSi_2 NNs. **e** Charge capacity and Coulombic efficiency of the Si/ TiSi_2 heteronanostructure at a rate of 8400 mA g^{-1} tested between 0.150 and 3.00 V. Inset: schematic of the Si/ TiSi_2 heteronanostructure. **f** Structure of Si–Ti framework and its electrochemical performance [72, 75, 77]

Park et al. [70] synthesized Ti_xSi_y -coated Si anode via the silicothermic reduction process, in which the titanium silicide enhances the electrical conductivity of Si nanoparticles and forms the basis for a highly stable solid electrolyte interphase layer during the cycling. Therefore, Ti_xSi_y -coated Si electrodes exhibit excellent electrochemical performance, including a high specific capacity and good rate capability [62]. Similarly, micro-assembled Si-titanium silicides nanotube was synthesized using a magnesiothermic reduction reaction of SiO_2 -coated carbon nanotubes (CNTs) and $\text{TiO}_2/\text{SiO}_2$ -coated CNTs [68]. The Si-based nanotube anodes exhibit a high capacity ($> 1850 \text{ mAh g}^{-1}$) and an excellent cycling performance (capacity retention of $> 99\%$ after 80 cycles) [76]. Li et al. [77] prepared a Si–Ti alloy with double framework which was fabricated on the basis of SiO_2 – TiO_2 gel network, due to its excellent structure the prepared Si–Ti alloy severs a good cycling stability at 0.5 A g^{-1} and a high rate capacity (1190 mAh g^{-1} at 2 A g^{-1}).

2.1.2.5 Other M_iSi_j Other transition metals such as Mn [78], Mo [79], W [80] and Cr [79] have also been investigated as a matrix to form alloys through mechanical milling. The electrochemical characteristics of Si–Mn composites prepared by different ball milling times has been investigated [78]. A reversible capacity of 455 mAh g^{-1} and an initial Coulombic efficiency of 52% were obtained by 60 h ball milling followed by annealing at 300 C for 2 h [78]. In Si–Mn composite electrodes, Mn can act as an inactive buffer for the active Si center and enhance cycling performance. However, the nanosized Si–Mn particles tend to merge together after the insertion/extraction of lithium ions, which decreases electrical contact between the active materials and the underlying copper current collector [78]. MoSi_2 and CrSi_2 synthesized by high-energy ball milling of the corresponding metals have also been investigated as anode materials for Li-ion batteries [79]. According to the evolution of their crystalline phases determined through XRD studies [79], 20 h of ball milling was necessary for the formation of MoSi_2 while 100 h for CrSi_2 . The prepared MoSi_2 powders showed a capacity of about 125 mAh g^{-1} whereas CrSi_2 powders provided a capacity of 340 mAh g^{-1} at $C/12$ ($1 \text{ C} = 469 \text{ mAh g}^{-1}$) [79]. Both of the prepared powders have shown better battery performance than commercial powders.

2.2 Ternary Metal Silicides

In this section, we mainly discuss ternary metal silicides. These were typically fabricated by melt spinning rapid solidification process to obtain nanosized Si particles embedded within a matrix. The matrix can buffer the mechanical stresses generated during volume expansion

Fig. 9 Comparison of the cycle performances of the Si/NiTi alloy and pure Si electrodes between 2.0 and 0.0 V (vs. Li/Li^+) at a cycling rate of 100 mA g^{-1} with coulombic efficiency. Inset: schematic microstructure of the Si/Ni–Ti matrix alloy [81]

and also provide good electrical contact with the current collector during lithiation and delithiation process. The characteristics of anode materials based on these materials for Li-ion batteries are dependent on the microstructure and the matrix phases, generated during rapid solidification. Thus, it is very important to explore suitable matrix phase compositions to evaluate the melt-spun alloys as candidates for anode materials.

2.2.1 Si–Ti–Ni Metal Silicides

Si–Ti–Ni ternary alloy system was a good choice for a high elastic strain matrix [81–84]. A nanosize Si embedded in super-elastic Nitinol alloy matrix composite was synthesized in large-scale using arc melting followed by rapid quenching [81]. Both XRD and high-resolution transmission electron microscope (TEM) with energy-dispersive spectroscopy analyses confirmed $\sim 50 \text{ nm}$ Si crystallites were surrounded by the Ni–Ti matrix [81]. This anode material showed a stable capacity of above 700 mAh g^{-1} after 50 cycles since the super-elastic Nitinol alloy matrix is able to withstand a deformation when a load is applied and return to the original shape when the load is removed, as shown in Fig. 9. Son et al. developed a Si–Ti–Ni ternary alloy where nano-Si particles were embedded in a $\text{Ti}_4\text{Ni}_4\text{Si}_7$ matrix [82]. As an anode material for lithium-ion batteries, this alloy exhibits a stable capacity above 900 mAh g^{-1} after 50 cycles and a high columbic efficiency of up to 99.7% during cycling. In this case, after the first cycle, the matrix of $\text{Ti}_4\text{Ni}_4\text{Si}_7$ is irreversible represented by $\text{Li}_x\text{Ti}_4\text{Ni}_4\text{Si}_7$ which results in faster and more efficient Li ion and electron transfer to nano-Si. The reduced formation of an SEI layer on the Si

surface due to $\text{Li}_x\text{Ti}_4\text{Ni}_4\text{Si}_7$ matrix also contributes to the excellent performance.

Kwon et al. [83] systematically investigated the electrochemical performance of various rapidly solidified Si–Ti–Ni alloys. Among the anode alloys, the $\text{Si}_{70}\text{Ti}_{15}\text{Ni}_{15}$ electrodes had the highest discharge capacity (974.1 mAh g^{-1}) after the 50th cycle. This research also revealed that the $\text{Si}_7\text{Ni}_4\text{Ti}_4$ crystal phase coexisting with an amorphous phase, could more efficiently act as a buffer layer than the fully crystallized $\text{Si}_7\text{Ni}_4\text{Ti}_4$ phase [83]. Ladam et al. [84] synthesized Si-rich $\text{Ni}_{0.12}\text{Ti}_{0.12}\text{Si}_{0.76}$ by one-pot ball milling, which the specific capacity is of 700 mAh g^{-1} with a coulombic efficiency of 99.8% at the 50 cycles. Song et al. [85] researched the performance of nitrated Si–Ti–Ni (STN) ternary alloy prepared by the NH_3 nitridation of STN alloy. The nitrated STN electrode shows 14% increased reversible capacity and 4 times higher rate capability at 3 C compared to those of pristine STN electrode. These improvements are attributed to the formation of nitride compounds (such as $\text{SiN}_x/\text{SiN}_x\text{O}_y$, $\text{TiN}_x/\text{TiN}_x\text{O}_y$ and $\text{NiN}_x/\text{NiN}_x\text{O}_y$) on STN alloy, which benefits both mechanic strength and kinetics [85].

2.2.2 Si–Ti–Fe Metal Silicides

The Si–Ti–Fe ternary alloy system has also begun to draw attention as a new anode material [86, 87]. Because the co-melting of Si, Ti, and Fe evolves various ternary compounds with very high tensile strength and good electronic conductivity, these alloys seem to effectively

accommodate the mechanical stress and strain of Si and its lithium-bearing compounds, as well as contribute to maintaining good electronic contact between the active Si and the current collector during lithiation/delithiation [87]. Kim et al. [75] reported a Si–TiFeSi₂ composite synthesized by arc melting followed by rapid quenching and the composite showed a reversible capacity of 1200 mAh g^{-1} over 50 cycles with a Coulombic efficiency of 89% for the first cycle. In this composite, nanosized cracks were observed only at the Si crystallites within the Si–TiFeSi₂ particles, indicating that the TiFeSi₂ matrix was hard enough to withstand the stress generated during lithiation which explained the excellent capacity retention [86].

Another nano-Si/FeSi₂Ti heterostructure has been synthesized for highly reversible Li-ion batteries by using a simple melt-spinning method [87]. As shown in Fig. 10a, in this nano-Si/FeSi₂Ti heterostructure, the FeSi₂Ti matrix can serve as an efficient electron transport pathway, facilitating homogeneous lithiation into Si, and also as a rigid mechanical support for Si domains in spite of their severe volume change. The pores surrounding its characteristic structure may be a second reason for the effective accommodation of the volume expansion of the Si domain during lithiation. Figure 10b shows the well maintained nano-Si/FeSi₂Ti composite after 50 cycles, verifying the continuous benefit of FeSi₂Ti matrix during lithiation and delithiation. Hence, this nano-Si/FeSi₂Ti heterostructure anode exhibited a significant enhancement in capacity performance, cycling stability and rate capacity compared with an electrode comprising bare Si particles (Fig. 10c, d) [87].

Fig. 10 **a** Schematic illustration of the nano-Si/FeSi₂Ti heterostructure during lithiation. **b** HRTEM images of the nano-Si/FeSi₂Ti heterostructure after 50 cycles. **c** The cyclic retention of the nano-Si/FeSi₂Ti heterostructure and Si nanoparticles at 0.1 C. **d** The dependence of discharge retention on the variation of current density for galvanostatic charge–discharge [87]

3 Metal Silicide/C Composites

In the metal silicides/C composites, the inactive metal component serves as a buffer matrix, and the addition of carbon materials such as graphite and CNT enhances the connection and conductivity of anode materials. Park and co-workers reported a Si–Ni–carbon composite synthesized using high-energy mechanical milling for an anode in lithium-ion batteries and the Si–Ni–Carbon composite demonstrated a large reversible capacity of ca. 960 mAh g^{-1} with an excellent cycling stability [77]. The reason for good electrochemical characteristics is that uniformly dispersed Ni improved electronic conductivity and induced fast charge transport significantly in the Si–Ni–Carbon composite [88]. Lu et al. [89] synthesized a CNT–Ni–Si anode, demonstrating a high capacity over 2500 mAh g^{-1} and a low fading rate of merely 0.2% per cycle over 110 cycles. Introduction of the rough Ni interfacial layer and utilization of the CNT cores lead to reinforced stability of the structure, well accommodated stress and enhanced charge transfer,

which are responsible for the improved performance [89]. In addition, pores and the disordered carbon layer played a role in accommodating the large volume change of Si during cycling. A composite comprising Si with a Si/Cu core in a carbon shell was investigated as an anode material in lithium-ion batteries [90]. The C/Si composite exhibits a reversible lithium storage capacity of 910 mAh g^{-1} and good cyclability, but the addition of Cu to the Si core in a carbon shell can further improve the cyclability of the composite, which reaches reversible capacity retention up to 94% after 20 cycles [90].

Li et al. [91] studied a FeSi_6 /graphite composite in which the FeSi_6 alloy particles consist of an electrochemically active silicon phase and inactive phase of FeSi_2 , distributed uniformly in the graphite matrix. Under the buffering effect of the inactive FeSi_2 phase and graphite layers on the volumetric changes of Si phase during lithium–Si alloying reaction, the composite anode offers a large reversible capacity (about 800 mAh g^{-1}) and good cyclability [91]. However, the contents of inactive metal component also affect the capacities of these composite anodes. In order to study the effect of Ti in the Ti–Si–C composite, various Ti–Si alloys ($\text{Ti}_{14}\text{Si}_{86}$, $\text{Ti}_{16}\text{Si}_{84}$, $\text{Ti}_{21}\text{Si}_{79}$) were mixed with carbon for electrochemical tests [92]. For the $\text{Ti}_{14}\text{Si}_{86}$ alloy, containing primary Si and Si + TiSi_2 eutectic phases, the matrix is identified as the primary Si phase [92]. Therefore, the buffering action of TiSi_2 phase in the $\text{Ti}_{14}\text{Si}_{86}$ alloy seems to be less effective than in the other Ti–Si alloys. It is likely that the pulverization of active alloy particles occurs more easily in the $\text{Ti}_{14}\text{Si}_{86}$ alloy compared to the $\text{Ti}_{16}\text{Si}_{84}$ and $\text{Ti}_{21}\text{Si}_{79}$ alloys, which leads to the inferior cyclability of the $\text{Ti}_{14}\text{Si}_{86}$ -carbon composite electrode [92].

The Cu_5Si -Si/C composites with different Cu content produced by high-energy ball milling of a mixture of copper–silicon alloy and graphite powder have been investigated [65]. Cu_5Si -Si/C composite with Si:Cu = 1 demonstrates an initial reversible capacity of 612 mAh g^{-1} and the capacity retention is 74.5% at the 40th cycle. However, increasing the amount of copper in the composites decreases reversible capacity but improves cycling performance.

Unlike inactive metals, the active metals may make a contribution to the anode capacity by reacting with Li^+ [93–97]. Some of these active metals also serve as a buffer matrix which enhances the connection of anode, carbon and conductor. For mechanically ball-milled Si–Zn–C composite, the first charge and discharge capacities are approximately 852 and 607 mAh g^{-1} , respectively, and that 91% of the initial discharge capacity of 607 mAh g^{-1} can be maintained for up to 40 cycles [93]. The superior cycling performance of the composite electrode is attributed to buffering of the mechanical stress generated during cycling and to improved electrical connection with the current

collector afforded by the synergistic effect between Li_2ZnSi , Zn and graphite.

The $\text{Sn}_{0.9}\text{Si}_{0.1}$ core/carbon shell nanoparticles were synthesized from butyl-capped particles for high-density lithium storage materials [94]. These $\text{Sn}_{0.9}\text{Si}_{0.1}$ core/carbon shell nanoparticles exhibited excellent lithium storage ability at a high current, resulting in a value of 964 mAh g^{-1} at a rate of 0.3 C ($1 \text{ C} = 1200 \text{ mA g}^{-1}$), and demonstrated good capacity retention after 50 cycles.

Zhou et al. [95] reported an Al–Si–graphite composite with low 7.9 wt% Si synthesized by ball milling eutectic Al–Si powder and graphite, for which the reversible capacity remained above 650 mAh g^{-1} after 10 cycles. In this case, addition of 7.9% silicon to an aluminum anode not only contributes to the total capacity but also improves the capacity retention. The Si also appears to form a superior surface layer in carbonate electrolytes that reduces the degradation of the bulk material.

A nanostructured $\text{Ni}_{0.14}\text{Sn}_{0.17}\text{Si}_{0.32}\text{Al}_{0.037}\text{C}_{0.346}$ composite has been synthesized by mechanical milling of element Si, Al and C graphite powders and $\text{Ni}_{3.4}\text{Sn}_4$ intermetallic precursor [96]. As a promising anode material for Li-ion batteries, it shows a high reversible capacity reaching 920 mAh g^{-1} with a good stability for 280 cycles [96]. The capacity is provided by lithiation of both Si and $\text{Ni}_{3.4}\text{Sn}_4$ phases, whereas the good stability is attributed to buffering of electrode volume variations by the Ni and C components.

Furthermore, the introduction of metal or metal silicides into Si-based anodes could improve the electrochemical property of anodes by optimizing their nanostructures. A novel layered zinc silicate/carbon composite was fabricated by embedding carbon into the interlayers of zinc silicate through a hydrothermal method [87]. The interlayer distance could be effectively tuned from 1.22 to 3.37 nm through the amount of carbon precursors, which has effects on the performance of the composite. Figure 11a shows the morphology of zinc silicate combined with moderately reduced graphene oxide. This composite can retain as high

Fig. 11 **a** HRTEM image of the layered zinc silicate/C composited nanomaterials. **b** Reversible charge capacities of the above electrodes cycled at various rates (50–1000 mA g^{-1}) [97]

as 778 mAh g⁻¹ at 50 mA g⁻¹ after 50 cycles and exhibit good rate capacity (Fig. 11b) [97].

4 Synthetic Methods of Metal Silicides

Indeed, metal silicide anodes have been successfully prepared by various approaches such as ball milling [41, 84, 98], melt spinning, magnetron sputtering, chemical vapor deposition (CVD) methods. Among them, mechanical ball milling is considered to be one of the most attractive methods. Since it can produce nanosized and non-equilibrium phases nanocomponents such as nanocrystalline or amorphous powder, Ruttart et al. [98] prepared Fe_xSi_y anode materials by controlling the milling time and Fe:Si ratio. In these alloys, nano-Si dispersed in intermetallic FeSi₂ matrix as an inactive buffer phase displaying excellent cycling stability. Ladam et al. [84] synthesized Ni–Ti–Si composites by one-step ball milling, showing a specific capacity of 700 mAh g⁻¹ with a coulombic efficiency of 99.8% at the 50th cycle. In addition to mechanical ball milling, CVD is another method to prepare metal silicides. Fukata et al. [99] synthesized Si–Fe nanocomposite by CVD. First, nano-germanium was formed on stainless steel substrates by GeH₄ at 300 °C, and then Si-based nanostructures were formed at 700 °C using SiH₄(100%) and PH₃(1%). In order to get more uniform nano-components, chemical reduction method is also used to prepare metal silicides, For

example, Yao et al. [39] prepared Si–Sn anode with NaBH₄ as reducing agent, and Li et al. [77] synthesized Si–Ti binary framework by reduction of Mg at 700 °C for 6 h under a 5% H₂/Ar atmosphere. While these metal silicides prepared by different methods can reduce volume change to a certain degree, it cannot completely eliminate volume expansion. Therefore, structure design is very important to alleviate the volume expansion, which often requires a good combination of multiple synthesis methods. Jia et al. [100] reported a facile synthesis for a porous core–shell NiSi₂/Si/C composite material. First, NiSi₂/Si composite material was obtained by ball milling with Li, Ni and SiCl₄ as rough materials, then heated at 900 °C at 2 h in argon atmosphere. Furthermore, a CVD method is deployed to coat the NiSi₂/Si phase with carbon. Usually the magnetron sputtering technique is often used to prepare high-performance metal silicides due to its ease of use and ability to produce large-scale uniform film. Zhang et al. [101] developed a composite anode of Cu/Si/Ge nanowire, which exhibited a stable capacity retention (81% after 3000 cycles at 2C) and doubled specific capacity at rate of 16C. The Cu/Si/Ge nanowires were fabricated by three steps. First, CuO was prepared on Ni foam by e-beam evaporation and furnace-heated, then Si and Ge were deposited on the surface of CuO nanowires by magnetron sputtering. Finally, the as-prepared CuO/Si/Ge nanowires were annealed at 300 °C in H₂/Ar to transform CuO/Si/Ge nanowire arrays into Cu/Si/Ge nanowire arrays.

Table 2 Electrochemical performance of some metal silicides

Materials	Discharge plateaus (V)	Initial coulomb efficiency (%)	Cycling stability (current rate, specific capacity, cycle numbers, capacity retention)	References
Mg ₂ Si	0.01–3.0	84.0	100 mAh g ⁻¹ , 1040 mAh g ⁻¹ , 35 cycles, 4.0%	[26]
Mg ₂ Si/C	0.02–2.0	60.6	100 mAh g ⁻¹ , 1199 mAh g ⁻¹ , 500 cycles, 39.2%	[28]
Ge _{0.1} Si _{0.9}	0.02–2.0	94.0	0.8 mA g ⁻¹ , 2022.12 mAh g ⁻¹ , 100 cycles, 52.8%	[30]
Ge _{0.25} Si _{0.75}	0.02–2.0	95.0	0.8 mA g ⁻¹ , 1992.10 mAh g ⁻¹ , 100 cycles, 62.8%	[30]
Ge _{0.5} Si _{0.5}	0.02–2.0	98.0	0.8 mA g ⁻¹ , 1934.12 mA g ⁻¹ , 100 cycles, 64.3%	[30]
Si/Ag/C	0.005–3.0	61.9	200 mAh g ⁻¹ , 988 mAh g ⁻¹ , 10 cycles, 71.0%	[102]
Si/Ni	0.0–2.0	82.4	233 mA g ⁻¹ , 650 mAh g ⁻¹ , 100 cycles, 72.9%	[57]
Si ₈₀ Ni ₂₀	0.0–2.0	59.0	50 mAh g ⁻¹ , 1304 mAh g ⁻¹ , 15 cycles, 7.7%	[56]
Si ₇₀ Ni ₃₀	0.005–2.0	80.9	240 mAh g ⁻¹ , 600 mAh g ⁻¹ , 30 cycles, 90%	[103]
NiSi ₂ /Si/C	0.01–1.1	81.0	2034 mAh g ⁻¹ , 765 mAh g ⁻¹ , 200 cycles, 86.7%	[100]
MP-Si/Ni/C	0.01–1.5	68.2	200 mAh g ⁻¹ , 1942.4 mAh g ⁻¹ , 120 cycles, 57.3%	[104]
Fe ₁₄ Si ₈₆	0.02–1.5	92.0	100 mAh g ⁻¹ , 1528 mAh g ⁻¹ , 100 cycles, 34.8%	[98]
Fe ₁₀ Si ₉₀ -G-C	0.0–2.0	87.0	200 mAh g ⁻¹ , 1201 mAh g ⁻¹ , 80 cycles, 88.5%	[105]
Fe ₂₀ Si ₄₀ -G	0.0–1.2	84.0	–, 800 mAh g ⁻¹ , 20 cycles, 75.0%	[63]
Si–Cu ₃ Si	0.0–1.5	93.5	100 mAh g ⁻¹ , 1310 mAh g ⁻¹ , 30 cycles, 83.0%	[106]
Si–Ti	0.02–1.5	77	0.1 mA cm ⁻³ , 1542 mAh g ⁻¹ , 50 cycles, 15.3%	[107]
Si–Mn/rGO	0.01–3.25	64.6	100 mAh g ⁻¹ , 1033 mAh g ⁻¹ , 50 cycles, 57.6%	[108]
Si/Co–CoSi ₂	0.01–3.0	77.9	100 mAh g ⁻¹ , 1200 mAh g ⁻¹ , 80 cycles, 79.3%	[109]

Fig. 12 Electrochemical performance of some metal silicides

5 Comparative Analysis of Metal Silicides

In the past 20 years, a large of number metal silicides have been explored as anode materials for lithium-ion batteries, and their insertion/extraction mechanisms of lithium have been reported in the literature. Generally, in the presence of Li-active metal in the M-Si alloy anodes, an obvious decrease in capacity retention was observed in spite of

high initial capacities. This is due to the increase in the pulverization of the anodes resulting from Li insertion into the active metal matrix. By comparison, the anodes of metal silicides containing Li-inactive metals usually give rise to lower reversible capacity since the inactive host matrix does not involve electrochemical reaction except for the low content Si-active material. But the inactive matrix present in such type of metal silicides can sustain the Si volume changes during the lithiation and delithiation process, which results in a good cycling stability.

Since the types of metal silicides and their composite materials and number of alloy compositions tested are large, the electrochemical data obtained from literature were tabulated (see Table 2) to determine material showing superior electrochemical performance. In order to facilitate comparisons, we drew a chart showing the specific capacity and initial coulombic efficiency of some metal silicide and their carbon composites, as shown in Fig. 12. It can be seen from Fig. 12 and Table 2 that the Li-active metals (Mg, Ge, Ca, Ag) have higher specific capacity but poorer cycling stability. For the Li-inactive metals (Ni, Fe, Cu, Ti), high specific capacity can be achieved at low operating voltage by adjusting the content of Si in the inactive matrix. Moreover, the capacity retention can be improved with the help of graphite addition and carbon coating. From the comparative analysis, the metals of Ge, Mg, Ni, Fe, Cu, Ti forming silicides are expected to be

Table 3 Electrochemical performance of different nanostructured metal silicides

Type of silicide	Nanostructure	Capacity (mAh g ⁻¹)	Cycle	Capacity retention (%)	Current density	References
Si _{0.5} Ge _{0.5}	Mixed particles	2022.12	100	64.3	0.8 mA g ⁻¹	[30]
Si/Ge	Nanotube	2362	100	24.8	200 mAh g ⁻¹	[110]
cpSG@C (canyon-like Si-Ge alloy@C)	Nanoparticles with canyon-like surface	1247	100	78.3	500 mAh g ⁻¹	[111]
Si ₅₃ Ge ₄₇	Core-shell	1692	60	90.0	5C	[112]
Si _{0.67} Ge _{0.33}	Nanowires	1709	250	79.6	C/5	[32]
Si/Ge	Heterostructure nanowires	1644	400	71.8	C/5	[33]
Ni ₃ Si/Si/NWs	Core-shell	3773	50	71.0	2.1 A g ⁻¹	[113]
Ni _x Si _y	Core-shell nanowire	1406	100	73.7	1 A g ⁻¹	[114]
NiSi _x /a-Si	Nanowire	1400	150	87.3	10 A g ⁻¹	[115]
Ni/Si	Core/shell nanosheet	2905	100	87.0	C/2	[116]
Ni ₂ Si/Si	Core-shell	1547	600	85.0	358 mA g ⁻¹	[117]
3DGF/Cu/Si (three-dimensional graphene foam/Cu/Si)	Core-shell nanoflowers	1647	500	65.1	3.2 A g ⁻¹	[118]
Si-Cu	Nanotubes	780	1000	88.0	20 A g ⁻¹	[68]
Cu-Si	Core-shell nanotube arrays	2473	400	60.9	C/2	[119]
HCS NW (hierarchical Cu-Si nanowire)	Nanowire hybrids	800	9000	60.0	20 A g ⁻¹	[69]
Si ₈₀ Ti ₂₀	Thin film	1017	300	≈ 100	2 A g ⁻¹	[120]
Si-Ti	Binary framework	960 (2nd)	200	82.1	2 A g ⁻¹	[77]

Fig. 13 Schema of a classification of metal silicides, corresponding challenges and solutions

the potential anode materials for Li-ion batteries. Besides, the initial coulombic efficiency (ICE) is a very important parameter to evaluate the performance of metal silicide anodes. From the dotted polyline of Fig. 12, the metal silicides containing Ge, Fe, Cu, Ti, particularly Si-Ge solid solution, exhibit a better initial coulombic efficiency. This indicates that more active Li can return to the cathode in a fully discharged state, and hopefully achieve a high energy density required for practical LIBs.

Although the metal silicides (Ge-Si, Ni-Si, Fe-Si, Cu-Si and Ti-Si alloy) have relatively high ICE and noticeable reversible capacity, their cycling stability is still unsuitable for commercial application. To further improve cycling performance, the integration of carbon and nanostructure to metal silicides is considered as an important combinatorial strategy. When carbon or graphite was added into a metal-silicide composite anode, a significant improvement in capacity retention has been reported. This is due to the compliant nature of carbon, which maintains contact and stability of the composite anodes during the volume changes, at least to a certain extent. Carbon and metal component permit formation of a conductive network outside and inside the anode particles, which resulted in improved electronic connection. The nanostructured approach to overcome poor stability is the design and synthesis of complex nanostructure which can not only release the volume expansion in the process of charging and discharging, but also enhance the conductivity of Li ion. The electrochemical performance of different nanostructured metal silicides were summarized in Table 3. It can be seen that most of the nanostructural design can significantly improve cycling stability and rate performance. However, the large-scale and cost-effective

nanostructured processing will face the challenge for metal silicide production in the future.

6 Summary and Perspectives

In summary, the combination of Si with a variety of different metals can form a large number of metal silicides. Basically these can be classified into two types: Li-active metal forming silicides and Li-inactive metal forming silicides, as shown in Fig. 13.

For the Li-active metal forming silicides, they can provide a high capacity due to the combined contribution of Si and the active metals like Sn, Ag, Zn and Al allowing Li reversible insertion/extraction, but cannot sustain large volume changes, and thus have poor capacity retention during cycling. As for the Li-inactive metal forming silicides, the size of initial capacity depends on the content of Si dispersed either in the inactive elemental state matrix (such as Ni, Fe and Cu) or in the inactive intermetallic compound matrix (such as NiSi_2 , CoSi_2 and FeSi_2). This type of metal-silicides has relatively good cycling performance due to the ability of the inactive phase to accommodate the Si volume changes. No matter what types, the combination of metal silicides with carbon can form a composite structure and further improve the capacity retention ability.

In the future, more effort should be put into excellent strategies for improving the electrochemical properties of metal silicide anodes toward the practical Li-ion batteries. One strategy is to create a composite structure consisting of high-strength inactive phases in order to withstand the volume change of Si on cycling through alloy composition design of multi-component metal silicides. Ideally, the inactive matrix phases have high electronic conductivity to allow charge transfer reaction occurring in the alloy anodes. Reducing Si particle size to nanoscale is still very important strategy for particular improvement in electrochemical performance. When nanoscale Si is dispersed in the inactive matrix, the metal-silicide anodes are usually amenable to obtaining high initial capacity and stable cyclability. Another strategy is to prepare carbon-containing metal-silicide composite anodes by adding carbon-based materials such as graphite, nano-carbon into the Si-active/inactive metal matrix in order to improve electronic conductivity and rate capacity.

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