# 碳+OA 摘引言

## [1] C. Jo, A.S. Groombridge, J. De La Verpilliere, J.T. Lee, Y. Son, H.-L. Liang, A.M. Boies, M. De Volder, Continuous-Flow Synthesis of Carbon-Coated Silicon/Iron Silicide Secondary Particles for Li-Ion Batteries, ACS NANO, 14 (2020) 698-707.

Because of their high energy and power density, lithium ion batteries (LIBs) are currently the most promising energy storage technology for mobile devices, electric vehicles, and large-scale energy storage. To further increase the energy density of LIBs, relentless research efforts have been invested in the development of new electrode materials and optimizing the electrode formulation.1−5 Commercial LIB anodes typically rely on Li-ion intercalation in graphite (372 mAh/g) or lithium titanate (175 mAh/g).5 However, much higher gravimetric energy densities have been achieved using anodes that react with lithium by alloying or conversion mechanisms (e.g., Si, Sn, GeO2, SnO2,Fe3O4, etc.).6−8 Unfortunately, these high capacity materials have disadvantages including poor cycling stability, large volume change during Li+ insertion/extraction, high voltage hysteresis, poor rate performance, poor Coulombic efficiencies (CE), and low electrical conductivity.9−12 To improve the ion and electron transport, as well as to alleviate mechanical stress, previous researchers have looked into nanostructuring these active materials. However, nanostructuring often introduces problems of its own such as low tapped and electrode density as well as irreversible reactions taking place on the high surface area of the nanostructured materials. Ongoing research is developing strategies to alleviate some of these challenges.13−15 In particular, attractive strategies have been proposed to address the poor conductivity of high capacity materials by advanced carbon coating processes. For instance, a number of promising carbon cages have been proposed to buffer the volume change of active materials,16−18 but these further reduce the tapped density of the electrodes. Alternatively, flexible high-aspect conductive carbons, such as graphene and carbon nanotubes (CNTs), have been studied.19−21 However, these materials tend to phase segregate after slurry mixing. This is because most carbon additives with high conductivity disperse well in NMP, whereas metal or metal oxides materials tend to disperse water well, which makes it difficult to codisperse them with battery binders such as PVDF in NMP or CMC/SBR in water.22,23 This phase segregation during the electrode coating and drying compromises electron conduction and results in poor material utilization and high ohmic losses. The phase segregation is particularly pronounced with high areal loading electrodes pursued in industry, which dry slower.24 Further, several researchers have shown that the interface between carbon additives and the active material can

degrade over time, which further accentuates the above problems.25,26 Industrially, time-consuming kneading and high intensity mixing processes are used to reduce the agglomeration of carbon additives,24 and academically, methods are developed to anchor active battery materials on the surface of carbon additives (e.g., by synthesizing the active material in the presence of CNTs or graphene).27,28 However, to nucleate the active material on the carbon additives, the carbon surface typically requires oxidation or other chemical modifications, which in turn decreases their electronic conductivity and is poorly scalable.

In this work, we combine several of the above principles to fabricate advanced silicon/iron silicide anodes coated with CNTs. In particular, we focus on a continuous fabrication process that structures nanoparticles into secondary micrometer-sized particles on which CNTs are synthesized. Si is a promising active material because of its high theoretical capacity (>3500 mAh/g), low reaction potential (∼0.35 V), and low cost.29−32 Because of these properties, Si is already mixed in very small amounts with graphite electrodes for commercial automotive applications.5Here, we start from nanosized silicon particles (Si NPs) and react them with iron precursors to form iron silicide for three reasons: (i) to decrease the electrical resistance, which is 2.6 × 101 Ω cm in FexSiy compared to 6.0 × 103 Ω cm in Si33 and (ii) to reduce the volume expansion during cycling. This comes at the cost of a lower capacity (iron silicides <100 mAh/g),33−35 but it should be noted that because of limitations in the capacity of current cathode materials (approximately 200 mAh/g), anode capacities in excess of 550 mAh/g do not substantially improve the overall battery performance.36 Here, we first optimize Si/ FeSi cores with a capacity of 1200 mAh/g and then blend them with graphite to obtain 550 mAh/g anodes. (iii) CNTs can be synthesized from iron/iron silicide domains on Si nanoparticles.37,38 The latter results in a strong anchoring of the carbon additive on the active material and fosters a better electric network in the electrode. This approach inverts the classic approach where carbon additives such as CNTs or graphene are first oxidized followed by active material synthesis from surface defects, which compromises the electrical conductivity of the conductive material. These three properties address electron-transport challenges as well as problems related to phase segregation during the electrode mixing but do not solve problems related to the poor tapped density and poor electrode coating properties of nanomaterials. In commercial battery electrodes, small primary battery particles are often aggregated in larger secondary particles to alleviate electrodecoating challenges and increase the volumetric density.39,40 Here, we follow a similar strategy using spray drying to pack our Si nanoparticles into micrometer-sized spheres. The electrical resistance of micrometer-sized pure Si secondary particles would be too high for good battery operation, but this work shows that CNTs can be synthesized inside the crevices of the secondary particles hereby providing a good internal short-range electrical network. In addition, CNTs extending from the surface of the secondary particles can help with the interparticle long-range conductivity, which is particularly important as industry shifts to thicker electrode coatings.24

Impressive results were achieved in previous reports where CNTs grown on the surface of Si particles for battery applications, however in these reports, CNTs were not structured in secondary particles.41−43 As a result, these batteries were only tested in low loading levels and show poor CE. In contrast, our CVD process on secondary particles reduces the BET surface area and therefore improves the CEs of the material.44 Further, we have performed blending experiments of our electrodes with commercial graphite anodes to balance the electrode capacity, density and areal loading. Finally, we demonstrate a continuous flow synthesis method that allows to continuously synthesize these complex materials from simple precursors. As summarized in Figure 1, our approach enables a hierarchical design for battery electrodes where at the nanoscale the chemical composition of the primary particles and their interface with carbon additives is controlled while at the microscale the secondary particle size and carbon additives are controlling the ion and electron transport, and finally, flow synthesis allows for continuous material production.

RESULTS

## [2] R.F.H. Hernandha, P.C. Rath, B. Umesh, J. Patra, C.-Y. Huang, W.-W. Wu, Q.-F. Dong, J. Li, J.-K. Chang, Supercritical CO2-Assisted SiOx/Carbon Multi-Layer Coating on Si Anode for Lithium-Ion Batteries, ADVANCED FUNCTIONAL MATERIALS, 31 (2021).

1. Introduction

To meet the surging demand for portable electronic devices and electric vehicles, efficient energy storage devices with high energy and power densities are urgently required. Lithium-ion batteries (LIBs) currently fill this need. However, despite decades of progress, the capacity and cycle life of LIBs remain unsatisfactory. [1,2] LIBs commonly use a conventional carbonaceous anode (e.g., graphite). [3]However, a graphite anode, whose theoretical capacity is limited to 372 mAh g −1 ,cannot meet the escalating application requirements. To improve LIB performance, several high-capacity anodes such as, those made of transition metal oxides,Si, Sn, Sb, Al, Mg, Bi, and their alloys have been studied. [4] Among them, Si is a promising anode material due to its high gravimetric capacity (theoretically 3579 mAh g −1 ), earth abundance, and low toxicity. [5] Moreover, its relatively high lithiation/delithiation potential compared to

that of graphite makes it safer to operate(i.e., lower risk of Li metal plating). [6]Thus, Si-based anodes have the potential for application in high-performance, ecofriendly, and low-cost LIBs. Nevertheless, the practical implementation of Si anodes is hindered by its fast capacity decay. [7] The severe volume change (i.e., ≈400%) of Si during lithiation/delithiation causes the mechanical degradation and pulverization of Si particles. Repeated volume expansion/contraction also results in an unstable solid electrolyte interphase (SEI). Low Coulombic efficiency (CE) and SEI accumulation gradually increase the interfacial resistance, leading to electrode performance decay. [8]

To prevent the fast degradation of Si anode, several strategies have been investigated, including size and morphology control, [9] nano-architecture design, [10] application of composites/hybrids, [11] and binder optimization. [12] A thin, uniform, and conformal carbon layer on the Si surface is highly desirable to boost Si conductivity and stabilize the interface. However, a conventional wet-chemical carbon coating method cannot form a high-quality surface covering layer. [13] Because of the high surface tension of the liquid reaction medium, Si aggregates are not easily dispersed, and thus carbon precursors are not effectively delivered between Si nanoparticles. [14] More advanced gas-phase carbon coating processes have thus been employed for Si particles. Magnetron sputtering deposition, [15] atomic/molecular layer deposition, [16] and pulsed laser deposition [17,18] have been applied to improve coating quality. However, these techniques require sophisticated facilities, complicate procedures, and high cost, which hinder their practical applications. A more facile, cost-effective, eco-friendly, and easily scalable carbon coating process is required. A SiOx coating can improve Si anode cycling stability. [19] SiO x shows a smaller volume change during lithiation/delithiation compared to that of Si. Moreover, the Li 2 O and lithium silicates in situ generated during the first lithiation buffer the volume variation and thus improve cyclability. [20] Nevertheless, creating a continuous and homogeneous SiO x coating layer is challenging and usually needs extra syn- thesis procedures. The formation of a SiO x /carbon multi-layer coating in one step, the goal of the present work, is thus highly desirable.

In this context, we believe that supercritical carbon dioxide (SCCO 2 ) synthesis is an appealing method for overcoming the aforementioned constraints. SCCO 2 fluid is characterized by its extremely low viscosity, gas-like diffusivity, and excellent mass transfer properties. [21] The near-zero surface tension of SCCO 2 allows excellent penetration between nanoparticles and the transport of reaction precursors throughout a sample. [22] The physicochemical properties of SCCO 2 , such as, density, viscosity, and the dielectric constant, can be tuned via temperature and pressure. [23] The control of coating layers can thus be achieved. Moreover, SCCO 2 is stable, nonflammable, non-toxic, and inexpensive; thus, the synthesis process is green and readily scalable. SCCO 2 has been used to exfoliate graphite, MoS 2 , and MoSe 2 to produce two-dimensional nanosheets for various applications. [24,25] It was also reported that SCCO 2 fluid could help disperse Si nanoparticles between graphene nanosheets. [26] The resulting silicon/graphene composite showed promising rate capability and cycling stability as a LIB anode. In addition, SCCO 2 fluid can act as a precursor carrier for the fabrication of various nanomaterials. For example, nano-size Ni, [27] Fe, [28] Pd, [22] Pt, [29] Au, [30] MnO 2 , [31] SnO 2 , [32] V 2 O 5 , [33] Fe 3 O 4 , [34] Co 3 O 4 [35] have been synthesized and anchored on

various nanostructured carbon materials. In addition, our team has demonstrated that SCCO 2 itself can serve as the precursor in the synthesis of a highly porous CoCO 3 /graphene nanocom-posite anode for Li + and Na + storage. [36] The charge–discharge properties were superior to those of the conventionally synthesized CoCO3 counterpart. To the best of our knowledge, using SCCO 2 to create coating layers on Si particles has not been previously attempted. We believe that this approach is worthy of investigation.

In the present work, three kinds of carbon precursor, namely, glucose, sucrose, and citric acid, are used in the SCCO 2 -assisted deposition process to produce carbon coating layers. SCCO 2

fluid can oxidize Si, producing a SiO x shell around the Si core. A SiO x /carbon multi-layer coating on Si is thus formed in a one-pot and single-step process, which is facile and easily scaled up for mass production. A control sample synthesized using a conventional wet-chemical route without SCCO 2 [37] is examined for comparison. The microstructure, crystallinity, chemical composition, and lithiation–delithiation behavior of various electrodes are systematically investigated. In addition, the effects of carbon precursors on the material and electrochemical characteristics are explored. The proposed SCCO 2 synthesis approach can fabricate high-capacity, high-power, and long-life Si@SiO x @C composite anodes for next-generation LIBs.

2. Results and Discussion

## [3] H. Su, A.A. Barragan, L. Geng, D. Long, L. Ling, K.N. Bozhilov, L. Mangolini, J. Guo, Colloidal Synthesis of Silicon–Carbon Composite Material for Lithium-Ion Batteries, Angewandte Chemie - International Edition, 56 (2017) 10780-10785.

Silicon is recognized as the most promising anode material to replace or complement graphite in lithium-ion (Li-ion) batteries.[1]However, the large volume change associated with lithiation/delithiation of Si causes significant challenges to practical Si-based anodes.[2]

Although particle pulverization may no longer be the primary problem since the use of Si of nanosize or with nanofeatures,[3] repeated volume change can degrade the electrical contact and destabilize the solid delithiation.[2a]

To date, Si–C composites with various nanostructures including yolk–shell Si–C,[2a, 8] sandwich-structured Si–graphene oxide,[9] pomegranate-like Si–C,[6c] graphene or carbon coated silicon nanoparticles or nanowires[10] have demonstrated excellent electrochemical performance. Clearly, incorporating Si into a carbon matrix does indeed improve the structural and electrical integrity of the Si–C composites.[11] However, most of the synthetic methods in use still face challenges in the uniform dispersal of the primary Si particles due to their poor solubility in any solvent. Herein we report aunique colloidal method to synthesize Si@C composites using Si nanoparticles (SiNPs) that are soluble in organic solvents. Using as calable non-thermal plasma synthetic method developed by the Mangolini group,[12] we synthesized SiNPs with hydrogen-terminated surface and an average particle size of approximately 5nmwith narrow size distribution (Figure S1 in the Supporting Information). Enabled by the surface H, dodecyl chains (C12H25)were tethered onto the SiNP surface upon reaction with dodecane. The obtained C12H25-SiNPs became readily soluble in many organic solvents. The Si content in C12H25-SiNPs is 86.5 wt% as measured with thermogravimetric analysis (TGA, Figure S2). To synthesize the SiNPs@C composite, C12H25-SiNPs were first dissolved in styrene, and the obtained solution was dispersed in the aqueous solution of hexadecyltrimethylammonium bromide by sonication to form astable emulsion. Free radical emulsion polymerization was then initiated to produce acolloid of SiNPs@polystyrene (SiNPs@PS) particles dispersed in water. The SiNPs@PS particles were subsequently coated with a layer of resorcinol–formaldehyde resin (RF) via a seeded sol–gel synthesis followed by carbonization to produce the SiNPs@C composite denoted as SiNPs@CPS.

The transmission electron microscopic (TEM) image, high-angle annular dark-field (HAADF) image, and the energy-dispersive X-ray spectroscopy (EDX) elemental mapping of the SiNPs@CPS are shown in Figure 1.

## [4] B. Chen, L. Zu, Y. Liu, R. Meng, Y. Feng, C. Peng, F. Zhu, T. Hao, J. Ru, Y. Wang, J. Yang, Space-Confined Atomic Clusters Catalyze Superassembly of Silicon Nanodots within Carbon Frameworks for Use in Lithium-Ion Batteries, ANGEWANDTE CHEMIE-INTERNATIONAL EDITION, 59 (2020) 3137-3142.

There is considerable demand to develop rechargeable lithium-ion batteries (LIBs) with high energy capacity and long cycle life for applications in portable electronic devices and electrical/hybrid vehicles. [1,2] Si is recognized as one of the most promising anode candidates because of its high theoretical lithium-storage capacity (4200 mAhg @1 for Li 22 Si 5 ) and moderate Li-uptake potential (0.4 V vs. Li/Li + ). [3–6] However, the serious volume variation (ca. 400%) of Si electrodes, coupled with poor conductivity, often cause electrode pulverization and active material loss, resulting in overall deterioration of battery performance. [7–11] Incorporating Si into a carbon matrix is recognized as an effective method by which to improve structural and electrical integrity of Si- based electrodes for enhanced LIB performance. [12–14] However, the Si/C composites prepared by physical mixing of the two components [15–18] generally results in weak interfacial interactions and uneven dispersion of the two components, which is adverse to electron transfer at interfaces and cycling stability of composite anodes.

Chemical vapor deposition (CVD) based on metal catalysts, where catalyst nanoparticles are dispersed on substrates as catalytic sites for in situ growth of Si nanowires with a vapor–liquid–solid (VLS) mechanism, [8,10,19–22] is a successful method by which Si can be uniformly anchored into the carbon matrix of Si/C composites. However, the introduction of metal catalysts to a carbon matrix is primarily achieved by physical sputtering or chemical deposition, and

such methods involve complicated processes and fail to distribute metal catalysts uniformly. Moreover, the catalytic growth of Si is usually carried out in an unconfined space where Si can be supplied without restriction, leading to poorly controlled growth of Si and the formation of long Si nano-wires (hundreds of nanometers–micrometers). In most cases, the catalysts employed are in the form of nanoparticles with relatively big diameters, which, according to the catalytic growth mechanism, [23] results in the generation of Si nano-wires with large diameters (>50 nm). In principle, Si nano-wires that are long and large in diameter are not conducive to electron transfer from Si to the current collector and also suffer from large volume changes upon cycling. Therefore, the development of a simple and effective metal catalytic strategy to construct Si/C composites with favorable structures for high-performance LIBs is highly desirable. [24,25]

Herein, we propose a novel strategy for the superassembly of a framework bearing Si nanodots (Si NDs) embedded in a carbon (Si NDs%C) framework for application in high-performance LIBs. The strategy was realized by copyrolysis of triphenyltin hydride (TPT) and diphenylsilane (DPS), during which Sn atomic clusters were produced from TPT pyrolysis and served as the catalyst for the pyrolysis of DPS and the catalytic growth of Si. The strategy breaks the Si @ C bonds of DPS and permits graphitization of the carbon framework at lower temperatures, thereby avoiding the generation of SiC. Moreover, the employment of Sn atom clusters can reduce the dimensions of Si product to form Si NDs as a consequence of the reported size-dependent correlation between the catalysts and the Si product. [26] The prepared Si%C composite made of Si NDs dispersed uniformly in a hybrid a/g carbon framework with a hierarchical pore structure (micropores of ca. 1.6 nm in diameter, large mesopores of 12.0–50.0 nm in diameter, and macropores over 50 nm in diameter is beneficial for stable, fast, and high-capacity Li storage. Significantly, the Si NDs%C framework demonstrates low lithiation stress

and an outstanding mechanical stability, revealed by finite element calculations. [27–30] As a result, the Si%C framework anode exhibited high reversible capacity, long cycling stability, and superior rate capability. Moreover, a series of full batteries containing Si%C framework anodes and commercial cathodes exhibited remarkable performance compared to commercial full cells.

The strategy for preparation of the Si NDs%C framework is simple and straightforward, governed by stepwise elevation of temperature from 25 to 800℃ (Figures 1a,b).

## [5] F. Wang, M. Gao, R. Hong, X. Lu, Magnetoelectric Plasma Preparation of Silicon-Carbon Nanocomposite as Anode Material for Lithium Ion Batteries, APPLIED SCIENCES-BASEL, 10 (2020).

1. Introduction

Nowadays, lithium-ion batteries (LIB) are the fastest developing energy storage systems, and have widespread application in mobile phones, laptops, electric vehicles, etc. [1–3]. However, the commercial graphite anode material has a limited theoretical capacity of 372 mAh g−1, which cannot meet the energy density requirements in certain applications [4,5]. Various studies have been carried out to find new high energy density materials, such as Sn- [6,7] or Si-based anodes [8–10], and transition metal oxides [11,12]. Among these, Si-based material is considered as a promising candidate owing to its high theoretical capacity of 4200 mAh g−1 [13,14]. At present, the main challenge is the enormous volumetric change of the Si during the cycle process, leading to structural failure and pulverization [15,16], and the low electronic conductivity of silicon also induces severe irreversible capacity loss.

At present, research has mainly focused on finding new Si-based structures to solve the problems of the volumetric changes. The utility of nanoparticles, nanosheets, nanohollows, nanowires, and nano-core-shells has been studied as well [17–21]. Among them, silicon/carbon composites are regarded as effective structures to alleviate the volumetric changes of the silicon. In them, the silicon acts as the active material to provide lithium storage capacity, and the carbon material acts as a buffer to resist the volumetric changes of silicon during the cycle process. In addition, the drastic capacity fading of the Si-based anode corresponds to the solid electrolyte interphase (SEI) films repeatedly formed during the cycles. It has been proved that the surrounding carbon material avoids direct contact between the silicon and the electrolyte, preventing repeated SEI formation [22–24].

To develop a high-performance anode material, Park et al. [25] synthesized a Si/carbon/graphite composite, and the Si nanoparticles were encapsulated by the carbonized coal-tar pitch and attached to the surface of graphite; the amorphous carbon layer avoided the direct contact between the Si nanoparticles and electrolyte and alleviated the volumetric changes of the Si nanoparticles during the cycles. The specific capacity of the composite was 712 mAh g−1 at a current density of 130 mA g−1, with a capacity retention of 80% after 100 cycles [25]. Wang et al. [26] proposed a sandwich-structured silicon nanoparticle/hollow graphite fiber/carbon-coated composite. In this work, the volume expansion of the Si nanoparticles was effectively controlled by the new sandwich-structure, and the specific capacity of the composite was maintained at 910.1 mA h g−1 after the 50th cycle.

Most silicon-carbon nanocomposites are embedded structures and are prepared by high-temperature pyrolysis of carbon materials, in which the Si nanoparticles are encapsulated by amorphous carbon layers to resists the volumetric change and enhance electrode conductivity. However, the further improvement of the electrochemical performance is limited by the non-uniform thickness of carbon coating and serious agglomeration of Si nanoparticles [27,28]. Moreover, the complex process, reagent pollution, and high cost make it difficult for industrialization.

Recently, plasma technology has been introduced to prepare silicon-carbon nanocomposites due to the rapid synthesis process without expensive materials or toxic reagents. However, the traditional plasma technology for the preparation of silicon-carbon nanocomposite is inadequate to achieve mass production. Herein we proposed a novel plasma process with a magnetron plasma generator, in which the addition of magnetic force increases the volume and density of the plasma reaction region and reduces energy consumption. Thus, it lays a good foundation for mass production. The silicon-carbon nanocomposite was prepared by one-step magnetoelectric plasma pyrolysis of the mixture of methane, silane, and hydrogen, in which methane acts as the carbon source, silane as the silicon source, hydrogen as the reducing gas, and argon as the carrier gas. Finally, a new composite structure was obtained in which the evenly dispersed Si nanoparticles were adsorbed on the surface of tremelliform carbon nanosheets, effectively preventing the aggregation and volume expansion of the Si nanoparticles and showing excellent electrochemical performance.

2. Experimental

## [6] S. Zhou, C. Fang, X. Song, G. Liu, Highly Ordered Carbon Coating Prepared with Polyvinylidene Chloride Precursor for High-Performance Silicon Anodes in Lithium-Ion Batteries, BATTERIES & SUPERCAPS, 4 (2021) 240-247.

1．Introduction

Lithium-ion batteries (LIBs) have long cycling life, high energy density, and high power capability, thus dominating the current energy storage market.[1,2]Significant research efforts have been devoted to development of next-generation rechargeable batteries to meet the demand of the rapidly growing energy storage market,[3–7]as the graphite anodes in current LIBs have a rather limited theoretical capacity of 372 mAh/g. Silicon materials, with a nearly 10-fold higher theoretical capacity of 3579 mAh/g, relatively low discharge potential (<0.5 V vs. Li/Li+ considered as promising anode materials for LIBs.[8–10]), and abundant resource, have been However, a major obstacle for silicon anodes is the dramatic volume change of silicon that occurs during lithiation and de-lithiation, which undermines the electrode’s integrity and disrupts the solid electrolyte interface (SEI). The breakdown of the SEI layers during cycling results in a range of problems, such as low Coulombic efficiency (CE), quick capacity fading and poor cycling stability.[11,12]

To address these challenges, many strategies have been proposed, including nanostructured silicon particles, coating of buffer layers, conductive binders, etc. Recently, various delicate nanostructures have been designed and fabricated, such as nanotubes,[13,14] structures.[17–19]

hollow sphere,[15,16] and yolk-shell These void-containing nanostructures can effectively alleviate the large volume change and improve the cycling performance, but they also suffer from additional demerits such as low tap density, large surface area, complicated synthesis process, and relatively poor electrical properties due to the high inter-particle resistance.[20]

Conductive polymer and carbon coating have proven to be a practical approach to enhance the electrochemical performance of the silicon materials for LIBs.[21] layers not only can improve the electrical conductivity, but also can serve as an electrolyte layer on the surface of silicon to alleviate the side reactions and minimize the volume changes. For example, Wu et al.[22] Conductive coating reported a stable Si/C anode material by in-situ polymerization of polyaniline (PANi) to conformally coat silicon nanoparticles with conducting polymer, delivering a capacity of 550 mAh/g after 5000 cycles at 6 A/g with a mass loading of 0.2–0.3 mg/cm2. The average CE of the Si/C electrode from the 2nd to 5,000th cycle was 99.8%. Lee et al.[23] investigated the pyrolysis of polyacrylonitrile (PAN) at the temperature of 300–500°C to attain the cyclization of PAN, which was achieved without carbonization while maintaining PAN’s polymeric properties. This Si/C material with homogeneous coating layer on the surface of Si nanoparticles could provide superior performance of ~1500 mAh/g after 150 cycles with a CE approaching 100% at a current rate of 0.1 C. Choi et al.[18] used sucrose as a precursor via spray drying process to attain Si/C composite particles in which silicon nanoparticles (~ 70 nm) were embedded in porous carbon particles. The composite electrodes exhibited excellent electrochemical performance of 1243 mAh/g after 150 cycles at 4 A/g with a mass loading of 1 mg/cm2. In the cycling range from first cycle to fifth cycle, the average CE was 98.5%. However, higher Coulombic efficiency and long-term cycling stability are still needed for these silicon-based anodes for practical applications.

Here, we introduce polyvinylidene chloride (PVDC), a polymer containing stoichiometric ratio of sacrificial H and Cl elements with the formula of (C2H2Cl2 )n , as precursor to attain ordered carbon coatings via a simple yet efficient sintering strategy to encapsulate the silicon nanoparticles. The Si/C composites with ordered carbon coatings show excellent electrochemical performance. The composition and preparation conditions of Si/C composites are examined systematically to identify the optimum protocols. The benefit of ordered and compact carbon coatings for silicon anode materials are demonstrated.

2.Results and Discussion

## [7] J. Wu, Y. Cao, H. Zhao, J. Mao, Z. Guo, The critical role of carbon in marrying silicon and graphite anodes for high-energy lithium-ion batteries, CARBON ENERGY, 1 (2019) 57-76.

1 INTRODUCTION

Lithium‐ion batteries (LIBs) have been dominant in the market for powering the portable electronic devices since they were first commercialized, due to their desirable energy and power densities. To meet the market demand for lighter batteries with longer service life, the energy densities of LIBs have to be continually increased. The recent development of electrical vehicles and their widespread use also call for LIBs with high energy. Therefore, there is always constant pressure on the relevant academic and industry communities to improve the energy density of LIBs.1-3 Nevertheless, the conventional LIBs using carbonaceous anode and lithium transition‐metal oxide cathode are approaching their theoretical energy density.

The energy density of LIBs is closely related to the electrode materials and their specific capacity. Compared to the cathode materials, there is more room in anode materials to increase the capacity. For example, the gravimetric capacity of conventional LiCoO2 cathode is around 165 mAh/g, which is 0.2 to 1 times lower than that of Ni‐rich or Li‐rich cathodes,4-6 while the gravimetric capacity of Si anode is 10 times higher than that of conventional graphite anode (372 mAh/g). With the same cathode material, replacing graphite with Si can significantly improve the energy density of LIBs. Therefore, Si has been considered as one of the most‐promising next‐generation anodes towards high‐energy LIBs because of its high theoretical capacity (3572 mAh/g), low working voltage (~0.2 V vs Li/Li+), and abundance in the earth’s crust.7 However, unlike the intercalation‐type anodes (eg, graphite), the alloying/dealloying reaction of Si with Li induces huge volume changes (>300%). Such huge volume changes during electrochemical cycling will lead to repeated cracking and pulverization of Si, and hence the disintegration and fracturing of the Si electrode, accompanied by electrical isolation. The repeated cracking and pulverization will also lead to the continual breaking up of the solid electrolyte interphase (SEI) layer and the explosion of new surface, which will quickly consume the electrolyte and Li ions. Therefore, the use of sole Si anode suffers from extremely fast capacity decay and low coulombic efficiency (CE) as a result of the severe volume changes and unstable SEI films. Design strategies for advanced materials, such as employing unique nanostructures (nanowire, nanotube, core/shell, yolk shell, nanoporous materials, etc) and forming composites with electrochemically inactive/less active materials, such as carbon, conductive polymer, and so forth, have been applied as academic approaches to significantly improve the cycle life.8-10 Nevertheless, the volumetric energy density of these materials and the areal mass loading on electrodes are generally too low for industrial implementation. The commercial goal of achieving high‐performance anodes to replace the existing commercial graphite materials in the near future, involves reaching a specific capacity of 500 mAh/g or higher with a capacity retention of 80% after 500 cycles, while the initial CE and average CE should exceed 90% and 99.8%, respectively (Figure 1). Accordingly, the pressing density should reach ~1.65 g/cm3, and electrode swelling should be restricted to ~10%.11

Recently, the co‐utilization of Si and graphite has emerged as the most practical anode for high‐energy LIBs. Graphite is a commercial anode with low cost, high CE, excellent cycle life, good mechanical flexibility, only small volume change, and high electrical conductivity. The addition of graphite into Si can buffer the volume change, increase the electric conductivity, and achieve high specific, areal and volumetric capacities at the same time. Moreover, the co‐utilization of Si and graphite can use the same commercial production lines, translating into high manufacturability and minimal investment. Therefore, the co‐utilization hybridizes two distinct anodes on the materials level into a single composite, retaining the advantages while circumventing the disadvantages of both, and can secure its success in the anode market. However, it is still a challenge to integrate the Si and graphite into a single system or composite to obtain the desired performance, since both of these materials are significantly different in terms of their physical and chemical properties. Growing research efforts have been devoted to improving and achieving high electrochemical performance with the design and development of Si/G/C composite. The carbon additives play important roles in integrating the Si and graphite from many aspects, such as increasing the interface bonding between the graphite and Si, alleviating the volume variations of Si, and improving the interfacial chemistry, conductivity, and mechanical integration. This review attempts to highlight the critical role of carbon additives, as well as the associated synthesis methods and structures for achieving high‐performance Si/G/C composites for developing high energy‐density LIBs, and aims to provide possible insights for the future development of practical Si/G/C anodes.

2． CHALLENGE OF THE INTEGRATION OF SILICON AND GRAPHITE ANODES FOR HIGH‐ENERGY LITHIUM‐ION BATTERIES

## [8] E.H. Chung, J.P. Kim, H.G. Kim, J.-M. Chung, S.-J. Lee, J.-S. Bae, E.D. Jeong, The Synthesis and Electrochemical Performance of Si Composite with Hollow Carbon Microtubes by the Carbonization of Milkweed from Nature as Anode Template for Lithium Ion Batteries, ENERGIES, 13 (2020).

1. Introduction

It has been known Silicon (Si) has many advantages such as high theoretical capacity (4200 mAh/g),non-toxic, low cost, and abundant reserve [1–6]. Therefore, Si is the one of the most attractive materials as an anode for lithium ion battery. Two main problems should be solved for Si to be used as an anode commercially, which are low electrical conductivity and significant volume expansion (~300%) during Li insertion/extraction [7–12]. In order to enhance electronic conductivity, many researchers have been studied on several of Si-based electrodes. Carbon materials, including artificial graphite, natural graphite, and hard carbon are widely applied for Si coating and the mixture of high carbon Si/carbon composite was synthesized [13–15]. However, it was shown a limitation in the number of times the cycle test. It is because of the lack of enough change in volume of the internal volume of Si. Core–shell structural Si/C composites prepared by the coating of polymer delivered outstanding electrochemical performance, such as good rate capability and a long cycling life, as anode for LIBs [6,13–15]. Yi’s group has synthesized a C-Si and C-Si@G and shown the performance as an anode for LIB. It was clearly seen that the Si/C could only deliver ~617 mAh/g at 0.5 A/g after 100 cycles. The charge specific capacity of C-Si@G at ~1987 mAh/g under the same rates. Other researchers have reported that the specific capacity for porous Si/C anode is 600~750 mAh/g for LIB after 100 cycles [2,4,13,14]. It is confirmed that carbon materials in the silicon–carbon composite can improve the electronic conductivity of composite. However, it is not enough for carbon to play as a role of buffer the huge volume expansion caused by the processes of intercalating lithium ions in silicon.

New types of carbon have been explored to improve the cycle ability and the electrochemical

performance due to their high surface area and good electrical conductivity. Many researchers have studied carbon nanomaterials, such as carbon nanofiber (CNF), a novel one-dimensional (1D) carbon nanomaterial, graphene, and carbon nanotubes (CNTs) [16,17]. Especially, several types of CNF have been manufactured fromdifferent sources, which also demonstrated good electrochemical performance [18,19]. However, most of the CNFs are from non-renewable precursors consequently limiting their large-scale application. Therefore, finding low-cost and renewable resources to manufacturing high performance CNF materials is a pressing problem for every researcher. Also, reducing the consumption of fossil fuel resources should be considered. Recently, biomass has become more attractive in preparation of useful carbonaceous materials as a bountiful renewable resource in nature. Biomass sources such as catkin, lignin, alginate, and wood sawdust have demonstrated excellent electrochemical performance as electrode materials for energy applications [20–25]. Some biomass materials such as pollen, lignin, chitin, cellulose, and catkin have been studied on batteries and supercapacitors [26–30]. They have many advantages of inexpensive, abundant natural resources, renewable, and huge specific surface area. Besides, they could directly serve as both a template with porous structure for LIB and a precursor for the preparation of carbon microfibers by simple carbonization [31,32]. Biomass is not widely applied as an anode for LIB. These day, Chen’s group has reported that HPC@Si@GS shows high rate capability that the electrode delivers a high and stable capacity of 435 mAh/g at a high current density of 1.6 A/g. When the electrode is measured at original current density of 0.1 A/g, it can deliver a capacity of 1003 mAh/g after the subsequent 100 cycles [1]. Zhu’s group has investigated that the Si@C@CNT electrode exhibits a specific capacity of 620 mAh/g at extremely high charging rate of 7.50 A/g. Furthermore, the Si@C@CNT-G electrode exhibits the capacity of 420 mAh/g at the rate of 0.2 C after 100 cycles [2]. MW is the one of the biomass sources and biomass has been studied as a supercapacitor. Recently, there are research papers that biomass has good conductivity, and there are also research publications applied to sulfur batteries. However, biomass is not yet widely used in LIB.

In this study, we used MW as a template with carbon porous structure and a precursor

to prepare HCMT by simple carbonization. HCMT can provide large surface area to load Si particles and buffer space to cushion the enough volume expansion for Si. Therefore, Si was accommodated to MW and calcinated with low-cost carbon sources such as Chitosan (CTS), Agarose, and polyvinylidene fluoride (PVDF) in N2 flow. Three different Si composites, HCMT@Si@C1, HCMT@Si@C1@C2 and HCMT@Si@C1@C3, were synthesized and discussed about electrochemical properties. Characterization for samples used after 100 cycle is in progress. In the future research, it will be the subject of future publication.

2. Materials and Methods

## [9] J.-C. Kim, K.-J. Kim, S.-M. Lee, Preparation and Characterization of Core-Shell Structure Hard Carbon/Si-Carbon Composites with Multiple Shell Structures as Anode Materials for Lithium-Ion Batteries, ENERGIES, 14 (2021).

1. Introduction

Lithium-ion batteries (LIBs) are widely used in many applications but there is an increasing demand for higher energy and power density. These characteristics are mainly determined by which cathode and anode materials are used. Among various anode materials, silicon has been investigated as one of the most promising alternatives to conventional graphite anodes because of its high theoretical specific capacity (about 4200 mAh/g) [1].

However, the practical application of Si as an anode material is currently impeded by its large volume change (~300%) during lithiation and delithiation, resulting in capacity fading and a limited lifecycle. Moreover, the rate capability of Si electrodes is limited by the low electronic conductivity of Si and low lithium diffusion rates in Si [ 2 – 4 ]. Great efforts have been devoted to achieving improved structural stability and electrical performance of Si based anodes [ 5 – 10 ]. Silicon-carbon composites using nanoscale Si have been recognized as a favorable approach to solve the abovementioned problems. Numerous studies have demonstrated that the drawbacks of Si as an anode material could be mitigated by reducing the size of the Si particle. The dispersion of nanoscale Si in a carbon matrix has been a favorable approach in synthesizing Si-based anode materials for LIBs because it improves the performance of Si through avoiding the direct contact with electrolytes [ 11 , 12 ]. On the one hand, the dispersion of nanosized Si particles in a carbon matrix is known to be challenging since these nanosized particles are prone to forming agglomerations [ 13 , 14 ]. On the other hand, it is anticipated that the problem in dispersion of nanosized Si particles will be overcome by synthesizing a Si-carbon black (CB) carbon composite [15].

Graphene(or graphite nanosheet) is regarded as a promising carbonaceous material for silicon–carbon composites due to its unique properties, in which graphene can provide an electrically conductive network and structural support for accommodating the mechanical stress, thus enhance the electrochemical performance of Si-based composites [ 16 , 17 ]. It also appears that the graphene could act as a protective barrier, inhibiting the Si particles from being directly exposed to the electrolyte [18].

To improve energy densities and simultaneously alleviate mechanical instabilities of electrodes, composite electrodes containing a small portion of Si have been increasingly researched [ 19 , 20 ]. However, little attention has been paid to an approach for improving their rate performance.

In this study, by combining several of the abovementioned aspects, a unique core-shell structure hard carbon/Si-carbon composites with multiple shell structures were synthesized to be applied as anode materials for LIBs. The concept was to improve the power density and energy efficiency by adopting a hard carbon with a high-rate capability as a core material and distributing Si nanoparticles in the shell layer. Thereby, it was expected that the utilization of active electrode materials would increase. In particular, we investigated the effect of the shell structure in the composite material on its electrochemical performance as an anode material for LIBs, in which we employed three types of shell structure: Si-carbon, Si-carbon black-carbon and Si-carbon black-carbon/graphite nanosheet. The resultant composite materials are denoted as Hard carbon/Si-carbon composite, Hard carbon/Si-carbon black-carbon composite and Hard carbon/Si-carbon black-carbon/graphite nano-sheet composite, respectively.

## [10] X. Zhou, H. Xie, X. He, Z. Zhao, Q. Ma, M. Cai, H. Yin, Annihilating the Formation of Silicon Carbide: Molten Salt Electrolysis of Carbon–Silica Composite to Prepare the Carbon–Silicon Hybrid for Lithium-Ion Battery Anode, Energy and Environmental Materials, 3 (2020) 166-176.

1. Introduction

Lithium-ion batteries (LIBs) are the key to underpinning the electrification of modern transportation and using intermittent renewable energies such as solar and wind. [1–3] To fulfill the requirements of batteries for electric vehicles and grid energy storage, it is necessary to increase the energy densities of LIBs. [4,5] The use of high-capacity electrode materials is one of the most effective ways to improve the energy densities of LIBs. Si is an earth-abundant element and of a theoretical gravimetrical capacity of 3579 mAh g-1 ,which is ten-fold of the commercially used graphite anode (372 mAh g-1 ). [6] This means that one Si atom can accommodate around four Li + to form Li 15 Si 4 at a fully charged state, resulting in a vast volume expansion (~300%) of Si. [7] During discharge, Li + ions will be extracted out from the Si and subsequently incur a significant volume shrinkage thus causing the collapse of Si framework. [8] After repeated charge and discharge cycles, pulverization of the Si anode becomes severe along with the continual formation of solid electrolyte interface (SEI) layers, so that the active electrode materials gradually lose contact from current collectors and consequently the capacity of the electrode decays. [9] Therefore, the central focus of developing the high-capacity Si anode is to minimize the capacity fading caused by the huge volume change.

To increase the life span of the Si anode, various approaches have been employed such as

designing nanostructured Si materials, [10–12] preparing Si-C hybrid materials, [13–18] using

buffering matrixes, [19,20] and engineering electrolytes and binders. [21–23] It has been proven

that the nanostructured Si can reduce the mechanical stress caused by the volume expansion, and a carbon layer on Si could remarkably stabilize the SEI layers and avoid the disconnection of the Si from the current collector. [24,25] The conventional approaches preparing nanostructured Si include physical vapor deposition (PVD), [26] chemical vapor deposition (CVD), [27] metallothermic reduction, [14,28,29] ball-milling, [30] and chemical etching. [31] In these methods, Si feedstocks are mostly organic Si compounds and Si halides, which require stringent synthesis conditions resulting in high energy consumption and cost. As we know, Si is the second most abundant element in the earth’s crust (26.4% by mass), and silica (SiO 2 ) is the most common natural Si resource. Thus, direct converting silica to nano-Si is of great interests due to the short process, low energy consumption, low cost, and sustainable raw materials.

In addition to the magnesiothermic reduction of solid SiO 2, [29] direct electrochemical reduction of solid oxides in molten salts offers a straightforward way to extract metals/alloys because the molten salts possess high ionic conductivity and wide electrochemical windows. [32–

34]

Si has been successfully prepared by electrochemical reduction of solid silica or soluble silicate in molten CaCl 2 -based molten salts. [35–39]However, the use of CaCl 2 -based molten salts could generate CO 3 2? At the graphite anode and then the CO 3 2? diffuses to the cathode and is then reduced to C, which decreases the coulombic efficiency of the electrolysis. [40–43] Jin et al. reported that the use of MgCl 2 -based molten salt can solve the parasite reactions caused by CO 3 2? in molten CaCl 2 - based molten salts. [44,45] Mai et al. [46] reported that Si nanowires can

be prepared by electrode position in molten NaCl-KCl-MgCl 2 -CaSiO 3 .Yin et al. [47] tested the Li storage properties of the electrolytic Si film obtained in molten CaCl 2 -nano SiO 2 , and the capacity retention of the Si film is only 50% after 40 cycles. Recently, Xiao et al. electrodeposited

Si nanowires on a carbon cloth and revealed that the surface oxide layer significantly plagued the performance of the electrolytic Si. [48] However, there are few studies reporting the use of the electrolytic Si from the electrochemical reduction of solid SiO2 for the anode in LIBs. Since the properties of the Si are highly related to its structures such as morphologies, particle size, and porosities, [46,49,50] the electrochemical reduction of solid SiO 2 involves both solid reduction and dissolution mechanism, [51] so that the morphologies of the electrolytic Si are difficult to control.

Precoating a carbon layer on SiO 2 (SiO 2 @C) could be an effective strategy to prepare the Si@viod@C because the voids can be created by the volume shrinkage from converting SiO 2 to Si. Unfortunately, the electrolysis of SiO 2 @C in molten CaCl 2 generates SiC but not the Si@C. [47,52–56] Likewise, the magnesiothermic reduction of SiO 2 @C generates SiC or Si@SiC but not the Si@C. [57,58] Xiao et al. designed a Si@C@Si structure by the electrolysis of SiO 2 @ polydopamine (PDA) in molten CaCl 2 -NaCl at 800 °C and revealed that the SiC could be retarded by the generated gas of thermal decomposition of the PDA. [48] The obtained Si@C@Si delivered a capacity of 904 mAh g ?1 at 500 mA g ?1 after 100 cycles. Yoo et al. [59] reported that the interface of C/SiO2 played a determining role in manipulating the products of the magnesiothermic reduction of the mixture of SiO 2 and C. Therefore, elimination of SiC by engineering the interface of SiO 2 /C in the process of the (electro-) reduction of SiO 2 @C is the key to preparing Si@C (Figure 1).

Note that Si@C could be prepared by magnesiothermic reduction of SiO 2 @void@C, but the reduction of the SiO 2 @C will concomitantly generate SiC. [59,60] Unlike the magnesiothermic reduction, the electrochemical reduction process could be engineered by alternating the electrochemical potentials and electrolytes. To suppress the formation of SiC by the electrolysis of SiO 2 @C, the MgCl 2 -based mol-ten salts were applied. In this work, the SiO 2 @C was prepared by pyrolyzing the mixture of silica and sucrose. Then, the Si@C was prepared by the electrochemical reduction of SiO 2 @C without generation of SiC in the Mg-based molten salts, and the electrochemical performances of the electrolytic C-Si composite were studied as the anode for LIBs.

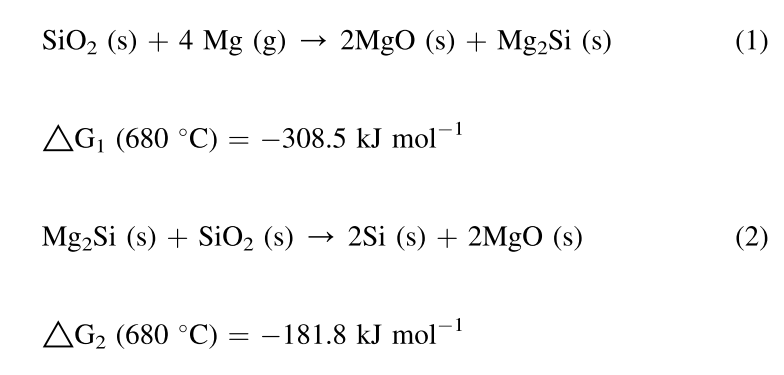
2. Results and Discussion

## [11] Z. Wu, J. Luo, J. Peng, H. Liu, B. Chang, X. Wang, Rational architecture design of yolk/double-shells Si-based anode material with double buffering carbon layers for high performance lithium-ion battery, GREEN ENERGY & ENVIRONMENT, 6 (2021) 517-527.

1. Introduction

Silicon (Si)-based anode materials as a glaring star among the all currently reported anode materials, and it has attracted more and more attention in the industry of LIBs. Especially, nowadays commercialized graphite anodes are hard to meet the ever-increasing need of higher energy and power densities for LIBs, which will restrict the further development of consumer electronics and electric vehicles [1,2]. Generally speaking, the Si-based anode materials in LIBs have many merits, such as the great rich in the earth, theoretical specific capacity（3580 mA h g1）is ten times higher than that of graphite, and the relatively low potential of 0.3 V vs. Liþ/Li, which can avoid the formation of lithium dendrites [3–5]. However, Si-based anode materials undergo the large volume expansion (300%) in lithiation/delithiation process, which will lead to the collapsing and pulverization of the active material, corresponded to the active materials break away from the current collectors [6,7]. Besides, the repeated fracture and formation of solid electrolyte interface (SEI) results in the irreversible consumption of Liþ and electrolyte [8,9], and it causes the low coulombic efficiency and large irreversible capacity loss [6]. In addition, the performance of Sibased anode materials is restricted by sluggish electrochemical kinetics due to the inherent low conductivity [10].

To overcome these thorny problems, many improvement strategies have been adopted. For instance, a variety of nanosized Si particles with different morphology and structures (nanoparticles [11,12], nanowires [13,14], nanosheets [15,16], hollow nanoparticles [17,18], and nanoporous networks [19,20]) have been designed and prepared. These solutions can buffer the huge volume change and enhance the mechanical integrity of Si electrodes to some degree. On the other hand, in order to improve the long cycling stability of Sibased anodes, the Si-based composites with different composite structures have also been designed, such as Si/carbon [21,22], Si/metallic oxide [23,24], and Si/carbon/metal oxide [25,26]. Compared with other modifications, core–shell Si/C and yolk–shell Si/C nanostructures are regarded as easier and higher efficiency strategies in the preparation of Si/C composite. In the Si/C composite structures, the carbon layer not only acts as a buffering shell to relieve the volume changes, but also decreases the contact resistance between Si particles with the current collector [27,28].

It is generally considered that the volume expansion of Si anodes can be limited in the initial lithiation process, when the diameter of particles is less than 150 nm [9]. However, with the decrease of the particles size, the price of commercial nanosized Si increases obviously, and the manufacturing technique of commercial nanosized Si particles is complex. Therefore, the selection of Si will directly affect the production cost of manufacturing Si-based anode materials. Fortunately, Si also can be obtained by making use of magnesium (Mg) to scavenge oxygen from silica (SiO2) at high temperature (500 C–900 C), and the microscale morphologies of the original SiO2 can be maintained, so magnesiothermic reduction have been used to prepare the nanosized Si particles [29–31]. The magnesiothermic reduction process can be summarized as follows: Eq. (1) and (2) [32]. 

The magnesiothermic reduction reaction is an exothermic process, and the obtained Si is melted and aggregated at high temperature. Therefore, the structural integrality of the reduced Si particles is related to the size of SiO2 nanoparticles. Besides, Yoo et al. reported that the Si nanoparticles (10 nm) were uniformly dispersed in MgO matrix via magnesiothermic reduction reaction, and Mg2Si still exists in the inner of product [32]. Moreover, the MgO matrix will contribute to form the ordered mesoporous structure, which will facilitate to enhance the electrochemical stability of Si. In this work, the mesoporous Si spheres were obtained from

SiO2 (St€ober method) particles via the magnesiothermic reduction reaction. The yolk/double-shells (YDS) Si/C anode material with double buffering resin-based carbon layers was fabricated via making use of HF to dissolve the SiO2 in intermediate layer. The unique architecture with double buffering layers can provide good electron/ion pathways and alleviate volume change during charge/discharge process. And the costing of phenolic resin-based carbon is much lower than other organic carbon sources, e.g., polydopamine-based carbon, polyaniline-based carbon and polypyrrole-based carbon. As expected, the new designed yolk/double-shells Si-based anode material with double buffering carbon layers demonstrated many advantages, such as higher initial coulombic efficiency, improved reversible discharge specific capacity, enhanced capacity retention, and good rate capability as well as low cost.

2. Experimental

## [12] L. Zhang, H. Guo, R. Rajagopalan, X. Hu, Y. Huang, S.X. Dou, H.K. Liu, One-step synthesis of a silicon/hematite@carbon hybrid nanosheet/silicon sandwich-like composite as an anode material for Li-ion batteries, JOURNAL OF MATERIALS CHEMISTRY A, 4 (2016) 4056-4061.

1. Introduction

Conventional lithium ion batteries (LIBs) based on carbon anodes, such as commercial graphite microspheres and mesophase carbon microbeads (MCMBs), with a theoretical capacity ofabout 372 mAh g1, have now reached their limits in terms of meeting the need for high energy storage.1–4To meet the increasing demand for energy storage capability, novel electrode materials with higher capacity, low cost, and the ability to be produced on a large scale are of great interest.5

Silicon (Si) and hematite (a-Fe2O3) have long been regarded as appealing anode materials for LIBs because of their much higher theoretical capacities ($4200 and 1007 mA h g1, respectively) than those of the commercially used ones, as well as their nontoxicity and natural abundance.3,6–14Despite all these advantages, the full utilization of silicon- or a-Fe2O3-based batteries to date has been hindered by a series of obstacles, including poor cycle life and rate performance, that resulted from their large volumetric expansion during cycling and low ionic/electronic conductivity.15–19Hence, great efforts have been made to further improve their electrochemical performance by using various silicon-containing (silicon nanowires,10,20,21Fe2O3 nanotubes,26 Fe2O3 and graphene@Fe2O3 composite9) materials. silicon nanotubes,22 porous structured silicon,23 and carbon coated silicon24,25)or aFe2O3-containing (Fe2O3 nanorods,15 nanosheets,6 Among them, porous carbon@Si or carbon@a-Fe2O3 composites in which the active particles are coated or embedded in a porous conductive carbon skeleton are quite promising, because the void space allows the expansion of silicon and a-Fe2O3 during the lithiation/delithiation processes, thus maintaining the structural and electrical integrity.7a carbon@void@Si (yolk–shell) composite system having a high capacity of $2800 mA h g1.27 a-Fe2O3/reduced graphene oxide (rGO) nanocomposites ($1100 mA h g-1) in which the a-Fe2O3 nanoparticles were uniformly anchored on the graphene nanosheets were fabricated by Zhang et al.28 through a facile microwave hydrothermal method. Therefore, the main problem for silicon and a-Fe2O3 can be addressed by combining porosity and the incorporation of carbon in one structure. Until now, some studies have reported that combining siliconwithmetal oxides or alloys in one system is an effective way to improve the electrochemical performance of the synthesized electrodes by taking advantage of the superiorities of both silicon and the active additions, such as Co2O3@Si,29 Ge@Si.32SnO2@Si,30 Fe3C@Si,31 and It is found that, the specific capacities of the composites were increased due to the introduction of silicon, and the cycling stability was also improved due to the specific structure of the metal oxides or alloys. However, to the best of our knowledge, most of the composite anodes explored so far contain either silicon or a-Fe2O3 along with carbon, and only a few reports are available in which both the materials are utilized in one system. Just as reported this year, David Zitoun synthesized Si@hollow gFe2O3 nanoparticles as anodes for LIBs.33As reported, theprepared Si with iron oxide grown on its surface showed a very high specific capacity (around 2600 mA h g1). However, the preparation process in this reported work is very complex and high cost. In addition, without the introduction of carbon or other kinds of conductive additions, the conductivity of this prepared composite is low. Therefore, it is envisioned that advances in LIB technology can be achieved by incorporating both silicon and a-Fe2O3 into one porous carbon skeleton.

Herein, we report a facile one-step synthesis of a carbon–silicon–hematite (C–Si–Fe2O3) composite. In our case, silicon nanoparticles (Si NPs) are sandwiched between a-Fe2O3embedded porous carbon sheets (C@Fe2O3). The electronic conductivity of both the silicon and the a-Fe2O3 NPs can be improved by using the conductive carbon layers.34,35

Meanwhile, the flexible carbon sheets are adaptable and can freely switch between the expansion and contraction of the active particles upon lithiation and delithiation.28,36 In addition, the space between the carbon layers allows the Si NPs to expand freely,37 and the C@Fe2O3 layers can prevent the Si and a-Fe2O3 nanoparticles from aggregating. These unique characteristics facilitate the collection and transport of electrons, resulting in high capacity and good cycling stability.38,39

2. Experimental section

## [13] D. Nan, Z.-H. Huang, R. Lv, Y. Lin, L. Yang, X. Yu, L. Ye, W. Shen, H. Sun, F. Kang, Silicon-Encapsulated Hollow Carbon Nanofiber Networks as Binder-Free Anodes for Lithium Ion Battery, JOURNAL OF NANOMATERIALS, 2014 (2014).

1. Introduction

To meet the increasing demands of rapidly developing market from cell phone to electric vehicles for the Li-ion batteries (LIBs), new anode materials with higher capacity have attracted significant attention. Graphite, the most commonly used commercial anode material, has low theoretical specific capacity (372mAhg−1) and poor rate capability. Silicon is considered as one of the most attractive and promising alternative anode materials to replace graphite in LIBs in the coming decades in virtue of its fascinating performance, such as relatively low working potential (∼370mV versus Li/Li+), rich abundance in earth, environmental benignity, and especially the highest theoretical capacity of4212mAh g−1 among the existing anode materials [1]. However, there still exist several challenges which restrict the commercialization of such silicon anodes. Firstly, the large volumetric expansion (∼400%) of silicon anodes upon the lithiation results in high internal stress, causes mechanical fracture and pulverization of electrode and subsequent losses of electrical contact between the active material and current collector, and leads to poor reversibility and rapid fading of capacity. Secondly, the huge and repeated volume change during the charge/discharge process prevents the formation of a layer of stable solid electrolyte interface (SEI). Hence it can easily continuously grow through the cracks till being too thick for Li-ions to diffuse through, and in turn results in a low Coulombic efficiency and a decrease in capacity. Moreover, silicon anodes possess poor electrical conductivity [2, 3]. Such drawbacks lead to serious capacity fade during cycles and thus hinder the practical applications of silicon anodes.

In order to address abovementioned challenges, it would be crucial to release the mechanical strains, as well as reducing the diffusion length of Li-ions in Si electrode materials during charge/discharge process. Nanostructured Si would be a good solution. So far, many nanostructured silicon and Si-based composites with various morphologies, such as nanoparticles [4–10], porous nanoparticles [11, 12], nanofilm [13–18], nanotubes [19–21], nanofibers [2, 22–37], and core shell structures [3, 38–42] have been prepared and evaluated. Among them, one-dimensional (1D) nanostructured Si or Si containing nanotubes, nanofibers, and core-shell structures showed very good electrochemical performance in virtue of the enhanced electric conductivity of the 1D nanostructures. Furthermore, they could easily form three-dimensional (3D) interconnected networks to buffer the huge volume changes of active Si, thereby preventing the degradation of the electrode integrity and the breakdown of electric conductive networks. However, such1Dsilicon nanostructures were usually synthesized by using toxic SiH4 as silicon precursor and costly Au particles as catalysts [22, 24, 39, 40]. Moreover, the synthesis of them seemed to be too elaborate and suffered from low yield. Thus, the most straightforward and practical approach recently to overcome these shortcomings is to directly utilize the commercially available Si nanoparticles incorporated into carbon matrix, for example, carbon nanofibers via electrospinning method [26–29, 31– 34]. Such products are typical interconnected nonwoven nanofiber networks with good mechanical integrity. The as-prepared free-standing fabrics can be directly used as anodes for LIBs without adding any other polymeric binders or conductive additives. They could increase the effective electrode-electrolyte interface area, facilitate the high-speed electron transport, and hold great potential to enhance the electrochemical performance. Nevertheless, in fact, their cycle stability is still inferior because the direct contact of carbon with silicon has the limited buffer capability, which is difficult to cope with about 400% of volume expansion.

More recently, to improve the cycling stability of silicon anode materials, some new nanostructures with Si nanoparticles encapsulated in continuous hollow carbon tube shave gained much attention due to the enhanced electrical conductivity and stable solid electrolyte interface (SEI). Moreover, particularly, the ample empty space inside the hollow tubes among the silicon nanoparticles allowed for silicon nanoparticles expansion freely during electrochemical cycling, supporting a stable cycling of the entire electrode as well as high charge and discharge rates [2, 3, 35–37, 42]. In addition, it is known that the low-cost phenolic resin (i.e., resol) has high carbon yield (over 50%) during carbonization and good anodic performance for LIBs by exhibiting a high reversible capacity of 550mAh g−1 [43]. More importantly, the resol could be solidified by occurrence of polycondensation reaction thus keeping the original morphology bymeans of solidification process. It is very favorable to generate the tubular nanostructure.

With a motivation to further increase the cycling stability of the silicon anode materials, in this work, we put forward a facile strategy to synthesize novel silicon-encapsulated hollow carbon nanofiber networks with ample space around the Si nanoparticles (hollow Si/C composites) by dip-coating resol on the surface of electrospinning Si/PVA nanofibers along with the subsequent solidification and carbonization. These freestanding membranous hollow Si/C composites can be used directly as anodes for LIBs without adding any carbon conductors or polymer binders. The as-prepared hollow Si/C composites display a high electrochemical performance with excellent cycle stability of ∼90% of discharge capacity retention after 50 cycles.

2. Experimental

## [14] N. Kobayashi, Y. Inden, M. Endo, Silicon/soft-carbon nanohybrid material with low expansion for high capacity and long cycle life lithium-ion battery, JOURNAL OF POWER SOURCES, 326 (2016) 235-241.

1. Introduction

Potential problems associated with natural resources including their depletion and increasing cost and challenges, such as global warming due to the increase in carbon dioxide generated by the combustion of natural resources, have become pronounced in recent years. This has accelerated the expansion of markets for environmentally friendly vehicles such as hybrid electric vehicles, plug-in hybrid electric vehicles, and fuel-cell vehicles. In particular, vehicles are highly anticipated owing to their environmental advantages stemming from their lack of carbon dioxide emissions; however, their actual ranges are still low compared to those of gasoline-powered cars, and the advanced batteries with high energy densities as the power sources of such vehicles are strongly desired to increase their range. In this context, solid-state and metal-air batteries have become increasingly active research and development areas; however, their practical use has not yet been realized.

In this study, we focused on silicon-based electrode materials for lithium-ion battery (LIB); theoretical capacity is approximately 10 times greater than that of graphite electrode of LIB. Hitachi Maxell commercialized SiO negative electrode which is composed of major component of graphite and SiO additives. Panasonic preliminarily released large capacity battery (4.0 Ah) with Si-based negative electrode, but not yet commercialized. Thus, no practical application of LIB, taking advantage of large capacity of Si, has been performed. The greatest challenges that obstruct the practical use of silicon-based materials for LIB is their short cycle life that arises from the alloying of silicon and lithium during their charging and discharging processes and the change in their big volume through large expansion and contraction during the repeated desorption of lithium from the alloy. In previous studies, these effects have been well documented to adversely affect the cycle life of LIB. In addition, vehicles require batteries that span the vehicles’ expected lifetime of as long as 15 years, which is similar to that of the automobiles based on gasoline internal-combustion engine.

Numerous studies to overcome this lifetime problem have already been conducted, including some reports that a longer battery lifetime can be achieved by lowering the absolute value of the volume change that occurs when silicon and lithium are alloyed; in these cases, longer lifetimes were achieved through the fabrication of thinned silicon electrodes [1e3] and micronization of the silicon [4,5]. However, the thin-film method has several shortcomings in terms of production costs that hinder its industrial development; specifically, the required manufacturing equipment is expensive, and its production speed is low compared to that of the method of applying an electrode paste, which is commonly practiced to produce LIB. Furthermore, micronized silicon forms SiO2 via oxidation by oxygen when handled in ordinary atmosphere, which results in increased irreversible capacity during the initial charging of LIB prepared using this method. A large number of studies have been conducted on the conjugation of silicon and graphite [6e21]; however, uniform silicon graphite composites are difficult to prepare, while the amount of added silicon is difficult to increase.

This study developed a new nanohybrid material, composed of carbon coated micronized silicon dispersed in soft-carbon matrix. It exhibited a long cycle life and suppressed the electrode expansion. These behaviors were discussed in connection with abundant nanovoids (diameter of ca. 70 nm) and hard bulk skeletal structure.

2. Experimental method

## [15] Z.P. Guo, E. Milin, J.Z. Wang, J. Chen, H.K. Liu, Silicon/disordered carbon nanocomposites for lithium-ion battery anodes, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 152 (2005) A2211-A2216.

1. Introduction

Lithium-ion batteries have become the power source of choice for consumer electronic devices such as cell phones and laptop computers due to their high energy density and long cycle life. In addition, lithium-ion batteries are expected to be a major breakthrough in the hybrid vehicle field. Despite their successful commercial application, further performance improvement of the lithium-ion battery is still required.

Graphitic or graphitization carbons have been used extensively as negative electrode materials for lithium-ion batteries. However, the lithium storage capacity of graphite as associated with its maximum LiC 6 stage 1 is limited to 372 mAh/g. Lithium alloys are also attractive anode candidates because they can incorporate large amounts of lithium. For example, Li 4.4 Si has a theoretical capacity of 4200 mAh/g. However, lithium alloys are brittle and hence easily pulverized by the large volume change in charge and discharge reactions. The resulting loss of connectivity with the conducting additive particles causes poor cyclability in practice. 2-5 To circumvent this problem, several research efforts have been focused on composites consisting of silicon and carbonaceous materials. For instance, Wilson and Dahn 6 have synthesized nanodispersed silicon in carbon using chemical vapor deposition (CVD). Although the Si–C anodes demonstrated a reversible capacity of 500 mAh/g, it is difficult to control the morphology of Si and C when using the CVD approach. Yoshio et al. 7 prepared carbon-coated silicon by a thermal vapor deposition (TVD) method, and a better cycle life than with the respective silicon has been achieved. Composite produced by mechanically mixing silicon and graphite? or acetylene black? Shows high capacity but its cycling is still poor. 8 More recently, research work by many groups has demonstrated that silicon/disordered carbon (DC) composite, obtained by mechanically milling and pyrolyzing organic precursors, such as polyparaphenylene (PPP) or polyvinyl chloride (PVC), in an inert gas atmosphere can reversibly insert Li atoms with a capacity (>500 mAh/g) greater than that of graphite (372 mAh/g). 9,10 Although the electrochemical performance is significantly improved compared with the respective silicon electrodes, the silicon-disordered carbon systems still pose some problems, such as a relatively high capacity fading rate and a relatively low capacity contribution from the disordered carbon (386 mAh/g from PVC-based disordered carbon; 451.3 mAh/g from PPP-based disordered carbon). Recently, it was reported that the disordered carbon prepared by pyrolyzing hexa(phenyl)benzene (HPB) demonstrated a stable capacity on the order of 500 mAh/g. 11 Carbon from pyrolyzed sugar under optimal conditions showed a large reversible capacity of 650 mAh/g. 12 Therefore, the optimization of the silicon-disordered carbon system and further improvement of the silicon-disordered carbon concept are necessary.

In this paper, a series of Si–DC samples were synthesized by mechanical milling of Si–sucrose and Si–polyvinyl alcohol (PVA) followed by pyrolysis. Here sucrose was chosen because the DC obtained by sugar pyrolysis shows a large reversible capacity (650 mAh/g); 12 PVA was used because it gives the maximum yield of amorphous carbon compared to other polymers. 13 The disordered carbon content in Si–DC nanocomposites was determined by thermogravimetric analysis (TGA) analysis for the first time. The electrochemical properties of the obtained Si–DC nanocomposites as anodes in lithium-ion cells were systematically evaluated.

2. Experimental

## [16] J. Ha, H. Park, M. Kim, Y.T. Kim, J. Choi, Liquefied-Natural-Gas-Derived Vertical Carbon Layer Deposited on SiO as Cost-Effective Anode for Li-Ion Batteries, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 169 (2022).

1. Introduction

Recently, the demand for Li-ion batteries (LIBs) with high energy density has increased. Si-based materials are the most promising candidates for LIB anode materials because of their high theoretical capacity (∼4200 mAh g−1 for Si, ∼2400 mAh g−1 for silicon monoxide (SiO), and ∼1680 mAh g−1 for silicon dioxide (SiO2)) compared to transition metal oxide1,2 and organic based electrode3 adequate lithium alloying–dealloying potential (∼0.5 V vs Li/Li+), and abundance in the Earth’s crust (15.1 wt%).4,5 However, because of their low conductivity and high-volume expansion rate during cycling (∼400%) leading to loss of electric contact via pulverization and electrolyte decomposition, Si-based electrodes exhibit poor cycling properties and fast capacity fading.6,7 Therefore, to overcome these shortcomings, recently, researchers have increasingly focused on coating the active material surface with a carbon layer that increases electrical conductivity and suppresses volume expansion by inducing the formation of a stable solid electrolyte interface (SEI).8–10 Typically, chemical vapor deposition (CVD) is the most effective method for large-scale manufacturing of carbon coating layers on active materials. Kang et al. fabricated a fibrous yolk–shell-structured Si–C freestanding electrode with a high areal capacity over 150 cycles via CVD using acetone.11 In addition, an amorphous carbon-coated porous Si–graphene–carbon composite anode with superior cycling performance compared with commercial Si–carbon materials were fabricated via CVD method using methane (CH4) under an Ar atmosphere.12 However, the use of expensive hydrocarbon-based carbon sources with high purity, including CH4, ethane (C2H6), acetylene, and n-butane (C4H10), during CVD leads to an increase in the overall electrode manufacturing cost13 To minimize the total production cost of CVD using expensive and high-purity hydrocarbon-based carbon sources, several researchers have attempted to obtain diverse carbon structures for decorating active materials using inexpensive carbon sources, such as liquefied petroleum gas,13,14 natural gas15 and coal gas.16,17

Herein, we deposited a vertical carbon layer on SiO as an anode material for LIBs via CVD using liquefied natural gas (LNG, 0.27 USD/L, based on the retail price in 2021, South Korea), which was 13 times less expensive than high-purity CH4 (3.52 USD/L, based on the retail price in 2021, South Korea). Furthermore, the physicochemical properties and electrochemical performance of the carboncoated SiO electrode prepared using inexpensive LNG (denoted as C-SiO-LNG) were compared with those of a carbon-coated SiO electrode prepared using high-purity CH4 (denoted as C-SiO-CH4).

2. Experimental

## [17] J. Kong, Y. Wei, Silicon Nanoparticles Confined in Thin Carbon Network: The Free-Standing Anode of Lithium Ion Batteries with High Performance and Easy Recyclability, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 166 (2019) A2013-A2020.

1. Introduction

As the one with exceptionally high gravimetric and volumetric capacity, low discharge voltage as well as abundant resource, silicon (Si) is a promising anode candidate as potential alternative to current commercial graphite in lithium ion batteries (LIBs). The exploration of Si-based anodes has been extensively carried out, as evidenced by hundreds of scientific papers published in the last 15 years and having been reviewed from varied perspectives.1–7 Despite the great potential, several issues of Si as anode severely hinder its practical use, including large volume expansion (more than 300% upon full lithiation) that irreversibly breaks the structural integrity, poor intrinsic electrical conductivity that causes sluggish electrochemical kinetics, as well as gradual pulverization of the anode along with lithiation/delithiation cycles.

Typical strategies to tackle the above issues mainly rely on stabilizing the Si nanostructure while maintaining its morphology/structure integrity during lithiation/de-lithiation. Firstly, introducing “nano-effect” by reducing at least one dimension of Si to normally less than 100 nm, such as Si nanoparticles/nanospheres/nanoflowers,8–10 nanocubes,11 mesoporous Si,12–14 Si nanowires,.15–18 The nanoscale dimension of the Si realizes faster and more complete alloying and de-alloying with lithium ions, and meanwhile suppresses the volume expansion during the process. Secondly, combining with structurally stable and electrically conductive components to produce Si-based composites. Among all the candidates (metals, polymers, etc.),19–22 carbon is the most promising one, acting as host/support of Si, that is capable of buffering/accommodating the volume change of Si during charging/discharging, as well as providing good electrical conduction to the composites. In addition, the carbon phase is also electrochemically active and contributes to the overall battery performance. So far, carbon nanofibers/carbon nanotubes,23–25 graphene/graphite,26–31 amorphous/doped carbon32–36 have been synergistically introduced into Si nanostructures. The ratio of Si/carbon in the composites and the effectiveness of the interaction between Si and carbon are the critical factors that determine the properties. Last but not the least, improving the fabrication/assembling process through, for instance, optimizing the binders,37–39 inkjet-printing of the anode,40 etc. Overall, the design/development of proper Si nanocomposites that could efficiently utilize the electrochemical activity of Si is still highly desired.

Nowadays, the recyclability of the used materials has been becoming a more and more important consideration in industry that favors the utilization efficiency of the materials and the environment protection. Yet this has rarely been investigated in the area of batteries, which the authors think it is worthwhile to unveil to add additional value to the good energy storage performance. In this work, we proposed a straightforward strategy to utilize Si via binding commercially available Si nanoparticles (NPs) within fibrous thin carbon network, achieving freestanding anode without the usage of any binder and carbon black. Interestingly, the Si NPs collapse into smaller ones instead of expanding in volume upon lithiation, leading to excellent electrochemical properties. Moreover, the used collapsed Si NPs can be easily recycled from the anode after battery test, offering opportunity for the further reuse of the Si material.

2. Experimental

## [18] Z. He, X. Wu, Z. Yi, X. Wang, Y. Xiang, Silicon/graphene/carbon hierarchical structure nanofibers for high performance lithium ion batteries, MATERIALS LETTERS, 200 (2017) 128-131.

1. Introduction

The capacity of the commercial graphite has reached its limit, which prevent lithium ion batteries to meet the increasing demand of higher energy density. Besides, the commercial or indevelopment cathode materials also display a low specific capacity [1–8]. Therefore, new anode materials should be developed to substitute the current commercial electrode materials. Silicon is a promising candidate for anode material because of its high theoretical capacity (about 4200 mAh g-1), low discharge voltage and natural abundance [9–14]. But a significant volume expansion and unstable solid electrolyte interphase (SEI) films occurred during the electrode process and results in particle fracture and loss of capacity with cycling [15–20]. Si nanoparticles (NPs) wrapped in carbon materials is an effective way to strengthen the electrochemical properties. Recently, porous carbon [17,21], grapheme [18,22], carbon nanofiber [23,24] etc. have been utilized to accommodate the volume change of the SiNPs, thus effectively avoiding the direct contact between encapsulated SiNPs and the electrolyte and enabling the interfacial and structural stabilization of encapsulated SiNPs during cycling. Though all of these carbon materials have their own advantages, the enhanced electrochemical performance of SiNPs has been limited depended on single coating materials. However, there are only a few of research referred to wrapping SiNPs in two different coating materials, in which different coating materials can make their respective advantages complementary to each other, and then improve the electrochemical properties of SiNPs dramatically.

In this work, we fabricated Si@RGO@C NFs with a hierarchical structure by encapsulating graphene coated Si nanoparticles in the interconnected carbon nanofibers. Firstly, for the Si@RGO, Si NPs were encapsulated into graphene shells with sufficient elasticity to accommodate the strain associated with volume change and enhance the conductivity of lithium ions and electrons. And then these as prepared Si@RGO powders have been wrapped in carbon nanofibers based on an electrospinning technology. This type of composite nanofibers as anode material possesses the advantages of high capacity and long cycle life.

2. Experimental

## [19] T. Azib, C. Thaury, C. Fariaut-Georges, T. Hezeque, F. Cuevas, C. Jordy, M. Latroche, Role of silicon and carbon on the structural and electrochemical properties of Si-Ni3.4Sn4-Al-C anodes for Li-ion batteries, MATERIALS TODAY COMMUNICATIONS, 23 (2020).

1. Introduction

Energy storage demands for current and future portable electronic devices and electrical vehicles are ever growing. Performances of Li-ion batteries in terms of specific power and density surpass other rechargeable battery systems but are still unsatisfactory for many applications such as extended-range electric vehicles [1–3]. The development of advanced anode materials exhibiting higher capacity than current graphite electrodes (C = 370 mAhg-1) remains very challenging [4]. Presently a lot of materials are studied as alternatives for carbonaceous ones to enhance the energy density of the negative electrode using various strategies such as conversion or alloying reactions [5,6]. For the latter, a special interest is brought to p-bloc elements that form lithiated compounds [7]. For instance Sn and Si can form Li4.4Sn and Li3.75Si compounds to store respectively 994 and 3600 mAhg-1 in electrochemical units, leading to much higher capacities than that of graphite [8,9]. In addition to their high theoretical capacity, these elements exhibit low potential and environmental friendliness, both suitable as anode properties.

However, electrodes made of pure p-bloc elements are considered inappropriate because of large capacity fading during electrochemical cycling [10]. The large volume expansion that accompanies Li insertion and extraction during cycle life results in electrode pulverization and loss of electrical contact [11,12]. To ensure mechanical stability, embedding capacitive elements into a buffering matrix that helps accommodating volume changes, while improving electronic conduction, has been proposed [13,14]. This concept can be implemented, for instance, using binary intermetallic compounds made of one element that reacts with lithium (e.g. Si or Sn) and another one that is inactive (e.g. Fe, Ni, Co or Cu). Some reported intermetallics to achieve this goal are Ni3Sn4 [15–17], Cu6Sn5 [18], CoSn2 [19,20], FeSn2 [20], FeSi2 [21] and NiSi2 [22]. This approach has been successfully extended to ternary silicides such as Ti4Ni4Si7 [23,24], TiFeSi2 [25] and Ti3Si2C2 [26]. Moreover, binary and ternary intermetallics have been associated to carbonaceous materials to form highly efficient multicomponent systems, such as Si/FeSi2/C [27] and Si/Cu3Si/C [28], for further improvement of both the mechanical cohesion of silicon and the electronic conductivity of the whole active material.

In this context, an efficient composite Si-Ni3.4Sn4-Al-C has been already synthetized by mechanochemistry [29]. It consists of sub-micrometric Si particles embedded in a nanostructured and complex matrix mainly formed by Ni3.4Sn4 intermetallic compound and disordered carbon. Si and Sn are the capacitive elements whereas Ni and C are expected to accommodate the volume changes and to insure good electronic as well as ionic conductivity of the electrode material. Al addition is based on reported beneficial effects on the cycle-life of Si-Sn-Al amorphous electrodes [30], best results being obtained for the composition 30Si67Sn-3Al which contains 3 wt.% of Al. This composite exhibits high reversible capacity (~ 700 mAhg-1) and long cycle life (over 280 cycles) [31,32]. Here we investigate the influence of silicon and carbon contents on the microstructure of this composite material and its electrochemical properties. Silicon and carbon contents were varied from 10 to 30 wt.% Si, and from 0 to 20 wt.% C, respectively.

2. Experimental

## [20] S. Song, J. Li, A. Zheng, Y. Yang, K. Yin, Facile Synthesis of Sponge-Like Porous Nano Carbon-Coated Silicon Anode with Tunable Pore Structure for High-Stability Lithium-Ion Batteries, MOLECULES, 26 (2021).

1. Introduction

With the rapid growth of energy demand in mobile devices and electric vehicles, etc., the development of lithium-ion batteries with a high capacity, long cycle life, and low cost has been paid much more attention around the world [1]. Silicon has become one of the candidates with the most potential to replace commercial graphite anode (theoretical specific capacity is only 372 mAh−1 for LiC6) due to the high theoretical specific capacity of 4200 mAh g−1 for Li22Si5 [2–4]. However, the extremely large volume expansion of silicon anode as high as 280% (vs. Li15Si4)~417% (vs. Li22Si5) causes severe problems such as pulverization, unstable solid electrolyte interface (SEI) film, etc. [5,6]. These issues lead to the rapid irreversible capacity decay of silicon anodes during the cycling, and then result in poor cycling stability.

Structure design is one of the main strategies to improve the cycling stability of siliconbased anodes. Carbon-coated silicon’s design exhibits improved structural stability and higher cycling stability due to the protection of silicon by the carbon coating layer [7–9]. For example, Liu et al. [10] proposed a hierarchical structure design inspired by the structure of pomegranate through a evaporation-driven self-assembly method combined with coating and etching processes. In this structure, the silicon nanoparticles are encapsulated by a conductive carbon layer that leaves enough room for expansion during lithiation. Owing to the more stable SEI film and relieved stress, this pomegranate-like silicon-based anode exhibited a superior cyclability (97% capacity retention after 1000 cycles). Ryu et.al. [11] introduced a two-dimensional silicon nanosheet coated with a thin carbon layer through chemical vapor deposition. This carbon-coated silicon nanosheet formed ripples upon delithiation, which effectively releases the induced stress, rendering the electrode much more stable and durable than the uncoated counterparts. However, although these improved carbon-coated silicon designs show excellent cycling stability, the complex synthesis methods and even uncontrollable structure adjustment still limit the practical application of carbon-coated silicon anodes.

Herein, we design a sponge-like porous nano carbon-coated silicon (sCCSi) anode with a tunable pore structure based on a facile synthesis method. It was found that the water adding strategy and the heating rate of pre-oxidation are the two key conditions for forming the sponge-like porous structure and maintaining the material integrity. Moreover, the sponge-like porous structure can be easily manipulated by changing the stirring temperature of precursor solution and the oscillation methods of precipitates. The sCCSi with normal and excessive silicon-to-carbon ratios, 1:5 and 1:2, both maintain high capacity retention up to 70.6% and 70.2% after 300 cycles at 500 mA g−1, respectively. Furthermore, the enhanced buffering effect on pressure brought from the sponge-like porous structure in sCCSi is revealed by mechanical simulation.

2. Results and Discussion

## [21] J. Chang, X. Huang, G. Zhou, S. Cui, S. Mao, J. Chen, Three-dimensional carbon-coated Si/rGO nanostructures anchored by nickel foam with carbon nanotubes for Li-ion battery applications, NANO ENERGY, 15 (2015) 679-687.

1. Introduction

Nanostructured silicon (Si) electrodes have shown great potential as lithium-ion battery (LIB) anodes. As the power demands in consumer electronics, transportation, and large-scale renewable energy storage continue to increase, LIBs with a greater power and a higher energy density are urgently needed [1–4].Sianodes [5–9] offer an alternative to commercial graphite, with Li storage capacity ten times higher than that of the graphite (372 mAh g-1)usedincommercialLIBs; thus, Si has been considered as a promising candidate for an anode material for next-generation LIBs. Unfortunately, practical applications of Si as an anode material are not yet a reality due to the huge volume change (4300%) during the lithiation/delithiation process, which leads to dramatic destruction of the initial particle morphology and the loss of electrical contact between active materials and the electrode framework. In addition, the low intrinsic electrical conductivity of Si leads to dramatic pulverization of the Si anode material, rapid capacity decay, and poor cyclability, and thus should be addressed before its practical application [10,11].

Significant efforts have been made towards mitigating the adverse mechanical effects of Si anodes and improving their overall electrochemical performance through diverse strategies, including engineering active material, current collector, binder and/or their interfaces [12–14]. A particularly attractive strategy is the use of in-situ polymerization to form a bifunctional conformal coating that binds to the Si surface and also serves as a short diffusion pathway for electronic conduction and three-dimensional (3D) interconnectivity [9,15].The Si nanoparticles (NPs) are trapped within the interconnected narrow pores of the polymer matrix, which can buffer the pulverization of larger particles during lithiation/delithiation and maintain good electrical connectivity among the fractured particles. Alternatively, hybrid nanostructures with carbon and various morphologies of Si have been created to tailor the nanostructure and buffer the mechanical strain. Nanometersized Si materials combined with carbon in the form of nanoparticles [16,17], nanowires [18], nanotubes [19], and core–shell nanofibers [20–22] have shown a long cycling life as candidate anode materials because they enable rapid Li transport with free volume around nanostructures and thus facilitate strain relaxation.

Carbon is a commonly used conductive additive in lithium-ion electrode materials, which can enhance electrical conductivity and constrain the large volume change of Si to maintain structural integrity by coating the Si surface with carbon [23– 27]. In the electrode structure viewpoint, we adopted Sigraphene with alternating multilayered composite structures, in which Si NPs are embedded in the in-between graphene films using a dip-coating method [28]. Nanostructured Si with graphene coating has been proven to be one of the most suitable Si anode designs because the graphene can accommodate the volume expansion of Si through its void space while enhancing the electrical conductivity [29,30]; however, fabricating those anodes is complex and time-consuming because the adhesion between the active materials and current collectors is not strong enough for longer cycling. Despite these issues, we have found a safer and more economical rapid fabrication method to improve anode performance by carbonating polymer on Si NPs and anchoring active materials on current collectors by carbon nanotubes (CNTs). This, in turn, forms cellular carbon coating and enforces interfacial contact between active materials and substrates by CNTs.

Here we report a novel anode composed of Si NPs trapped in a 3D cellular carbon framework with reduced graphene oxide (rGO) as the electronic fortifier. The polymer, in which Si NPs and GO sheets are well distributed, can be carbonized to become amorphous carbon on Si NPs loaded on nickel (Ni) foams; CNTs rooted from Ni forms, can help active materials stabilization during cycling of LIBs. Such an electrode offers several advantages as LIB anodes: (1) the approach opens a new pathway for scalable, low-cost, and binder-free fabrication of carbon-coated Si/rGO/CNT (SiGC) nanostructures using a viscous solution method, which can assist with the mass loading of active materials; (2) the carbonized polymer generates a dense cellular carbon on Si NPs/rGO surfaces and an Ni foam through the entire electrode [31], attributing to the enhanced electrode integrity; (3) carbon coating and rGO wrapping on Si NPs restrict volume expansion and improve electrical conductivity, thereby enhancing lithium ion transport and electrical contact with Si NPs during the charge/discharge processes; and (4) the catalyzed CNT growth on Ni foams using the CVD method results in a strong interface connection, thereby helping to maintain the stability of the Si anode and improve its cyclability. In addition, the fabrication method using a polymer solution process leads to the uniform distribution of Si NPs and GO sheets in the carbon framework and thus high performance in cycle stability and rate capability. More importantly, CNTs grown on the Ni foam, like nails, can stabilize the active materials on the Ni foam and result in desirable structure integration.

2.Experimental section

## [22] K. Feng, W. Ahn, G. Lui, H.W. Park, A.G. Kashkooli, G. Jiang, X. Wang, X. Xiao, Z. Chen, Implementing an in-situ carbon network in Si/reduced graphene oxide for high performance lithium-ion battery anodes, NANO ENERGY, 19 (2016) 187-197.

1. Introduction

The ever soaring market of portable electronic devices has triggered significant demand and unprecedented research interests for high performance batteries. Lithium ion batteries (LIBs) have been dominating the market for electronic devices due to its relatively higher working potential, higher specific power and energy densities, and better environmentally friendliness compared to previous battery technologies such as lead acid, nickel cadmium, and nickel metal hydride batteries [1,2]. However, the development of LIB technology has fallen far behind the pace of the advancement of electronic devices, which roughly follows Moore's Law [3]. Electric vehicles have emerged as a potential replacement of traditional vehicles due to the limited supply of fossil fuels, long-term increasing oil prices, and the environmental benignity and sustainability of electricity generated from green energy technologies. To meet the demands of increasingly sophisticated electronic devices and competitive electric vehicles, which require both high energy density and power density, tremendous efforts have been devoted to developing high-performance electrode materials in LIBs [4,5]. As increase of specific electrode capacity can greatly reduce a battery's mass and volume.

Silicon (Si) has been regarded as a promising candidate anode material for next-generation LIBs due to its outstanding properties. The theoretical gravimetric capacity of Si is approximately 4200 mAh g-1 – more than ten times that of the commercial graphite (372 mAh g-1) [6]. In addition, Si's high natural abundance, environmental compatibility, low working potential (0–0.4 V vs. Li/Li+), and maturity in the Si semiconductor industry all make it highly desirable as an anode material for LIBs [7–9]. However, several intrinsic drawbacks of Si have prevented it from being widely commercialized as LIB anodes. One of the critical challenges is that the large volume expansion of Si upon lithiation (up to 400% of its original volume) can cause it to crack and pulverize, resulting in the loss of contact points between the active material and the current collector [10–12]. This large volume change also leads to the continuous formation of an unstable solid electrolyte interphase (SEI) which consumes a considerable amount of electrolyte and lithium in a battery [13]. Columbic efficiency and electrode capacity are hence lowered due to these continuous side reactions. Furthermore, the repetitive growth of the SEI may severely block the conductive pathway of electrons between Si and the current collector. These phenomena significantly decrease the electrode's integrity and electron conductivity and, ultimately, the battery's rate performance [14]. Although the pulverization of Si can be prevented by engineering nano-sized structures, the severe volume variation can still lead to the displacement and the detachment of Si from the electrode's original conductive network during cycling [15]. The above disadvantages consequently result in poor cycling and rate performance of Si electrodes. To circumvent the aforementioned problems with Si electrodes, several strategies have been proposed by researchers. One of the potential solutions is to design various nanostructured Si electrodes. Nano-sized Si can better accommodate mechanical strain during lithiation and delithiation processes, and avoid cracking and fragmentation [16]. Improved cycling stability has been demonstrated with mechanically-milled nanostructured particles, [17] and chemically synthesized nanostructures including nanowires, [18] nanotubes, [19] nanoporous structures, [20] and core– shell nanostructures [21]. Another effective strategy to improve Si's performance in batteries is to build an efficient conductive network for Si. Si/C, [22] Si/Graphene, [23] Si/ CNT [24] and Si/conductive polymers [25] have been reported to exhibit enhanced performance compared to bare Si. Recent reports of novel binding materials in electrode fabrication have also shown significant improvement in Si electrode's performance [26–28]. Although these results have shown some promise, there are some significant issues regarding their synthesis. Many of these procedures are highly complex and expensive. For example, the synthesis of Si nanowires (Si NWs) usually requires complex procedures and dangerous precursors such as silane gas. Template growth of Si usually involves multi-step template synthesis and removal steps, adding to the cost of the final Si product. All these factors make it merely impossible for these materials to be widely commercialized [29].

rGO has been intensively studied in the electrochemical field because of its unique structure and superior physical properties including conductivity, mechanical strength and flexibility. It has recently been combined with Si to form composite anode materials in LIBs [30]. Wrapping rGO around Si NPs significantly improves the electrochemical performance of Si NPs in terms of both cycle and rate performance. However, despite the good contact between rGO and Si, the composite still fails to maintain long-term stability. Reported Si–rGO composites generally suffered considerable degradation after certain cycles [31,32]. The degradation of the above Si–rGO anode can be explained by the fact that many of these composites are synthesized using physical mixing, which does not lead to strong chemical bonding between Si and rGO. In addition, the size of rGO sheets is usually much larger than that of Si NPs. These make it difficult to homogeneously wrap Si NPs with rGO. Poor wrapping of Si with rGO and migration of Si NPs from rGO during cycling result in most of the reported unsatisfactory performances.

Herein, we present a highly efficient Si reduced graphene oxide carbon (Si–rGO–C) composite with good Si wrapping and thus improved electrochemical performance compared to commercial Si NPs and regular Si–rGO composite. In order to take advantage of both carbon coating and rGO wrapping, a facile freeze-drying method and a subsequent chemical vapor deposition (CVD) process were conducted using commercially available Si NPs. Si NPs were well embedded onto the GO layers, and the sponge-like composite served as the precursor of the next step carbon incorporation. The following advantages of the obtained Si–rGO–C composite were first proposed and proved based on the electrochemical performances presented in the context. First, a layer of carbon on exposed Si NPs provides enhanced electron conductivity between particles and other rGO flakes with wrapped Si NPs. Second, the carbon rods between the rGO flakes create an effective conductive network in the whole electrode, helping electrons transfer from one rGO sheet to another and eventually to the current collector. Moreover, the flexibility of rGO and the carbon network can also help restrain the electrode morphology change during cycling, avoiding significant detachment of the active material from the conductive network and helping to maintain contact between the electrode material and the current collector. Various physical and electrochemical measurement techniques were adopted to characterize the samples.

2. Experimental

## [23] J. Yang, Y.-X. Wang, S.-L. Chou, R. Zhang, Y. Xu, J. Fan, W.-x. Zhang, H.K. Liu, D. Zhao, S.X. Dou, Yolk-shell silicon-mesoporous carbon anode with compact solid electrolyte interphase film for superior lithium-ion batteries, NANO ENERGY, 18 (2015) 133-142.

1. Introduction

Developing rechargeable lithium ion batteries (LIBs) with a long cycling life, high energy density, and excellent ratecapability is of critical importance for electric vehicles and renewable energy storage [1–4]. The traditional graphite anode with its limited theoretical capacity of $372 mA h g-1 is unable to meet the high energy needs of such applications. Various anode materials and strategies have been explored and proposed for increasing the specific capacity of LIBs [5–7]. Due to its high theoretical capacity (Li4.4Si=4200 mA h g-1) and low discharge potential ($0.5 V versus Li/Li+), silicon has been considered as an attractive and promising candidate for LIBs [8]. The practical application of Si-based anodes, however, is still hindered by two critical problems: the relatively low electric conductivity and the huge volume expansion ($400%) upon lithium insertion and extraction [9]. These often cause fracturing, pulverization, and loss of electrical contact, leading to rapid capacity fading and poor cycling performance [10].

It is a common and effective strategy to adopt nanoscale silicon materials with various morphologies, including nanoparticles [11,12], nanowires [13], nanotubes [14,15], and hollow spheres [16,17]. Compared to bulk silicon, such nanostructured Si is able to accommodate elevated mechanical stress, resulting in prolonged cycling stability. Nanostructured silicon materials, however, still suffer from poor electric conduction [18]. Further optimization is achieved by incorporating nano-silicon materials with various conductive matrixes, such as graphene [19,20], carbon nanotubes [21], and carbon [22,23] to form core-shell and yolk-shell nanocomposites [24]. The most promising carbon coating strategy has been explored to promote the electrochemical performance [25–28]. The obvious advantage of carbon shells is intensive improving the overall electrical conductivity of the Si-based anodes. In addition, the introduction of such a carbon shell plays a key role in alleviating the agglomeration of nano-silicon particles [29,30]. However, the well-established carbon coating methods are based on the chemical vapor deposition, hydrothermal of carbohydrates and polymerization of phenolic resin from sol–gel process, all of them unfortunately result in the compact carbon shells without open and connecting mesopore channels for fast transport of Li+ ions between the electrolyte and silicon. This could be the reason that Si NPs covered with carbon layer matrix as an anode present unsatisfactory rate-capability [18,29,31]. Furthermore, the crucial impact of SEI is usually be neglected and the formation of SEI is hard to control. Importantly, if a stable and compact SEI is constructed, the electrolyte molecules would not penetrate through SEI layer into the active material for further growth, thereby avoiding continual lithium loss and ensuring higher Coulombic efficiency.

Here, aiming at outstanding cycling stability and ratecapability, we report a novel large-void-containing Si@mesoporous carbon yolk-shell structure from commercial silicon NPs for LIB anodes. This unique design has multiple attractive advantages: (i) the special design of the void spaces (10 and 50 nm) between the silicon NPs and the mesoporous carbon shells highlights the superiority of the unique yolk-shell structure and allows us to optimize the cycling stability while maintaining a reasonable storage capacity; (ii) the open-ended mesoporous carbon shells with accessible channels are able to facilitate the fast diffusion of Li+ ions, and guarantee the full immersion of active materials in the electrolyte, thus contributing to excellent rate capability; (iii) the mesoporous carbon shells are beneficial for the formation of a homogeneous and compact SEI-layer film on the external surface, retaining the internal void space for silicon yolk expansion and rendering superior capacity retention at a high current density. With this design, such elegant mesoporous carbon-encapsulated Si yolk-shell NPs address the challenges of rapid capacity decay and unsatisfied rate capability for Si-anodes, and deliver a high reversible capacity of $1000 mA h g-1 with outstanding cyclability during 400 long-deep cycles, as well as superior rate-capability at a very high current density of 8.4 A g-1.

2. Experimental section

## [24] J. Lu, D. Wang, J. Liu, G. Qian, Y. Chen, Z. Wang, Hollow double-layer carbon nanocage confined Si nanoparticles for high performance lithium-ion batteries, NANOSCALE ADVANCES, 2 (2020) 3222-3230.

1. Introduction

Lithium-ion batteries (LIBs) have been considered as one of the most important energy storage devices owing to their high energy density and lack of the memory effect.1,2 However, the commercial anode material, graphite, has got a low theoretical specific capacity (LiC6, 372 mA h g-1), and it is challenging to meet the ever-growing demands of portable electronics and electric vehicles.3,4 Therefore, to improve the energy density of current LIBs, it is urgent to develop a high specific capacity electrode material instead of commercial graphite anodes. Among the emerging anode materials, silicon (Si) is a promising candidate for next-generation LIB anodes due to its high specific capacity (Li15Si4, 3579 mA h g-1), low Li-uptake voltage (-0.5 V vs. Li/Li+) and natural abundance (second largest resource).5–7 Unfortunately, the application of Si-based anodes has been impeded because of its inferior intrinsic conductivity and large volume effect (~300%) during lithiation.8,9 The huge volume variation produces high mechanical stress that causes the powdering of the electrode materials and formation of an unstable solid electrolyte interphase (SEI), resulting in fast capacity fading and poor coulombic efficiency.10

Researchers have developed various strategies to resolve Researchers have developed various strategies to resolve simple and multi-strategic coupling methods to mitigate the volume change of Si and form a stable SEI layer. Metal–organic framework compounds are constructed using metal ions/ clusters and organic ligands through coordination bonding, showing great potential in energy storage.22 The application of MOFs as a derivatized carbon shell in the field of energy storage has been reported.23,24 MOFs not only heighten the mechanical integrity of materials, but also derivate the heteroatom doping and porous structure of the carbon shell, which increases the conductivity, allowing rapid transfer of lithium ions. Furthermore, MOFs can form hollow structures through heterogeneous shrinkage during high temperature heat treatment.25 Thus, it is foreseeable that the combination of Si and MOFs will be a suitable method for the preparation of multifunctional materials.

Herein, a Si-hollow double-layer hybrid carbon nanocage (Si@H-NC@GC) has been successfully prepared based on electrostatic self-assembly, seed-induced growth and heterogeneous shrinkage. The double hybrid carbon shells are obtained during heat treatment where a N-doped microporous carbon (NC) inner shell is derived from ZIF-8 and a mesoporous graphitic carbon (GC) outer shell is derived from ZIF-67.26,27 At the same time, the material is heterogeneously contracted during the high-temperature treatment to form the internal hollow, denoted as Si@H-NC@GC. In the novel structure of Si@H-NC@GC, GC has the effect of stabilizing the SEI, good electrical conductivity and rapid transfer of lithium ions, while hollow NC effectively accommodates the volume expansion of Si nanoparticles and increases lithium storage active sites.28–30 Si@H-NC@GC displays a high reversible capacity of 1052 mA h g-1 (92.5% capacity retention) after 550 cycles at a high current density of 1 A g-1 when used in LIBs. With the successful synthesis of Si@H-NC@GC, the employment of MOFs to synthesize double-layer and even multi-layer anode materials from self-templates will pave a new way for the manufacture of various anodes with high capacity and superior stability for next-generation LIBs.

## [25] B. Li, F. Yao, J.J. Bae, J. Chang, M.R. Zamfir, L. Duc Toan, P. Duy Tho, H. Yue, Y.H. Lee, Hollow carbon nanospheres/silicon/alumina core-shell film as an anode for lithium-ion batteries, SCIENTIFIC REPORTS, 5 (2015).

1. Introduction

Electrochemicalenergystoragehasattractedmuchattentionandreceivedincreasingresearchinterestworldwide for a variety of applications such as portable electronic devices and electric vehicles. The lithium-ion battery (LIB) has become one of the most promising energy storage devices because of its relatively high energy density and reasonable rate capability 1,2. Since the development of the first commercial LIB in the early 1990s by Sony Energytech 3, graphite has been widely used as the anode material. However, the specific capacity of graphite is relatively low due to its intercalation mechanism 4. To further increase the energy density of LIBs for more demanding applications, novel electrode materials with higher specific capacity are required. Silicon is an exciting and promising alternative anode material to replace graphite due to its highest theoretical specific capacity of 3579 mA h g -1 among all of the alloy type anodes, which is almost ten times that of graphite anode (372 mA h g -1) 5. However, two major scientific and technical challenges have hindered its practical applications. First, due to the alloying mechanism, a large number of lithium atoms are inserted into Si and chemical bonds between Si atoms are broken. The structural pulverization induced by the large volume change (>300% at room temperature) during Li insertion and extraction leads to the loss of electrical contact between the

active material and the current collector, eventually resulting in capacity fading and short battery lifetime 6,7. Second, due to the volume expansion and shrink, a thick solid-electrolyte interphase (SEI) layer can be formed deriving from the irreversible side reactions with the organic electrolyte 8. This causes the degradation of battery performance due to the consumption of electrolyte and lithium ions, the electrically insulating nature and the rather long lithium diffusion length through the thick SEI 9. Thus, to make silicon a good anode candidate for LIBs, two major issues must be settled: minimizing the degradation of the mechanical integrity and maintaining the stability of the SEI.

Numerousworkshavebeenconductedontheresearchofsiliconanodetomeettheabovechallenges.Reducing the size of active materials into nanoscale could be one efficient way to alleviate the mechanical fracture. Various structures synthesized by different methods have been proposed, including nanoparticles 10,11 , nanotubes 12,13, nanowires 14,15, nanospheres 16, core-shell nanofibers 17,18 and thin films 19. These nanostructures have demonstrated superior performance compared to bulk silicon because of their ability to release the strain. Moreover, nanostructured silicon has settled the issue of the active material detachment from the current collector, resulting in significant improvement of electrochemical cycling. In spite of this, the surface of silicon is still directly exposed to the electrolyte and therefore unstable SEI is still formed.

To tackle this problem, conformal coatings on silicon anode have been explored. Amorphous carbon is a good candidate and often used as a coating layer because of the relatively simple and inexpensive fabrication process, and more importantly it is both electronically and ionically conducting 20. Recently Al2O3 was used as a coating material fabricated by atomic layer deposition (ALD) 21–23. ALD is a mature technique for conformal coatings. The process is quite easy and the thickness of the deposited materials can be well controlled. Metallic and SiOx coatings have also been studied 9,24. These coatings prevent silicon from being exposed directly to the electrolyte. As a result, a thin SEI layer can be formed. Nevertheless, in some cases, these coatings will fracture upon the volume expansion of silicon, and therefore the silicon surface will be exposed to the electrolyte again. To maintain a stable SEI layer on the surface of the electrodes, void space around silicon inside the coatings is necessary to be built. Recently, numerous relevant structures have been designed to fulfil this requirement 25–35. The free volume allows silicon to expand without rupturing the outer coating layers, and thus the stable SEI is possibly maintained.

In this report, hollow carbon nanospheres/silicon/alumina (CNS/Si/Al2O3) core-shell structure was fabricated to overcome the above issues. The CNS thin film substrate was fabricated by electrophoretic deposition technique, followed by the deposition of amorphous Si and Al2O3 thin layer. The CNS/Si/Al2O3 hollow structure not only provided a conductive film connecting a series of CNSs into 3D network, but also accommodated large silicon volume expansion due to the existence of void space provided by CNSs. Moreover, the electrochemical performance was further improved by the reduced SEI formation due to the coated Al2O3 layer and the efficient electron transport facilitated by the surface-to-surface contact mode.

2.Results

## [26] L.Y. Yang, H.Z. Li, J. Liu, Z.Q. Sun, S.S. Tang, M. Lei, Dual yolk-shell structure of carbon and silica-coated silicon for high-performance lithium-ion batteries, SCIENTIFIC REPORTS, 5 (2015).

1. Introduction

Recently, the rapidly rising price of petroleum and growing concerns about global warming have brought a great deal of attention to lithium-ion batteries with high capacity and energy density for future electric vehicles and portable electronics1–6. Nevertheless, the performance of currently commercialized lithium-ion batteries must be further improved to meet the increasing demand for high energy storage capacity. Therefore, novel electrode materials with higher capacity and higher power density are urgently needed.

Among the various anode materials, silicon is one of the most promising candidates due to its high theoretical capacity (~3580 mA h g−1, Li15Si4) among alloy type anode materials and relatively low discharge potential (~0.4 V vs. Li/Li+)4,5. Despite these advantages, silicon anodes have two major disadvantages that have prevented their widespread use. First, the large volume changes (~300%) in silicon upon insertion and extraction of lithium-ions lead to severe electrode pulverization, which results in the loss of contact between the active materials and the current collector, leading to rapid capacity fading. Second, the continual pulverization of silicon during cycling causes the electrode surface to be cyclically exposed to the electrolyte. This generates continual formation of solid-electrolyte interphase (SEI) films, contributing to capacity fading and poor coulombic efficiency.

In an attempt to overcome these limitations of silicon, much attention has been devoted to the design and fabrication of silicon nanostructures, such as silicon nanowires6–8 and nanotubes9,10, three-dimensional (3D) porous silicon11–14, and silicon in composites with carbon or oxides15–20. Encouraging results have been achieved through these efforts. In particular, Si/SiOx composites21,22, Si/SiO2/C23–25, and yolk-shell structured Si/C26–28 have demonstrated excellent electrochemical performance. These performances can be ascribed to the C or SiOx shell on the outside of the silicon, which can offer a static surface for the formation of a thin and stable SEI, preserving the anode from irreversible reaction with the electrolyte29–31. Additionally, the existing hollow structures in the yolk-shell structure can provide extra space for the volume expansion of silicon, which guarantees the structural integrity of the electrode29–31. These distinguishing features provide enlightened guidance for nanostructured design of high-performance silicon batteries. In this paper, we uniformly coated silicon with a silica layer via the Stöber method and then coated Si/SiO2 composites with a carbon layer. Taking advantage of the inhomogeneous nature of silica shells prepared by the Stöber method32, proper etching conditions were chosen for selectively etching the SiO2 shell by means of a hydrofluoric acid (HF) treatment. By this process, a small portion of the outer layer and a large portion of the interior layer of the SiO2 shell were removed. The novel Si/void/SiO2/void/C structures were obtained. The advantages of dual yolk-shell silicon structures lie in the presence of internal void spaces and the mechanically strong SiO2 layer, which limits the degree of volume expansion of silicon during lithiation. In addition, the amorphous SiO2 and C intrinsically have advantages as shell materials due to their chemical inertness, porous structure, and size-selective permeability33–37. They can provide a double barrier to prevent the electrolyte from reaching the surface of the silicon nanoparticles and protect the anode from subsequent irreversible reaction with the electrolyte31. With the help of the dual yolk-shell structures, the capacity of the silicon half-cell could be stabilized at 956 mA h g−1 at 0.46 A g−1 after 430 cycles with capacity retention of 83%, while the capacity of the Si/C core-shell structures rapidly decreases in the first ten cycles under the same experimental conditions. Therefore, such dual yolk-shell structures can also be extended to other battery materials that undergo large volume changes.

2.Results

# Iseec

## Modelling human–natural systems interactions with implications for twenty-first-century Warming

Most studies on climate mitigation address the question of what society should do. Such normative approaches have led to aspirational solutions such as achieving carbon neutrality by 20501 , reducing short-lived climate pollutants (SLCPs) and extracting up to one trillion tons of CO2 from the air, among others. These prescriptive solutions have been enormously helpful in guiding mitigation policies. However, the reality is that the growth of CO2 emissions and global warming have continued unabated2 . Part of the problem is that the aspirational mitigation goals do not always fully factor in interactions between human and natural systems. Such interactions create barriers against redesigning energy and economic systems3,4 .

Many have concluded that it is now time for a new approach5,6 , which explicitly allows for interactions between natural systems and social systems7–13. Examples of human–natural interactions that have been considered include societal response to perceived climate risks such as providing support for mitigation policies and changing personal behaviours that reduce individual greenhouse gas emissions7 ; the role of finance and other macroeconomic agents in sustaining economic development and shaping the dynamics of transition to low-carbon energy sources9 ; the role of positive tipping points in the societal transformation towards stabilizing climate10; negative feedback on the economics of energy production due to climate risks12; and constraints on carbon emission reductions due to legacy technologies10 and climate change11. Another recent development in coupling human and natural systems is the modelling of the feedbacks between warming, land use and land-cover policy14,15, which has paved the way for an integrated Earth system model16.

The increasing use of integrated assessment models (IAMs)9 has substantially influenced climate mitigation actions proposed in the most recent Intergovernmental Panel on Climate Change (IPCC) Working Group III report17. Most IAMs, however, are still in the early stages of development for fully coupling nature and human systems. As concluded by Peng et al.18, “IAMs have to get real about people”. For example, a recent review19on integrated human–Earth system modelling stated that ‘many potential human–Earth system feedbacks were not explored in these studies’ and ‘none of the studies look at the interactions between energy and climate.’ The present study attempts to fill this gap by focusing on energy–climate interactions

# MDP-Multiagent+water

## Assessing Adaptive Irrigation Impacts on Water Scarcity in Nonstationary Environments—A Multi-Agent Reinforcement Learning Approach

Since the launch of the Harvard Water Program in 1955, the field of water resources management has been dedicated to providing practical solutions for complex water systems (Reuss, 2003). However, these efforts are hindered by the uncertainty and nonstationarity rooted in both the human (demand) and natural (sup ply) systems (Brown et al., 2015; Cosgrove & Loucks, 2015; Herman et al., 2020). Several planning approach es have emerged to address this issue, which can be grouped into three categories: dynamic planning, risk based planning, and robust planning. The first category, dynamic planning, seeks a set of decision rules that yields the optimal outcomes (Castelletti et al., 2010; Harrison, 2007; Higgins et al., 2008). Risk-based plan ning aims at generating solutions under different risk levels and explores tradeoffs between risks and man agement objectives (Borgomeo et al., 2018; Hall et al., 2020; Lund, 2002), whereas robust planning looks for strategies that are robust (acceptable) across a variety of future conditions (Lempert & Collins, 2007). These categories are not mutually exclusive as several hybrid methods have been proposed. For instance, Dynamic Adaptive Policy Pathways incorporates robust decision-making into dynamic planning to determine the timing and actions for adaptation (Haasnoot et al., 2013; Kwakkel et al., 2015, 2016). Many-objective Robust Decision Making explores robust planning alternatives, plans that perform well in a set of future condi tions, and the tradeoffs among management objectives (including risks) (Kasprzyk et al., 2013; Watson & Kasprzyk, 2017; Yan et al., 2017). Another example is risk-based stochastic programming which enhances dynamic planning by considering risk-aversion to avoid undesirable outcomes (Piantadosi et al., 2008) and learning by doing to improve decision-making adaptively (Hung & Hobbs, 2019). Nevertheless, the meth ods adopted in these studies often do not acknowledge the active interactions among human water users (stakeholders) and natural water supply. Water systems are inherently complex human-nature systems as stakeholders can interact with each other and the environment. Neglecting or simplifying the dynamics among stakeholders and stakeholders' adaptive behaviors may lead to biased conclusions.

Studies have indicated that incorporation of stakeholders objectives (Gold et al., 2019; Hadjimichael et al., 2020; Quinn et al., 2017) and consideration of stakeholders' cognitive beliefs and values (Glynnet al., 2018; Moallemi et al., 2020), are critical for managing complex human-nature systems. Originat ing from the Artificial Intelligence community, agent-based modeling (ABM) was introduced to the water resources field in the late 2000s (Berglund, 2015). Since then, ABMs have emerged for assessing human systems dynamics and impacts on water systems (e.g., Al-Amin et al., 2018;

Berglund, 2015; Ng et al., 2011; Yang et al., 2009). ABM is a distributed, bottom-up planning approach for understanding human impacts on system performance. An agent in an ABM is an object that interacts with other agents and the system of interest (a virtual environment, e.g., water resources models). et al., 2018; Moallemi et al., 2020), are critical for managing complex human-nature systems. Originat ing from the Artificial Intelligence community, agent-based modeling (ABM) was introduced to the water resources field in the late 2000s (Berglund, 2015). Since then, ABMs have emerged for assessing human systems dynamics and impacts on water systems (e.g., Al-Amin et al., 2018; Berglund, 2015; Ng et al., 2011; Yang et al., 2009). ABM is a distributed, bottom-up planning approach for understanding human impacts on system performance. An agent in an ABM is an object that interacts with other agents and the system of interest (a virtual environment, e.g., water resources models).

the collective behavior of the water users in that group, but it may not represent the individual water users' decision-making. In summary, this paper's contribution includes: (a) a modeling approach for studying human adaptation impacts on nonstationary water resources systems with a focus on the human cognitive aspect, and (b) an RL algorithm for simulating agriculture water users’ adaptive water consumption decisions that incorpo rate additional water availability information. Moreover, RL-ABM parameters can better characterize an agent's cognitive processes comparing to Hyun et al. (2019), which can provide information about agents’ reactions to environmental changes. The remainder of this paper is organized as follows. Section 2 describes the modeling framework for agri culture water users’ adaptive policy and the ABM-CRSS coupling. Section 3 introduces the case study. The results are shown in Section 4, followed by the discussion in Section 5. Finally, we present our conclusions and final remarks in Section 6.

Berglund (2015) summarized earlier ABM development and developed case studies of two distinct agent types for water resources planning: the reactive agents respond to environmental signals based on behavio ral rules, and the active agents pursue strategies to optimize their objectives. The former is also known as a descriptive model, and the latter a normative model (Smith, 1991). Recently, several ABM frameworks have been proposed to address the natural uncertainties and nonstationarity of complex human-natural systems. Giuliani et al. (2016) proposed a normative ABM framework to investigate the coevolution of agricultural water systems under climate change. Hyun et al. (2019) and Yang et al. (2020) applied psychological the ories to simulate farmers’ irrigation decision-making under uncertainty. Al-Amin et al. (2018) coupled a descriptive ABM with a groundwater model to evaluate water restriction programs in a watershed with mul tiple cities under future climate scenarios. Castilla-Rho et al. (2015) developed a similar ABM-groundwater model framework with a focus on participatory modeling. Generally, normative ABMs assume rationality and disregard human cognitive activities (e.g., learning and risk attitude), while descriptive ABMs only simulate encoded behavior rules that may misrepresent human response when the environment changes. We believe this research gap can be addressed, at least partially, by reinforcement learning (RL) algorithms.

RL is an area of machine learning where an intelligent agent can learn and improve its decision-making to optimize the long-term reward (Sutton & Barto, 1998). Depending on the context of the problems, RL meth ods can be either learning algorithms for searching optimal policy (a set of rules that guides an agent's ac tions in RL's terms) or decision-making models for simulating human adaptive behaviors (Seo & Lee, 2017; Sutton & Barto, 1998). The former is termed as learning methods, and the latter termed planning methods in the RL community (Sutton, 1992). RL has two essential characteristics: trial-and-error search and delayed reward, which enable agents to adapt their strategies by interacting with the environment. Since the intro duction of RL to the water resources field, it has been extensively applied for optimal reservoir operations (Castelletti et al., 2010; Dariane & Moradi, 2016; Lee & Labadie, 2007; Madani & Hooshyar, 2014; Rieker & Labadie, 2012), with a few exceptions in dam sizing (Bertoni et al., 2020) and water and natural resource allocations (Bone & Dragićević, 2009; Ni et al., 2014). However, despite its increasing popularity, these appli cations only focus on RL's learning aspect for finding optimal policies in a stationary environment.

Focusing on the RL's planning aspect, this paper proposes an RL-ABM framework that equips agents (i.e., the agriculture water users in the case study) with the ability to adapt to a changing water system. The agents' decisions are the water quantity requests submitted to the water resources administration, and the water system is assumed under the impacts of climate change and growing water consumption. Rooted in psychology and cognitive science, the RL algorithm is advantageous, compared to the aforementioned methods, in simulating the constant changes in human beliefs and strategies through interactions with the environment. This feature is critical for the simulation of human reactions in nonstationary systems. Moreover, RL's parameters are relevant to human cognitive activities and can be used to characterize agents’ behaviors (i.e., water diversion patterns in response to signals of environmental changes from the water system).

The RL-ABM framework is applied to the Colorado River Basin (CRB), United States (US), as an illustrative case study. The CRB is one of the most critical water sources in the Western US and Mexico and is facing increasing water stress due to recent droughts and the warming climate (US Bureau of Reclamation, 2012). The Colorado River Simulation System (CRSS), a water resources management model for CRB developed by the US Bureau of Reclamation (USBR) for reservoir operations and policy evaluations (US Bureau of Reclamation, 2007a; Zagona et al., 2001), is adopted in the case study as the virtual environment to be coupled with the RL-ABM for the assessment of water system response to dynamic agriculture water demands. The RL-ABM agents (agriculture water users in the CRSS) can be a single farm, an irrigation ditch, an irrigation district, American tribal water users, or a group of farming entities. Therefore, an agent represents only the collective behavior of the water users in that group, but it may not represent the individual water users' decision-making.

In summary, this paper's contribution includes: (a) a modeling approach for studying human adaptation impacts on nonstationary water resources systems with a focus on the human cognitive aspect, and (b) an RL algorithm for simulating agriculture water users’ adaptive water consumption decisions that incorporate additional water availability information. Moreover, RL-ABM parameters can better characterize an agent's cognitive processes comparing to Hyun et al. (2019), which can provide information about agents’ reactions to environmental changes.

The remainder of this paper is organized as follows. Section 2 describes the modeling framework for agriculture water users’ adaptive policy and the ABM-CRSS coupling. Section 3 introduces the case study. The results are shown in Section 4, followed by the discussion in Section 5. Finally, we present our conclusions and final remarks in Section 6.

# Pnas文章

## Reinforcement learning–based adaptive strategies for climate change adaptation: An application for coastal flood risk management

Effectively adapting to climate change necessitates the development of robust policies and public investments within systems that are complex, interlinked, and characterized by manifold uncertainties. Planners therefore need to be able to adapt their plans to the changing reality ( 1 ). Dynamically responsive, flexible adaptation strategies generally outperform rigid, fixed strategies by incorporating evolving knowledge about risks and uncertainties. First, phased investments can be planned, facilitating relatively low-cost initial actions. Second, dynamic investments enable adjusting actions or plans in response to unexpected future states, forestalling catastrophic failures. Third, possible future actions can be considered in current decision-making to avoid overestimating lifetime risks

Flexible adaptation frameworks are diversely referred to as “adaptation pathways” ( 2 , 3 ), “dynamic adaptation” ( 4 , 5 ), or “real options analysis” ( 6 , 7 ). Several analytical approaches have been developed for modeling these policy frameworks ( 8 – 10 ) and applied to evaluate the benefits and costs of adaptation measures, but they do not account for the full potential of flexible adaptation. Table 1 categorizes quantitative methods applied to environmental policy design according to their ability to a) develop dynamic policy, b) incorporate obser vational data, and c) systematically consider future observations and strategy adjustments in current decision-making.

Methods in category (a) can design a dynamic path for decisions over time. For example, ref. 13 used the dynamic programming (DP) method, a classical sequential decision-making framework, to estimate the optimal path of coastal protection based on current projections of the future climate. Ref. 14 employed heuristic algorithms, stochastically generating thousands of potential paths of the coastal protection and selecting better paths. These heuristic algorithms improve DP’s ability to handle the curse of dimensionality for multistep decision-making ( 14 ). Such methods, however, assume a static base of information and do not directly address a key advantage of flexible policy design: The capacity to learn and thus update and improve decisions as exogenous information is collected.

Methods in category (b) can design dynamic decision paths that adapt to new observations. In extreme cases, they account for the possibility that new information could shift scientific beliefs away from correct climate outcomes, a phenomenon known as negative learning ( 21 ). Specifically, Bayesian dynamic programming (BDP) methods ( 15 , 16 ) extend traditional DP by integrating new obser vations and projections into the estimation of optimal paths. Although BDP can incorporate observations and learning into current decision-making, future learning and updating are not considered, and thus, lifetime risks to be addressed may be inac curately estimated. In other words, the potential for future decision adjustments can affect the optimality of current decisions

Decision trees or real options methods which generate flexible plans by searching over scenario trees can overcome this limitation ( 7 , 17 , 18 ). However, the real options approach involves an event tree with scenarios exponentially increasing with the total number of time steps in the policy pathway. Real options analysis is tractable only under a limited number of potential solutions and scenarios. Direct policy search (DPS) approaches ( 19 , 20 ) lower the compu tational cost by modeling the decision at each time step as a specified function of the observation, with the parameters of the function optimized through simulations. Consequently, the intricate stochas tic sequential decision is treated as a parameter optimization prob lem. Despite their computational efficiency, DPS approaches may still fail to deliver true optimality in adaptive climate decision-making.

RL is an area of machine learning regarding how agents should act in changing environmental states to maximize their cumula tive rewards ( 22 ). RL approaches systematically incorporate observations, consider future outcomes and reactions, and sup port policy designs over a continuous range of future environ mental states. Also, various approximations (e.g., in characterizing states and rewards) can be made in RL for numerical efficiency. RL has been successful in fields including chess playing ( 23 , 24 ), autonomous driving ( 25 ), and robotics control ( 26 ), and it has been employed to address sequential environmental decisions with large decision spaces, including electric power storage ( 27 ) and water resource management ( 28 ). However, it has not yet been used to address uncertainties in climate change risk man agement. We investigate the potential and performance of RL when applied to adaptive climate decision-making. Broadly speaking, we examine the value of systematic learning and updat ing in climate adaptation.

To illustrate, we apply the RL method to model adaptive strategies to address coastal flood risks. Potential coastal adaptation strategies include “protection,” such as building structures such as seawalls along the coastline or dikes on higher lands; “accommodation,” such as retrofitting structures (encouraged through incentives and insur ance regulations); and “retreat,” or withdrawing from harm (which can be encouraged through subsidized “buyouts”) ( 29 ). We account for projected changes in tropical cyclones (TCs), which may induce higher storm surges under climate change ( 29 – 33 ), and sea-level rise (SLR), which has been and will remain primarily responsible for increasing coastal flooding. However, future SLR projections are characterized by large and deep uncertainties, associated par ticularly with human emissions and with ice-sheet physics, that currently impede modeling optimal risk mitigation strategies ( 29 , 34 – 38 ). We develop RL methods to identify optimal coastal risk mitigation strategies (including adaptive seawall construction and combined strategies involving withdrawing, retrofitting, and diking) for Manhattan, New York City, USA (NYC), that incorporate con tinuous SLR observations over the 21st century (Materials and Methods ). RL efficiently handles the computational costs (which grow exponentially in traditional algorithms as the number of SLR scenarios and temporal resolution of decision updates increase) through state and reward approximation methods [Materials and Methods ; ( 39 )].

We focus on coastal flood risk management to evaluate the effectiveness of RL in the wider optimization frameworks for climate adaptation strategies. Comparison to DP, BDP, and DPS shows RL’s superiority in deriving flexible strategies that minimize cost and tail risk. The RL framework also demon strates the greatest ability to minimize “regret” when the actual climate conditions deviate far from initial belief. The results highlight the importance of continuous learning and systematic adaptation in addressing the large uncertainty in climate pro jections and RL’s potential in modeling optimal climate adap tation strategies.

# Ste

## Social tipping dynamics for stabilizing Earth’s climate by 2050

Preventing dangerous climate change and its devastating con sequences is a defining task for humanity (1, 2). It is also anindispensable prerequisite for achieving sustainable development(3, 4). Limiting global warming to 1.5 °C as stipulated in theParis Climate Agreement (5) scientifically implies a complete netdecarbonization of the world’s energy and transport systems, in dustrial production, and land use by the middle of this century. Intheir “roadmap for rapid decarbonization,” Rockström et al. (6)highlight that rapid increase of the share of zero-carbon energywithin the global energy system would be needed to achieve thisobjective, likely alongside a considerable strengthening of terres trial carbon sinks. In one scenario, the zero-carbon share of theenergy system doubles every 5 to 7 y for the next several decades(6). Carbon emissions that are currently still on the rise at rates of0 to 2% per year, despite decades-long efforts in international cli mate negotiations, would thereby need to pivot to a rapid decline ofultimately 7% per year and more. These emission reduction rateswould surpass by far even those experienced only during periodsof massive socioeconomic crisis in the 20th century, such as WorldWar II and the collapse of communism (Fig. 1).

Here, the historically decisive question is whether and how such rapid rates of deployment can be collectively achieved. Current deployment rates of low-carbon energy sources are compatible with the required shift but when scaled up are expected to encounter considerable resistance due to the rigidities inherent in political and economic decision making (7, 8), as well as new technological demands (9, 10). Although an increasing number of countries have already introduced or are committed to introducing carbon pricing, the initiatives covered by carbon pricing included only 15% of global greenhouse gas emissions in 2017 (11) and have so far driven only marginal emission reductions (12). It is increasingly recognized that business-as-usual technological progress and carbon pricing alone are not likely to lead to rapid and deep reductions in greenhouse gas emissions (13).

At the same time, there is evidence from various scientific fields demonstrating that rapid rates of change can be observed under certain critical conditions in natural (14–16), socioeconomic (17–20) and social-ecological systems (SESs) (21, 22). Increasing attention is being given to the concept of tipping dynamics as a nonlinear mechanism behind such disruptive system changes. Based on a review on social-ecological tipping points research, Milkoreit et al. (23) propose a common definition of social tipping points (STPs) as points “within an SES at which a small quanti tative change inevitably triggers a non-linear change in the social component of the SES, driven by self-reinforcing positive-feedback mechanisms, that inevitably and often irreversibly lead to a qual itatively different state of the social system.” There are historical examples of dynamic social spreading effects leading to a large self-amplification of small interventions: For example, the writings of one man, Martin Luther, injected through newly available printing technology into a public ready for such change, triggered the worldwide establishment of Protestant churches (24). An exam ple in the field of climate policy is the introduction of tariffs, subsidies, and mandates to incentivize the growth of renewable energy production. This has led to a substantial system response in the form of mutually reinforcing market growth and expo nential technology cost improvement (25, 26)

In this paper, we examine a number of potential “social tipping elements” (STEs) for decarbonization (27, 28) that represent specific subdomains of the planetary social-economic system. Tipping of these subsystems could be triggered by “social tipping interventions” (STIs) that could contribute to rapid transition of the world system into a state of net zero anthropogenic green house gas emissions. The results reported in this study are based on an online expert survey, an expert workshop, and an extensive literature review (SI Appendix).

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# 1+RL+ABM

# Stand2019-ays

## Deep reinforcement learning in WorldEarth system models to discover sustainable management strategies

I. INTRODUCTION

Efforts invested in identifying pathways toward global sustainability need to account for critical feedback loops between the socioeconomic and sociocultural World and the biophysical Earth

system.1,2 These pathways may require novel, yet undiscovered, multilevel policies, from the local to the global scale, for the governance of this coupled World-Earth system leading toward a safe and just operating space.3,4 Striving for a safe and just operating space, policymakers of the United Nations agreed on global political cooperation for a sustainable future at the resolution of the 17 Sustainable Development Goals (SDG)5 and the adoption of the Paris Agreement on Climate Change.6 The safe and just operating space is based on a set of biophysical planetary boundaries (dened on dimensions such as climate change or biosphere integrity loss) as they are formulated by Rockström *et al.* in Refs. 3, 4, 7, and 8, extended by social foundations (e.g., poverty alleviation) by Raworth.9 If respected together, staying within these boundaries is seen as a prerequisite to ensuring sustainable human development. The eld of Earth system model ing develops computer models to show possible pathways toward a sustainable future. However, the identication and characterization of concrete trajectories within the planetary boundaries and above social foundations remains a problem requiring ongoing research e‑orts.10,1

In this paper, we consider this problem on a globally aggregated level assuming the following basic structure: An abstract single decision-maker interacts with a dynamical, in most cases, nonlinear environment to nd sustainable trajectories within certain boundaries. The eld of Integrated Assessment Modeling (IAM) addresses this issue via optimizing a social welfare function in order to estimate the design of sustainable management strategies.12 IAM models

integrate data and knowledge from established climate models.13,14 To identify pathways in IAM, numerical solvers such as GAMS15 are frequently used. However, these IAM models are highly dependent on the choice of the target function of the optimization. In many cases,

this choice may not be obvious and depends on the IAM developers.16 As another approach, optimal control theory (OCT) can be used to solve problems where dynamical systems are supposed to stay within certain constraints. In these systems, OCT tries to nd an optimal choice for some control variable by optimizing a specic objective function.17 Applied to Earth system models, the focus has been set on the design of climate regulators and their impact on climate modication.18,19 Viability theory (VT) as a subeld of OCT can be stated as an example. In this eld, such problems of identifying trajectories are typically addressed by methods that rely on a

discretization of the state space, followed by the application of local linear approximations.20 It is, however, not well applicable in systems with more than just a small number of variables due to the curse of dimensionality.2

The use of reinforcement learning (RL)22 can also be considered as a possible approach for intelligent decision-making within World-Earth system models.23 It is designed for nding optimal policy strategies as well. However, in contrast to the previously presented approaches, RL does not detect solutions based on numerically solving an optimization problem, but by a dynamic search process via exploration and exploitation of past experiences, guided by a reward

function. However, tabular methods, which are mainly used for classical RL solutions, cannot be straightforwardly applied to the systems of interest here, due to the continuous state spaces that we mostly nd in World-Earth system models.

The common point of all the presented methods outlined above is that they reach their limits as the complexity of the environments increases. However, deep reinforcement learning (DRL)24 algorithms have been shown to detect solutions in other highly complex environments surprisingly well.24,25 In this paper, we propose using DRL as a novel approach for Earth system analysis. Even though rst successful reinforcement learning experiments by using neural networks as nonlinear function approximators were reported already in 1995,26 the breakthrough of DRL was achieved only in 2013.24,25 Since then, DRL algorithms have become increasingly popular in the eld of arti- cial intelligence.27,28 The key to the success of this approach lies in the combination of Q-learning,29 neural networks,30 and experience replay,31 which has been shown to learn policies up to a super human performance in a variety of di‑erent environments.24,25 Often DRL applications come up with unexpected and novel solutions.32,33 Many extensions have been proposed addressing both speed and eciency.34 Due to its general applicability to various environments, DRL is used in a wide range of di‑erent elds, e.g., resources management in computer clusters,35 optimization of chemical reactions,36 playing abstract strategy games like chess and Go,32,33 autonomous driving,37 and, in particular, robotics.38–41

Due to the wide applicability of DRL, we propose a framework that uses DRL as a tool that is both robust and easy to use at the same time to identify and classify trajectories in Earth system models e‑ectively. As a proof of concept, we use our DRL framework within various stylized World-Earth system models.2,42 These models are designed to investigate the coevolutionary dynamics of humans and nature in the Anthropocene. Some rst applications of reinforce

ment learning methods within resource use models have been carried out,43–45 but as far as we know, there are no approaches yet applying DRL to Earth system models. We believe this approach will open so far unused possibilities to discover so far unknown management

strategies that keep the Earth system within planetary boundaries, while, at the same time, respecting social foundations of the world’s societies. Recently, various ways of how to tackle problems related to anthropogenic climate change by using machine learning techniques have been outlined.46 Our work proposes a novel strand to this list.

II. METHODS

# C-切入点-ClimateRL-theo

## Can Reinforcement Learning support policy makers? A preliminary study with Integrated Assessment Models

**1 Introduction**

Climate is a high dimensional dynamical system with strong inter-dependent components and

long time dependencies, all of which interact to produce highly non-linear responses and behavior. Climate is also highly conditioned on human behavior – another greatly complex system – such that is now necessary to reason about climate change from a socio-climatic perspective [Moore et al., 2022]. To make progress towards achieving some kind of solution in the face of extreme consequences, policymakers and advisory groups employ *Integrated Assessment Models* (IAMs), state of the art models for climate change that combine knowledge about human development (such as economical theories) together with planetary sciences such as ecology and geophysics [Parson and Fisher-Vanden, 1997]. Exploring and analysing the properties of the IAMs employed for large scale assessments [Pörtner et al., 2022] - to e.g. measure fidelity against the real world – is generally intractable from a computational perspective, which leads researchers to implement poor simplifying assumptions and decrease their effectiveness [Asefi-Najafabady et al., 2021]. Smaller IAM models aim to provide an alternative by employing fewer state variables and simpler sets of dynamics, making them amenable to mathematical probing and analysis [Kittel et al., 2017, Nitzbon et al., 2017]. Th literature commonly explores these models with ODE solvers; however recently [Strnad et al., 2019] has shown that it is possible to employ them as environments in standard Reinforcement Learning (RL) [Sutton and Barto, 2020], and explore models using trained policies. These can be used to understand the system, and provide upwards insight towards improving more complex IAMs or even our understanding of climate change policies.

We build on this work, testing more RL algorithms, reward functions, as well as different experimental setups. Among others, we show that (a) modern RL can learn effective policies with a variety of reward functions in this environment (b) that different agents and reward functions generate a significantly diverse set of solutions, thus exploring the IAM in different manners, and (c) that it is necessary to apply care when designing reward functions as they show different success rate in reaching the desirable state for different initialisation points, finally - (d) that RL helps us gain a deeper understanding of the properties and limitations of the applied models.

**2 AYS environment, RL reward functions and agent**

## Climate Change Policy Exploration using Reinforcement Learning

Introduction

1.1 Motivation

1.1.1 A Safe Space for Humanity

“It is unequivocal that human influence has warmed the atmosphere, ocean, and land. Widespreadand rapid changes in the atmosphere, ocean, cryosphere, and biosphere have occurred.” according to the latest Intergovernmental Panel on Climate Change (IPCC) report [2].

The relatively stable climate of the last 10-12 millennia, the Holocene, has seen the majority of human advancement: from the first agricultural societies to the start of the industrial revolution. The geological period before the Holocene, is known as the Pleistocene, colloquially known as the Ice Age [3]. Recently, due to the consequential effect of humans on the climate, scientists have started naming the era of human industrialisation the Anthropocene [4, 5]. This proposed geological era is characterized by the effects of humans on the environment and the climate.

Tipping Points refer to certain thresholds at which small perturbations can drastically change a system [6]. For the climate, different tipping elements can cause dramatic changes to the overall climate balance. According to scientists, the climate of the Holocene has a delicate balance [6, 7], one that should not be perturbed lest disastrous consequences for life on Earth, which would be difficult to counteract. It is understood that the climate is a part of a complex coupled socio-ecological system that is also adaptive [8]. So, any actions taken by humans can have many cascading and unpredictable effects [7]. Therefore, the coupled system has to be considered when constructing policy that relates to the climate [9].

To mitigate the effects of future climate change, scientists recommend staying within Planetary Boundaries [10, 11]. These boundaries define limits for measurable quantities, that are linked with significant tipping points, such as keeping warming below +2◦C above pre-industrial levels. Crossing planetary boundaries can provoke feedback loops (or “snowballing” effects) in the climate system that can lead to rapid and uncontrollable climate destabilisation [7]

1.1.2 Climate Change as a Control Problem

The IPCC uses SSP (Shared Socioeconomic Pathways) to make predictions on the possible pathways for the climate given different behaviours of humans. There are five pathways described, ranging from heavily reducing Green House Gas (GHG) emissions, to heavily increasing them. Each potential behaviour has consequences for the Earth and the life on it. Predicting these pathways requires models that have incredibly high uncertainties attached to them, since modelling all the complexities of the Earth is infeasible. The IPCC does not give exact probabilities for each scenario; instead, they predict using terms such as “very high probability”, “low probability”, “medium probability”. These SSP are generated by Integrated Assessment Models (IAM). These models encompass a wide range of scientific knowledge in different fields such as climate, biology, and economics [12].

We know that the weather system and, consequently, the climate are dynamical systems where small changes in initial conditions can lead to startlingly different answers over time [13, 14]. Dynamical systems are deterministic. If the initial conditions are perfectly known, then we can predict outcomes accurately. Having fully accurate data and models is not technically possible, so meteorologists start multiple simulations at different initial conditions and then average the answers, also called ensembles models. This is the approach also taken by the IPCC to generate SSP, they use information from multiple IAMs from the Integrated Assessment Model Consortium and average them out. In dynamical systems, this can yield an incredibly wide range of answers with enough time, which is why weather predictions are often inaccurate further in the future.

Climate is defined as the “general weather conditions usually found in a particular place”1

. The global climate is then the general weather patterns of the Earth. The global climate is easier to predict than the weather over long periods, since it is an average of the weather over long periods. However, due to human influence, this system is being perturbed very fast [15]. Adding perturbations to a dynamical system makes the system even harder to predict. Perturbations can include a change in human carbon emissions, which has cascading and unpredictable effects. Ideally, if we can predict accurately, we can control accurately. We would like to control the climate to negate its most disastrous effects for humans by staying within planetary boundaries. Control would be done by policymakers and worldwide organisations by changing the actions of humans to enable a sustainable future.

The task of keeping a dynamical system within certain boundaries is called Optimal Control Theory (OCT), often referred to more simply as control [16]. This sub-field of mathematics looks at methods that aim to optimise some objective function in a system by controlling the variables of the system. In the case of the climate, we would like to minimise climate destabilisation by staying within planetary boundaries

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