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► **To cite this version:**

Xi Chen, Laure Monconduit, Vincent Seznec. 2D Si-Ge layered materials as anodes for alkali-cation (Na⁺, K⁺) batteries. *Electrochimica Acta*, 2023, 462, pp.142756. 10.1016/j.electacta.2023.142756 . hal-04255205

HAL Id: hal-04255205

<https://hal.science/hal-04255205>

Submitted on 23 Oct 2023

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2D Si-Ge Layered Materials as Anodes for Alkali-Cation (Na⁺, K⁺) Batteries

Xi CHEN, Laure MONCONDUIT*, and Vincent SEZNEC*

ABSTRACT: Recent studies have shown that two-dimensional (2D) materials, such as siloxene and germanane, as electrode in alkali metal ion batteries can lead to excellent performance. The improved electrochemical behavior of these 2D active materials could be due to the limited volume change during charge and discharge, based on an intercalation rather than an alloying mechanism. In addition, if Si is effective in reducing costs due to its low price and abundant resource reserves, its conductivity is low, while Ge can provide higher electronic conductivity than Si, but is more expensive. In this respect, in order to integrate their cheapness and excellent conductivity, we propose a series of layered materials (named siliganes, *i.e.*, Si_{1-x}Ge_x, 0.1 ≤ x ≤ 0.9), which consist of 2D Si-Ge composites. Through a simple method, the Ca²⁺ cations were completely removed from the precursor Ca(Si_{1-x}Ge_x)₂, and the lamellar siliganes were obtained. The layered materials were tested in Na- and K- ion batteries. Based on the better electrochemical performance, we identified siligane_Si_{0.1}Ge_{0.9} as the best candidate. At a current density of 0.05 A g⁻¹, its reversible capacities of the Na ion and K ion cells were 276 mAh g⁻¹ and 132 mAh g⁻¹ after 50 cycles, respectively.

Keywords: Layered materials, Siloxene, Siligane, Germanane, Anode, Sodium-ion battery, Potassium-ion battery.

INTRODUCTION

In order to enhance electrochemical performances, numerous routes have been proposed[1–4]. For example, to address the phenomenon of dissolution, migration and deposition (DMD process) of transition metal ions during cycling, Peralta et al. [5] coated or doped the electrode surface of silicon-graphite/lithium-rich layered oxide (Si-Gr/Li_{1.2}Ni_{0.2}Mn_{0.6}O₂) systems with electrochemically inert cations and/or anions to enhance the electrochemical performance/. The coating technique was not so effective to prevent the dissolution of transition metal cations. Fugattini et al. [6] used Plasma Enhanced Chemical Vapor Deposition (PECVD) to grow a germanium film on a molybdenum substrate followed by hydrofluoric acid electrochemical etching to acquire nanostructured Ge film. The nanostructured binderless Ge-based anode exhibited high specific capacity and very good capacity retention (1624 mA h g⁻¹ at 1 C after 1600 cycles). Although surface coating and film preparation methods are significant for electrochemical performance enhancement, there are still many problems to overcome, and layered materials are one of the promising candidates for energy storage technology. Zhang et al. [7] designed a novel layered composite Zn₂SiO₄/C by a simple one-pot. The Zn₂SiO₄/C has good electrical conductivity and stability, and exhibits good electrochemical properties in sodium storage mechanism (374 mA h g⁻¹ at 0.1 A g⁻¹).

Noteworthy, over the past few years, two-dimensional (2D) materials have been investigated due to their unique characteristics both physically and chemically. [8] The space between their interlayers can be used to insert/extract ions and does not change significantly the materials' original structure, making it ideal for use in batteries. [9–11] It has been demonstrated in several studies that siloxene (2D Si) [12,13] and germanane (2D Ge) [14,15] are both capable of storing large amounts of lithium and have good cycling stability. Our proposal is to synthesize a 2D single-phase composed of Si and Ge to combine the advantages of both in a 2D electrode material, *i.e.*, the low cost of Si and the high electronic conductivity of Ge.

Some related studies have been conducted in the past. Zhang et al. [16] examined the nonlinear elastic properties of Si and Ge 2D hexagonal lattices by using density generalized function theory (DFT), which revealed

that Si and Ge are capable of forming stable 2D hexagonal lattices with low buckling properties as a result of the reproduced structure optimization and phonon dispersion curves. Arindam et al. [17] used DFT to study the application of 2D SiGe sheets for Na and K ion batteries, demonstrating the possibilities of fast charge/discharge rates and high capacities by modulating alkali-metal atom migration energy barriers. Using epitaxial growth deposition, G. Vogg et al. [18] synthesized Zintl phase $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ ($0 \leq x \leq 1$) and studied their properties. The a parameter is linearly proportional to the Ge content and the c parameter is linearly proportional to the x value with a triangular rhombohedral crystal structure in a TR6 stacking sequence. Recently, we have prepared the 2D ($\text{Si}_{1-x}\text{Ge}_x$) siligane materials [11] by chemical synthesis for the first time. These layered siliganes were obtained by deintercalation of Ca cations from the $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ precursor by acid leaching. The siligane_ $\text{Si}_{0.9}\text{Ge}_{0.1}$ showed a reversible capacity of 1325 mA h g^{-1} with high-capacity retention and coulomb efficiency after 10 cycles at a low current density of 0.05 A g^{-1} for Li-ion battery anode materials.

In this study, we used this series of materials as anode materials for Na- and K- ion batteries. Aiming at the improvement of synthesis method and electrochemical performance, a series of Si-Ge based 2D materials, including siloxene, siligane_ $\text{Si}_{1-x}\text{Ge}_x$ ($0.1 \leq x \leq 0.9$) and germanane was prepared. The as prepared materials were electrochemically tested in Na- and K- ion batteries. Due to the unique structural advantages of 2D materials. These versatile 2D electrode materials have shown stable cycling performance.

EXPERIMENTAL SECTION

Preparation for siloxene, siligane_ $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.1, 0.5, 0.9$) and germanane.

The synthesis method of CaSi_2 , $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ ($x=0.1, 0.5$ and 0.9) and CaGe_2 was firstly performed by mixing Ca (99% ACROS Organics), Si (325-Mesh, 99% ACROS Organics), and Ge (100-Mesh, 99% Alfa Aesar) in different specific ratios in a sealed 50 mL jar of tungsten carbide (WC), respectively. With a ratio of 10 balls:1 gram, the mixture was ground at 600 rpm for 20 hours in a planetary ball miller (RETSCH PM 100). The ball milled powder was transferred into a sealed stainless-steel reactor under argon atmosphere, and annealed at $800 \text{ }^\circ\text{C}$ for 50 h at a heating rate of $1.5 \text{ }^\circ\text{C}/\text{min}$. Then the siloxene, siliganes and germanane were prepared through the Wöhler method by soaking 300 mg of respective Zintl phase ($\text{CaSi}_2/\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2/\text{CaGe}_2$) in acid solution (40 ml hydrochloric acid 35% VWR Chemicals) for 10 hours. Then, the resulting powders were washed sequentially with distilled water ($\times 3$ times), ethanol ($\times 1$ time) and acetone ($\times 1$ time), separated by centrifugation and dried under vacuum overnight.

Both raw Si and Ge powders were ball milled and annealed with the same parameters, respectively.

Electrochemical measurements

This electrode contains a 1:1:1 ratio of synthetic 2D active material $\text{Si}_{1-x}\text{Ge}_x$ ($x=0, 0.1, 0.5, 0.9, 1$), carbon C_{45} (SN2A, Y50A), and carboxyl methyl cellulose binder (CMC, Aldrich, $M_w = 700,000$, $DS = 0.9$). To make the slurry, distilled water ($\text{pH} \approx 4$) containing 0.4% Triton X-100 dispersant was added and magnetically stirred. The slurry was coated on copper foil with a $30 \text{ }\mu\text{m}$ thickness doctor-blade and dried overnight at room temperature. Finally, the electrodes were punched into 15 mm-diameter disks, and dried overnight at 70°C under dynamic vacuum. The control electrode group was made by treating previously treated bulk Si and bulk Ge with the same process, respectively.

Using Argon-filled glove boxes (with H_2O & $\text{O}_2 < 0.1$ ppm) to assemble coin cells (CR2032). Sodium & Potassium foil were used as the reference and counter electrodes for Na-ion & K-ion batteries, respectively. The electrolyte for Na-ion batteries was 1 M NaPF_6 in EC: DEC (ethylene carbonate / diethyl carbonate) (1:1 w/w) + 1% FEC (fluoroethylene carbonate); while for K-ion batteries, 0.8 M KFSI in EC: DEC (1:1 w/w) was used. Each coin cell uses Whatman glass fiber as the separator (GF/ D, 675 μm).

Galvanostatic testing was performed using MPG2 (Biologic) at a current density of 0.05 A g^{-1} with a voltage range of 0.001 to 2.0 V. All rate performance was evaluated at current densities of 0.05, 0.1, 0.2, 0.5, 1, 2 and 0.05 A g^{-1} . The expected capacities of the batteries were calculated based on the active material mass of the electrodes. The cyclic voltammetry (CV) experiment was conducted by a VMP3 Multichannel Potentiostat at a scan rate of 0.01 mV s^{-1} between 0.001 and 2.0 V.

RESULTS AND DISCUSSION

Preparation of samples

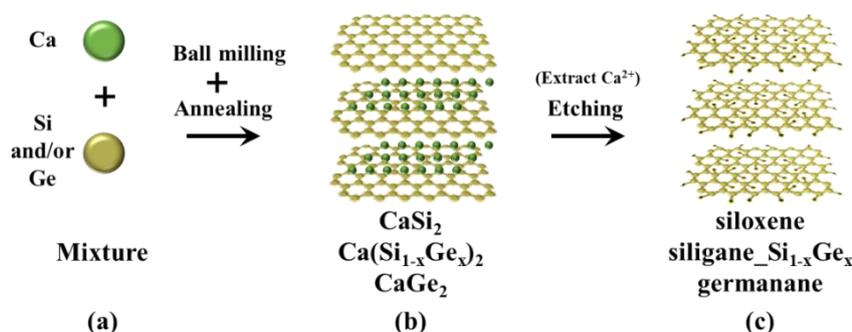


Fig. 1. Preparation process of siloxene, siligane and germanane: (a) Mixing Ca metal with bulk Si and/or bulk Ge, (b) after ball milling and annealing at $800 \text{ }^\circ\text{C}$ to obtain CaSi_2 , $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ or CaGe_2 , (c) acid leaching (Wöhler method) to remove Ca ions to obtain siloxene, siligane or germanane.

Fig. 1 briefly illustrates the preparation process of the 2D materials, and the following reactions (1) [19] and (2) [14] express the process of forming siloxene and germanane, respectively.



Based on the above two chemical equations, the synthesis process of siligane_ $\text{Si}_{1-x}\text{Ge}_x$ can be derived as follows:



The preparation and characterization of these 2D materials have been elaborated in our previous research work [11]. It was confirmed by SEM (**Fig. S10**) that all this series of materials showed layered structure. The successful preparation of solid solutions of $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ series materials was confirmed by XRD (**Fig. S9**), Raman and IR spectroscopy [11]. Besides, the cell parameters of these materials follow a perfect Vegard's law [18,20] as the ratio of silicon to germanium varies. It is worth noticing that the number of interlayer functional groups ($-\text{OH}$, $-\text{H}$) is dependant of the silicon and germanium content. [11]

Electrochemical performance

The whole series of 2D materials was electrochemically evaluated in Na and K batteries. The galvanostatic charge/discharge curves measured at the current density of 0.05 A g^{-1} between 0.001 and 2.0 V are shown in **Fig. 2**, for Na- and K-ion batteries (the whole series curves are plotted in **Fig. S1** and **Fig. S2**). It can be observed that both Na-ion and K-ion batteries have high irreversible capacities in the first cycle, and the specific capacity of Na-ion batteries is generally higher than that of K-ion batteries with the same sample, likely simply due to the lower atomic mass of Na (23 g/mol) than that of K (39 g/mol). From **Table 1**, in Na- and K-ion batteries, the ICEs of all 2D materials are very low, between 35 and 63%. Possible reasons for the low coulombic efficiency are: (1) Na and K metal counter electrodes are very reactive and the formed SEI layer is expected to be large and unstable. The electrolyte degradation species could also dissolve in electrolyte and migrate to the surface of the working electrode; (2) the functional groups on the surface and between the interlayers can cause many side reactions which accelerate the electrolyte degradation.

For Na-ion batteries, higher ICE is obtained for the Ge-rich group than that of the Si-rich group. This trend may be due to the better electrical conductivity of Ge than Si and the smaller amounts of interlayer functional groups of the Ge-rich group leading to less SEI formation. However, this phenomenon is not obvious in K-ion batteries, which does not show better performance with Ge rich materials. In that case, reversible capacities are still lower, perhaps due to the larger radius of K ions, which hinders the ion transport process, and to the stronger reactivity of potassium with electrolyte leading to a thicker solid electrolyte interphase (SEI) layer. The SEI would cause severe volume expansion, eventually leading to the destruction of the electrode material structure, and reducing the cycling stability. [21] Generally, from literature, Ge reacts more with Na and K than Si [10,22], leading to higher capacities and cyclability. In bulk $\text{Si}_{1-x}\text{Ge}_x$ materials the specific capacity of the Ge-rich group was also shown to be significantly higher than that of the Si-rich group in both Na- and K-ion batteries [23].

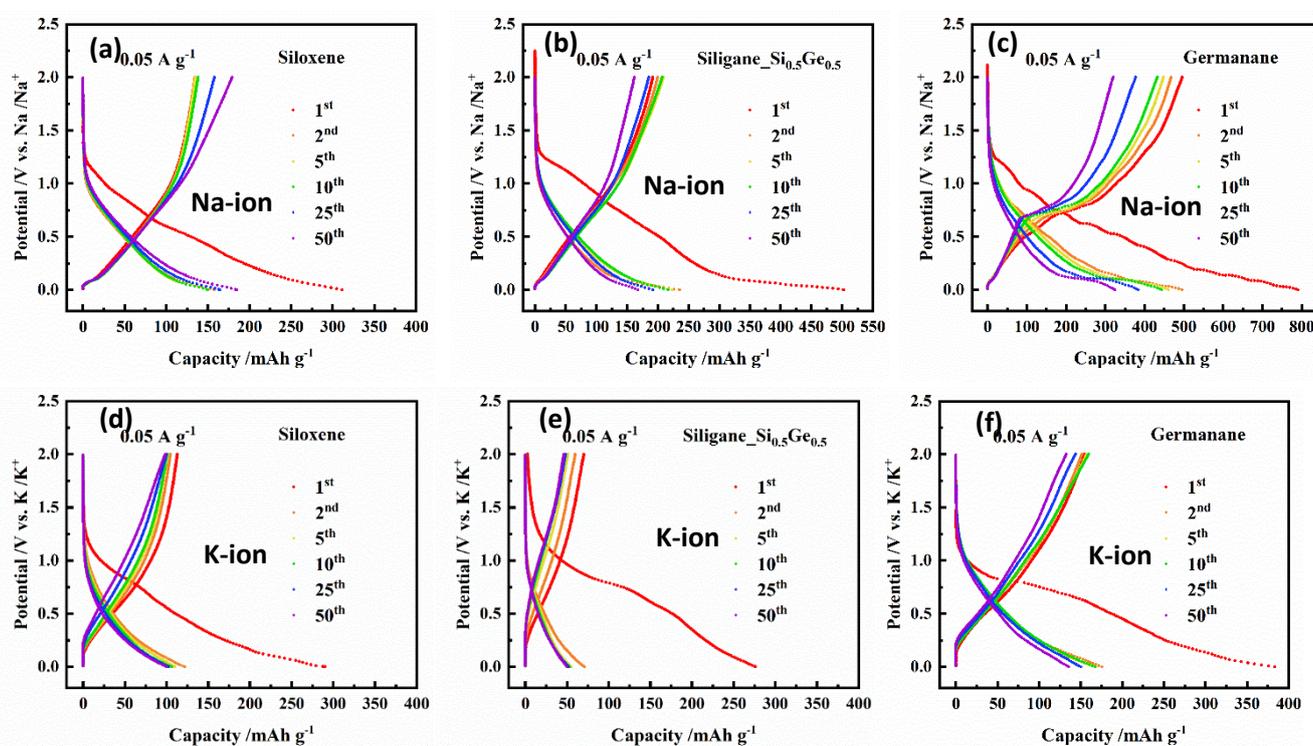


Fig. 2. Charge-discharge curves of (a) siloxene, (b) siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$, (c) germanane in Na-ion batteries & (d) siloxene, (e) siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$, (f) germanane in K-ion batteries at a current density of 0.05 A g^{-1} between 0.001 and 2.0 V.

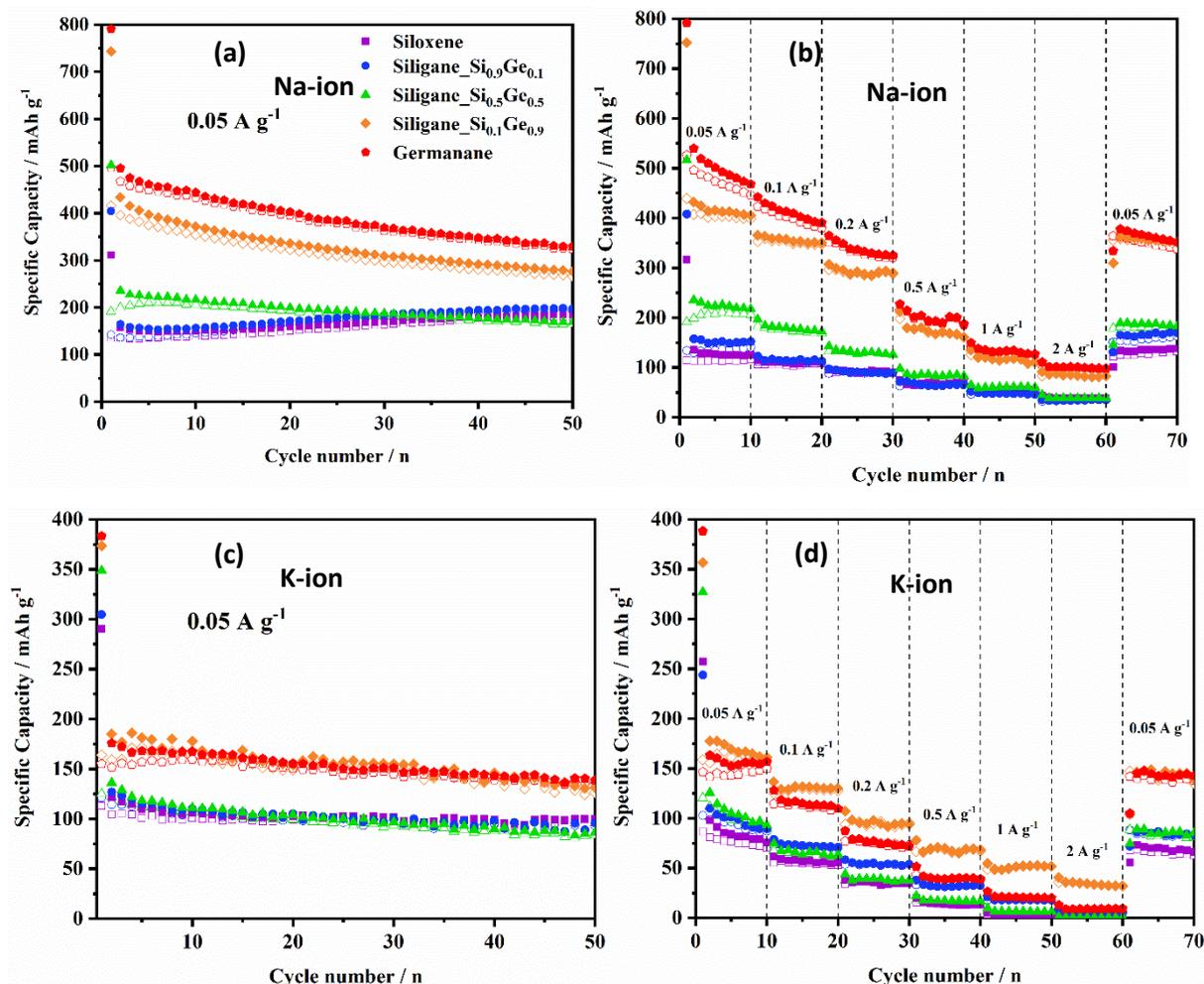


Fig. 3. The cycling performance (0.05 A g^{-1}) and (b) rate performance in Na-ion batteries & (c) the cycling performance (0.05 A g^{-1}) and (d) rate performance in K-ion batteries of siloxene, siliganes ($\text{Si}_{0.9}\text{Ge}_{0.1}$, $\text{Si}_{0.5}\text{Ge}_{0.5}$ and $\text{Si}_{0.1}\text{Ge}_{0.9}$), and germanane between 0.001-2.0 V. Filled symbol represent the discharge and empty symbols the charge.

Fig. 3-a, c shows the cycling performance corresponding to the charge and discharge curves of $\text{Si}_{1-x}\text{Ge}_x$ vs. Na and K, respectively. For the cycling capability in Na-ion batteries (**Fig. 3-a**), the specific capacities of the Ge-rich group gradually decayed with the increase of the number of cycles, while the specific capacity of the Si-rich group, lower than the former, gradually increased. This kind of activation processing has also been observed in Li-ion batteries (**Fig.S5-b**), surprisingly it does not take place in K-ion batteries. In the K-ion batteries (**Fig. 3-c**) for the whole series the specific capacity is very low ($< 180 \text{ mAh g}^{-1}$), but the Ge-rich group shows slightly higher capacities (**Table 1**). For the latter, capacity decay with cycles is observed as in Na-ion batteries, but less pronounced, while the specific capacity of the Si-rich group remains stable (but very low, $< 100 \text{ mAh g}^{-1}$). Besides, rate performance is also an important consideration for batteries. In **Fig. 3-b**, for Na-ion batteries, the Ge-rich group exhibits higher capacity than Si-rich groups at a low current density of 0.05 A g^{-1} ($136, 157, 236, 432$ and 540 mAh g^{-1} for $x = 0, 0.1, 0.5, 0.9$ and 1), but it rapidly decays, especially when current increased. Siligane_ $\text{Si}_{0.9}\text{Ge}_{0.1}$ shows better rate stability than germanane. Contrarily the siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$ sample and Si-rich groups show smoother capacity

decay but for a very limited capacity (44, 36, 45, 92 and 110 mAh g⁻¹ for x = 0, 0.1, 0.5, 0.9 and 1). It is worth mentioning that, each 2D material is more or less able to restore original capacity once the current density returns to 0.05 A g⁻¹.

Table 1. The first discharge specific capacity, initial coulomb efficiency (ICE) and charging specific capacity of all 2D materials at the current density of 0.05 A g⁻¹ for Na-/K-ion batteries.

Na-ion batteries, EC+DEC (w:w=1:1) + 1%FEC+1 M NaPF ₆ , Current Density: 0.05 A g ⁻¹					
	Siloxene	Siligane Si _{0.9} Ge _{0.1}	Siligane Si _{0.5} Ge _{0.5}	Siligane Si _{0.1} Ge _{0.9}	Germanane
First discharge capacity (mAh g ⁻¹)	311	404	502	743	791
Initial CE	43 %	35 %	38 %	56 %	63 %
Specific capacity (Charge at 50 th cycle, mAh g ⁻¹)	180	193	164	266	324
K-ion batteries, EC+DEC (w:w=1:1) + 0.8 M KFSI, Current Density: 0.05 A g ⁻¹					
	Siloxene	Siligane Si _{0.9} Ge _{0.1}	Siligane Si _{0.5} Ge _{0.5}	Siligane Si _{0.1} Ge _{0.9}	Germanane
First discharge capacity (mAh g ⁻¹)	290	305	349	374	383
Initial CE	39 %	40 %	36 %	44 %	40 %
Specific capacity (Charge at 50 th cycle, mAh g ⁻¹)	98	93	83	126	134

In order to observe the activation process in the Si-rich group (siloxene and siligane_Si_{0.9}Ge_{0.1}) in Na-ion batteries, we tested the long-term cycling performance at 0.1 A g⁻¹ (**Fig. S5-c**), where the specific capacity of the Si-rich group gradually increased during the first 50 cycles and then decreased super slowly till 1000 cycles, which exhibit very robust properties. Siligane_Si_{0.9}Ge_{0.1} continues showing a stable capacity after 1000 cycles. On the other side, the K-ion batteries in **Fig. 3-d** possess an alike rate performance but with lower overall specific capacity (98, 110, 126, 178 and 163 mAh g⁻¹ for x = 0, 0.1, 0.5, 0.9 and 1 at 0.05 A g⁻¹). Yet, siligane_Si_{0.1}Ge_{0.9} provides a higher specific capacity and better rate stability than germanane in the Ge-rich group. In particular, only siligane_Si_{0.1}Ge_{0.9} can retain some specific capacity when the current density reaches 2 A g⁻¹, while the rest of the 2D materials all performed poorly. Interestingly, when the current density returned to 0.05 A g⁻¹, the specific capacities of all 2D materials returned to their initial values and present a lower decay in further cycles.

The cycling performance and coulombic efficiencies of each 2D series materials in Na- and K- ion batteries are listed in **Fig. S3** and **Fig. S4**, respectively.

The coulombic efficiencies in the Na-ion batteries are measured between 96 % - 97 % after 20 cycles. Intriguingly, as already mentioned, the specific capacity of the Si-rich group shows a gradual increase trend at the beginning, while the specific capacity of the Ge-rich group and siligane_Si_{0.5}Ge_{0.5} sample decays as the cycling proceeds. The coulombic efficiency in K-ion batteries is more fluctuating, likely due to the high reactivity of K metal and the rapid formation of K dendrites and huge SEI. Anyway, specific capacity of all 2D materials shows a gradual decay trend.

Furthermore, the cycling performances (**Fig. S5-a**) of bulk Si, bulk $\text{Si}_{0.5}\text{Ge}_{0.5}$ and bulk Ge were tested in Na-/K- ion batteries under the same measurement conditions and compared with the corresponding 2D materials (siloxene, siligane and germanane). It can be seen that for the whole series, the specific capacities in both Na- and K- ion batteries (**Fig. S6-a, b and Fig. S6-c, d**) are relatively similar, but siloxene and siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$ showed better cycling stability and capacity retention than bulk Si and bulk $\text{Si}_{0.5}\text{Ge}_{0.5}$. However, for Ge-based electrode materials, the capacity of germanane is significantly better than that of bulk Ge in both Na- and K- ion batteries (**Fig. S6-e, f**), with however a more rapid decay with cycles.

Last, to facilitate the comparison, we have directly compared the electrochemical performance of each 2D material in LIB [11], NIB and KIB in the same figure. **Figs. 4** show the cycling performance as well as the coulomb efficiencies of the 2D materials, while **Fig. 5** shows the rate performances (all data are listed in **Fig. S7** and **Fig. S8**). Li-ion batteries clearly show the highest specific capacity, followed by Na-ion batteries and the lowest by K-ion batteries. In addition, if all CE (**Fig. 4**) gradually stabilize in the first 10 cycles, it is higher for siloxene in LIB, followed by the NIB and finally KIB. However, CE of germanane in the three alkali metal ion batteries are relatively similar. It is noticeable that in the rate performance of **Fig. 5**, all samples possess a convenable specific capacity retention even at high rate (2 A g^{-1}) in LIB and exhibit limited rate performance in NIB and KIB. This may be related to the radius and atomic mass of each cation (Li: 1.55 \AA , 6.94 g/mol ; Na: 1.9 \AA , 22.99 g/mol ; K: 2.35 \AA , 39.10 g/mol), making it more difficult to be inserted in 2D materials.

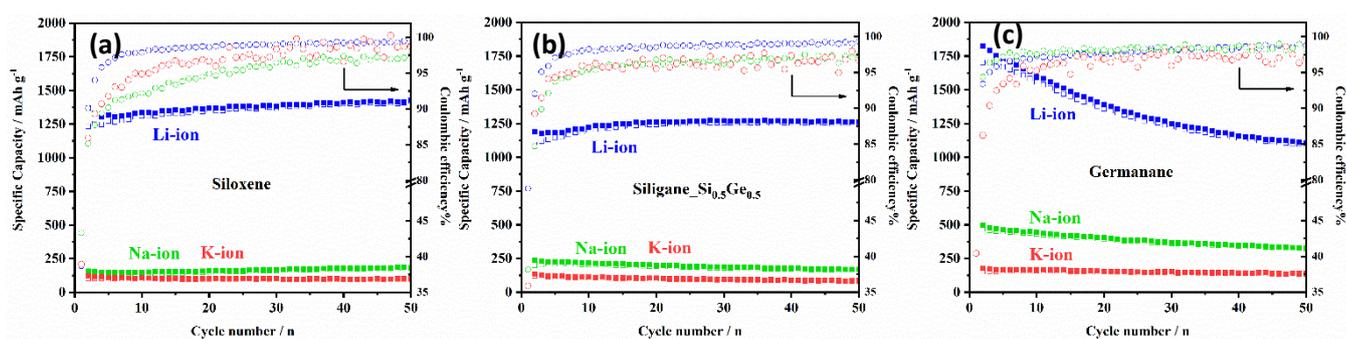


Fig. 4. Comparative cycling performance (start from 2nd cycle) and coulombic efficiency of (a) siloxene, (b) siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$ and (c) germanane in Li-, Na- & K- ion batteries with current density of 0.05 A g^{-1} between $0.001\text{-}2.0\text{ V}$.

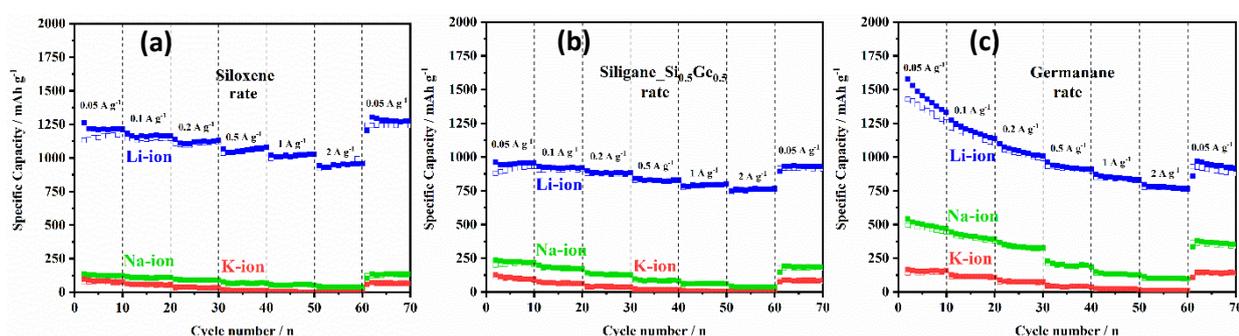


Fig. 5. Comparative rate performance (start from 2nd cycle) of (a) siloxene, (b) siligane_ $\text{Si}_{0.5}\text{Ge}_{0.5}$ and (c) germanane in Li-, Na- & K- ion batteries between $0.001\text{-}2.0\text{ V}$.

CONCLUSIONS

In summary, siligane layered materials obtained by complete deintercalation of Ca from $\text{Ca}(\text{Si}_{1-x}\text{Ge}_x)_2$ can be used as anode materials for Na- or K- ion batteries technology. Despite the high initial irreversible discharge capacity, after the second cycle, they provided capacity values between 300 and 500 mAh g^{-1} , with good cycling stability. The Ge richer electrodes present the best performance of the series, which could be attributed to the better electronic conductivity of Ge, and further impedance measurements are planned to confirm this point. For instance, the siligane $\text{Si}_{0.1}\text{Ge}_{0.9}$ achieve reversible capacities close to 400 mAh g^{-1} and 160 mAh g^{-1} in Na-ion and K-ion batteries, respectively, with acceptable cycling stability and coulombic efficiency. The expected advantage of this family of 2D compounds was the ability to insert ions between Si/Ge-based layers of the 2D structure with limited volume change compared with Si/Ge bulk materials and improved cycling stability. Dilatometry measurements are planned to confirm this hypothesis. Moreover, huge SEI is formed during the first discharge, likely limiting intercalation in further cycles. Again, here the goal was to synthesis a new family of 2D materials combining Si and Ge.

ACKNOWLEDGEMENTS

Research for this project has been supported by LABEX-STOREX and has been conducted within the French Research Network on Electrochemical Energy Storage (RS2E), National Center for Scientific Research (CNRS).

REFERENCE

- [1] J. Guo, Y. Zhao, T. Ma, Electrostatic self-assembly of 2D delaminated MXene (Ti_3C_2) onto Ni foam with superior electrochemical performance for supercapacitor, *Electrochim Acta*. 305 (2019) 164–174.
- [2] W. Dang, W. Wang, Y. Yang, Y. Wang, J. Huang, X. Fang, L. Wu, Z. Rong, X. Chen, X. Li, One-step hydrothermal synthesis of 2D WO_3 nanoplates@ graphene nanocomposite with superior anode performance for lithium ion battery, *Electrochim Acta*. 313 (2019) 99–108.
- [3] H. Liu, X. Chen, L. Deng, X. Su, K. Guo, Z. Zhu, Preparation of ultrathin 2D MoS_2 /graphene heterostructure assembled foam-like structure with enhanced electrochemical performance for lithium-ion batteries, *Electrochim Acta*. 206 (2016) 184–191.
- [4] W. Li, X. Sun, Y. Yu, Si-, Ge-, Sn-Based Anode Materials for Lithium-Ion Batteries: From Structure Design to Electrochemical Performance, *Small Methods*. 1 (2017) 1600037.
- [5] D. Peralta, J. Salomon, Y. Reynier, J.-F. Martin, E. De Vito, J.-F. Colin, A. Boulineau, C. Bourbon, B. Amestoy, C. Tisseraud, Influence of Al and F surface modifications on the sudden death effect of Si-Gr/Li1.2Ni0.2Mn0.6O2 Li-Ion cells, *Electrochim Acta*. 400 (2021) 139419.
- [6] S. Fugattini, U. Gulzar, A. Andreoli, L. Carbone, M. Boschetti, P. Bernardoni, M. Gjestila, G. Mangherini, R. Camattari, T. Li, Binder-free nanostructured germanium anode for high resilience lithium-ion battery, *Electrochim Acta*. 411 (2022) 139832.

- [7] M. Zhang, D. Cheng, G. Qiu, M. Ning, Z. Duan, B. Wan, S. Tang, L. Miao, Z. Li, H. Zhang, Superlattice-like alternating layered Zn₂SiO₄/C with large interlayer spacing for high-performance sodium storage, *Electrochim Acta*. 449 (2023) 142163.
- [8] D. Chimene, D.L. Alge, A.K. Gaharwar, Two-dimensional nanomaterials for biomedical applications: emerging trends and future prospects, *Advanced Materials*. 27 (2015) 7261–7284.
- [9] L.C. Loaiza, L. Monconduit, V. Seznec, Siloxene: A potential layered silicon intercalation anode for Na, Li and K ion batteries, *J Power Sources*. 417 (2019) 99–107.
- [10] L.C. Loaiza, L. Monconduit, V. Seznec, Towards Germanium Layered Materials as Superior Negative Electrodes for Li-, Na-, and K-Ion Batteries, (2020).
- [11] X. Chen, L.C. Loaiza, L. Monconduit, V. Seznec, 2D Silicon–Germanium-Layered Materials as Anodes for Li-Ion Batteries, *ACS Appl Energy Mater*. 4 (2021) 12552–12561.
- [12] Q. Guo, Y. Han, N. Chen, L. Qu, Few-Layer Siloxene as an Electrode for Superior High-Rate Zinc Ion Hybrid Capacitors, 29 (2021) 2022.
- [13] P. Pazhamalai, K. Krishnamoorthy, S. Sahoo, V. Kumar Mariappan, S.-J. Kim, Understanding the Thermal Treatment Effect of Two-Dimensional Siloxene Sheets and the Origin of Superior Electrochemical Energy Storage Performances, (2018).
- [14] L.C. Loaiza, L. Monconduit, V. Seznec, Towards Germanium Layered Materials as Superior Negative Electrodes for Li-, Na-, and K-Ion Batteries, (2020) 1–11.
- [15] Complex Lithiation Mechanism of Siloxene and Germanane: Two Promising Battery Electrode Materials, (2021).
- [16] H. Zhang, R. Wang, The stability and the nonlinear elasticity of 2D hexagonal structures of Si and Ge from first-principles calculations, *Physica B Condens Matter*. 406 (2011) 4080–4084.
- [17] A. Sannyal, Y. Ahn, J. Jang, First-principles study on the two-dimensional siligene (2D SiGe) as an anode material of an alkali metal ion battery, *Comput Mater Sci*. 165 (2019) 121–128.
- [18] G. Vogg, C. Miesner, M.S. Brandt, M. Stutzmann, G. Abstreiter, Epitaxial alloy films of Zintl-phase Ca(Si_{1-x}Ge_x)₂, *J Cryst Growth*. 223 (2001) 573–576.
- [19] A. Weiss, G. Beil, H. Meyer, The Topochemical Reaction of CaSi₂ to a Two-Dimensional Subsiliceous Acid Si₆H₃(OH)₃ (= Kautskys' Siloxene), *Zeitschrift Für Naturforschung B*. 35 (1980) 25–30.
- [20] A.R. Denton, N.W. Ashcroft, Vegard's law, *Phys Rev A (Coll Park)*. 43 (1991) 3161–3164.
- [21] Y. Zhang, Y. Wang, L. Hou, C. Yuan, Recent Progress of Carbon-Based Anode Materials for Potassium Ion Batteries, *The Chemical Record*. (2022) e202200072.
- [22] L.C. Loaiza, L. Monconduit, V. Seznec, L.C. Loaiza, V. Seznec, L. Monconduit, Si and Ge-Based Anode Materials for Li-, Na-, and K-Ion Batteries: A Perspective from Structure to Electrochemical Mechanism, (2020).
- [23] L.C. Loaiza, E. Salager, N. Louvain, A. Boulaoued, A. Iadecola, P. Johansson, L. Stievano, V. Seznec, L. Monconduit, Understanding the lithiation/delithiation mechanism of Si_{1-x}Ge_x alloys, *J Mater Chem A Mater*. 5 (2017) 12462–12473.

