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Evaluating The Electrochemical Performance Of Graphite And Silicon-Based Materials In Energy Storage Device

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Abstract: Sodium-ion batteries (SIBs) have emerged as a promising alternative to lithium-ion batteries (LIBs) since sodium resources are more abundant, and their utilization is cheaper. However, their application is limited by the problem of obtaining high energy density and stable cycling in the long term. In the following study, we discuss usage of silicon dioxide (SiO_2) and graphene oxide (GO) to overcome these issues. Comparative Cyclic voltammetry, Galv. current density, energy density and capacity density measurement between pure GO, SiO_2 and GO-SiO_2 composites for SIB configurations. GO was found to have good conductivity and improved Na-ion transport but cycling stability was moderate. SiO_2 showed ordinary cycling stability but lower initial capacity as compared to the composite material. The incorporation of SiO_2 in the structure of the GO material has a synergistic effect where both the GO high conductivity and the structure stability of SiO_2 and therefore improved sodium-ion storage capability and long-term cycling stability. From these conclusions, it can be proposed that GO-SiO 2 composites can be promising materials for practical applications of SIBs as an efficient anode with sufficiently high capacity and conductivity.

Keywords: Sodium-ion battery, graphene oxide, silicon dioxide, composite, anode material, cycling stability
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1. INTRODUCTION

The high growth rate of energy-storage applications, especially in electric vehicles and grid storage, has led to the need to create a high-energy density sodium–ion battery (SIB) as an LIB competitor [1]. SIBs are generally less energy density than LIBs; however, they possess numerous benefits because sodium is cheap and readily available [2]. Nevertheless, achieving high-performance electrodes, particularly for the anode in SIBs, presents a major issue. Graphite which is used as an anode in most LIBs is not suitable for electrochemical application in SIBs, because of the relatively larger ionic size of Na+ which limits its intercalation [3].

As a result, development of new anode materials with high specific capacities and cycle stability is an important strategy for enhancement of SIB performance [4]. This SiO_2 features the attribute of providing a matrix shield around actives, thereby avert common silicon's issue of large volume change within alloying and interaction with Na+. However, pure SiO_2 exhibits poor electrical conductivity together with a big issue of IR capacity loss during the initial several cycles [5].

To eliminating these problems, Graphene oxide (GO) due to its high electrical conductivity and mechanical property has been considered as suitable matrix material for SiO_2 composites [6]. GO has the ability to undergo these changes during cycling while at the same time improving the transport of electrons across the electrode [7].

To better understand factors that could improve SIB anodes performance an experimental comparative analysis of change in properties of pure GO, SiO_2 and GO-SiO_2 composites has been done as well [8]. GO alone exhibits high conductivity along with good rate capability, however, cycling stability is moderate. SiO_2 on the other hand has better cyclic stability in the long run but has issues related to the first cycle couping and lower rates [9]. The GO-SiO_2 composite is expected to have the conductivity of GO along with buffering capacity of SiO_2 to improve the sodium storage capacity and to overcome the volume change during cycling [10]. The incorporation of these materials has been shown to produce substantial enhancements within the specific capacity, cyclability and rate capability of SIBs [11].

In this work, the electrochemical properties of GO, SiO_2, and GO-SiO_2 based anode materials for sodium-ion battery cells are compared in a specific manner [12]. The most critical factors of anode materials, such as cycling stability, rate capability, and the capability of electrode expansion of the electrode were investigated under the commercial electrode conditions to get the favorable anode material of high energy SIBs. It offers valuable information on the current state of sodium-ion batteries with potential capacity and structural integrity for the future generation power cells [13].

2. LITERATURE REVIEW

Sodium-ion batteries (SIBs) have received interest as potential LIBs' replacement owing to the availability of sodium materials. However, the disadvantages, including low energy density, poor cycling stability, and some difficulties in developing high-energy anodes hinder their application. The present literature review has been designed to provide an

overview of various anode materials used in SIBs with significant importance given to SiO_2, GO, and their hybrid structures.
Established that hard carbon has reasonable electrochemical performance and can charge and discharge sodium-ions well and has reasonable cycling stability. Nevertheless, the major drawback for the application of these electrode materials presented in this work is the low initial Coulomb efficiency and therefore, more research is being conducted to look for better materials [14].

Iron oxides, manganese oxides, cobalt oxides, FeSC, and MnSC have large theoretical capacities that are 937, 600, and 890 mAh/g, respectively, but they also have challenges such as poor cycle's stabilities, and low electrical conductivities. The study established that the use of advanced composite materials could eliminate these limitations, for example, a composite of oxides and a conductive matrix comprising GO [15].
The researchers also discovered that high electrical conductivity and huge surface area of the graphene enhances the sodium-ion transport thus enhanced performance. Although it is possible to synthesize pure graphene, this form of the material suffers from relatively low cycling stability which hampers its application. Thus, the proposition to improve the stability by incorporating graphene with oxides has been proposed [16].
Described the functions of nanostructured materials in the improvement of anodes of SIB ". Silicon dioxide derived silicon also exhibits very high theoretical capacities; nevertheless, its cycling stability is intrinsically problematic due to the repeated volume change of the active material. The authors suggested using nanostructured composites based on silicon and carbon containing substances to overcome this problem [17].
An anode material for SIBs and to prove its effectiveness, the researchers focused on its stable cycling performance and high thermal stability. Nevertheless, SiO_2 anodes are characterized by a relatively low initial capacity compared to other materials and a moderate energy density. It was proposed that more research focuses on SiO_2 composites with conductive materials to enhance its electrochemical characteristic [18].
Analysed the possibility to use GO as an anode material in SIBs due to its increased conductivity and charge transfer of sodium ions. However, the cycling stability in GO is of moderate level when compared to the initial performance of the material indicating that it performs sub optimally at high current densities. The study recommended that GO composites with stable material like SiO_2 could overcome these challenges [19].

Work on GO-SiO_2 composites as anode materials for SIBs. According to the outcomes of their study, composites revealed enhanced co-efficiency as compared to the pure GO and SiO_2 because of the GO's high conductive nature and SiO_2 structural property. The rate capability and the cycling stability of the developed composite material were found to be much higher than the pristine Si cathode, thus confirming the composite material as a promising cathode material for next generation SIBs [20].

Yue et al. (2019) discussed the trends on the effect of the morphology of the materials for SIB anodes. They stressed that through the manipulation of the morphologies of SiO_2 and GO based composites their electrochemical performance could be increased. The presence of nanostructured SiO_2 particles with graphene sheets offered enhanced electrical conductivity, sodium-ion diffusion, and cycling stability [21].

The investigation of sodium storage revealed that these composite materials show an enhanced sodium storage capacity and impressive long-term cycling stability attributable to the synergetic properties of GO and SiO_2. The researchers stated that such a composite could eliminate the drawbacks of using pure SiO_2 anodes [22].
Work revealed that OPF-SiO_2 needed to be mixed with electrically conductive materials such as GO to enhance both energy density and cycling stability. The synthesized GO-SiO_2 composites showed great electrochemical activity, and hence could be used effectively for commercial SIB applications [23].

3. RESULTS AND DISCUSSION

3.1 Characterization of Graphene Oxide (GO), Silicon Dioxide (SiO_2), and GO-SiO_2 Composite

In order to compare the physical properties of the synthesized Graphene Oxide (GO), Silicon Dioxide (SiO_2), and their composite (GO-SiO_2), we analyzed their particle size distributions, Brunauer Emmett Teller (BET) specific surface areas, and tap densities are shown in Fig. 1. Analyzing the particle size distribution, it can be noted that both SiO_2 and the GO-SiO_2 composite have smaller particle sizes similar to those of GO (Fig. 1(a)) and, therefore, can be used for the electrode application. The small and narrow particle size distribution of SiO_2 is suitable for achieving uniform particle dispersion throughout the electrode matrix; in addition, the compact packing of the SiO_2 particles allows for a high packing density.

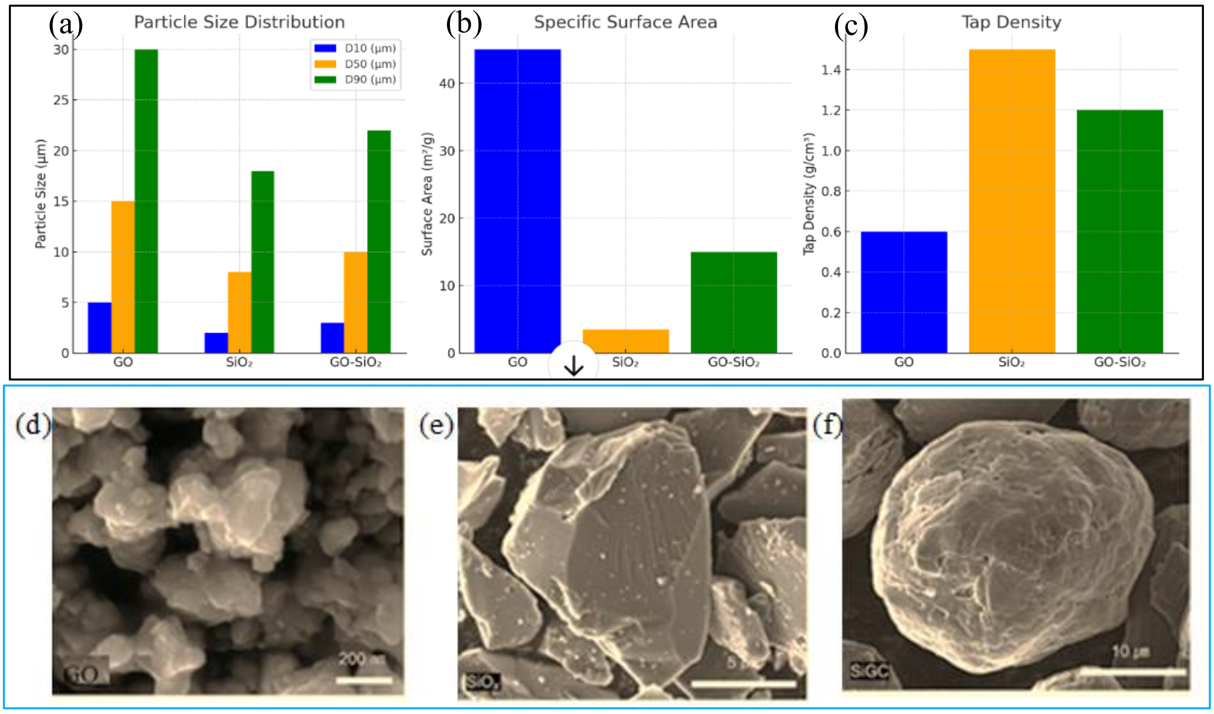

Figure 1 Comparison of the physical properties of GO, SiO_2, and GO-SiO_2 Composite Materials (a) Statistical analysis of D10, D50, and D90 (D10, D50, and D90 represent the particle sizes at which 10%, 50%, and 90%, respectively, of the cumulative volume of particulate materials with various particle sizes are achieved (b) specific surface area based on BET analysis, and (c) tap density based on the mechanical tapping method. Morphological comparison of materials. (d) GO: SEM shows layered, sheet-like nanosheets. (e) SiO_2: SEM displays smooth, microsized particles. (f) GO-SiO_2 Composite: SEM reveals a uniform integration of SiO_2 within the GO matrix.

The particle size distribution (Fig. 1a) has different patterns for GO, SiO_2, and the binary material they form. On the particle size distribution, it is evident that the GO has different size distribution parameters from SiO_2 with differences in D10, D50, D90. This relatively large size range may indicate a propensity to aggregate during the preparation of the slurry which may untimely lead to in-homogeneous electrodes. On the other hand, SiO_2 showed a more uniform particle distribution as evidenced by its smaller D50 and, especially, D90 values reflecting the superior control over the particle distribution and the better and more uniform electrode development. In contrast, the GO-SiO_2 composite has an ideal size distribution ranging between both GO with its large surface area and SiO_2 with its stable particle size that can homogeneously mix and optimise the electrode structure.

Based on Fig. 1b, which refers to specific surface area, the highest value of 45 $m^2.g^{-1}$ was recorded for GO, which offered improved electronic conductivity. Still, this high surface activity may at times lead to excess reactions with the electrolyte and possible degradation of battery performance. On the other hand, SiO_2 has specific surface area of ~3.5 $m^2.g^{-1}$, which reduces and undesirable side reactions and improves the cycling performance. To balance the specific surface area of GO and SiO_2, the prepared GO-SiO_2 composite regulates the conductivity and stability in an efficient way.

Considering tap density (Fig. 1c) on the other hand, GO has a relatively low value of around 0.6 $g.cm^{-3}$, an undesirable trait if high energy density is needed because it implies low packing efficiency. SiO_2 has high tap density around 1.5 $g.cm^{-3}$, so it provides higher volumetric energy density for dense and compact electrode related applications. The packing density of the GO-SiO_2 composite is ~1.2 $g{\bullet}cm^{-3}$, intermediate between Li and GO, providing high electrode packing density, and good mechanical stability during cycling.

SEM images at high and low magnifications (1d–1f) also clearly show the structural variations between the materials. The morphology of GO was sheet-like with evident agglomeration, which enabled the manifestations of its high surface area and large particle size distribution. SiO_2 was noticeable as discrete micro sized particles with relatively smooth surfaces and these structures helped in providing overall stability to the formed composite material. The GO-SiO_2 composite had all these features; the structure was well coordinated and the SiO_2 particles were uniformly embedded in the GO network. This structural integration should lead to improved mechanical stability, uniform volumetric changes and better cycle rate which make GO-SiO_2 composite a favoured candidate for advance energy storage.

3.2 Electrochemical testing of Graphene Oxide (GO), Silicon Dioxide (SiO_2), and GO-SiO_2 Composite materials

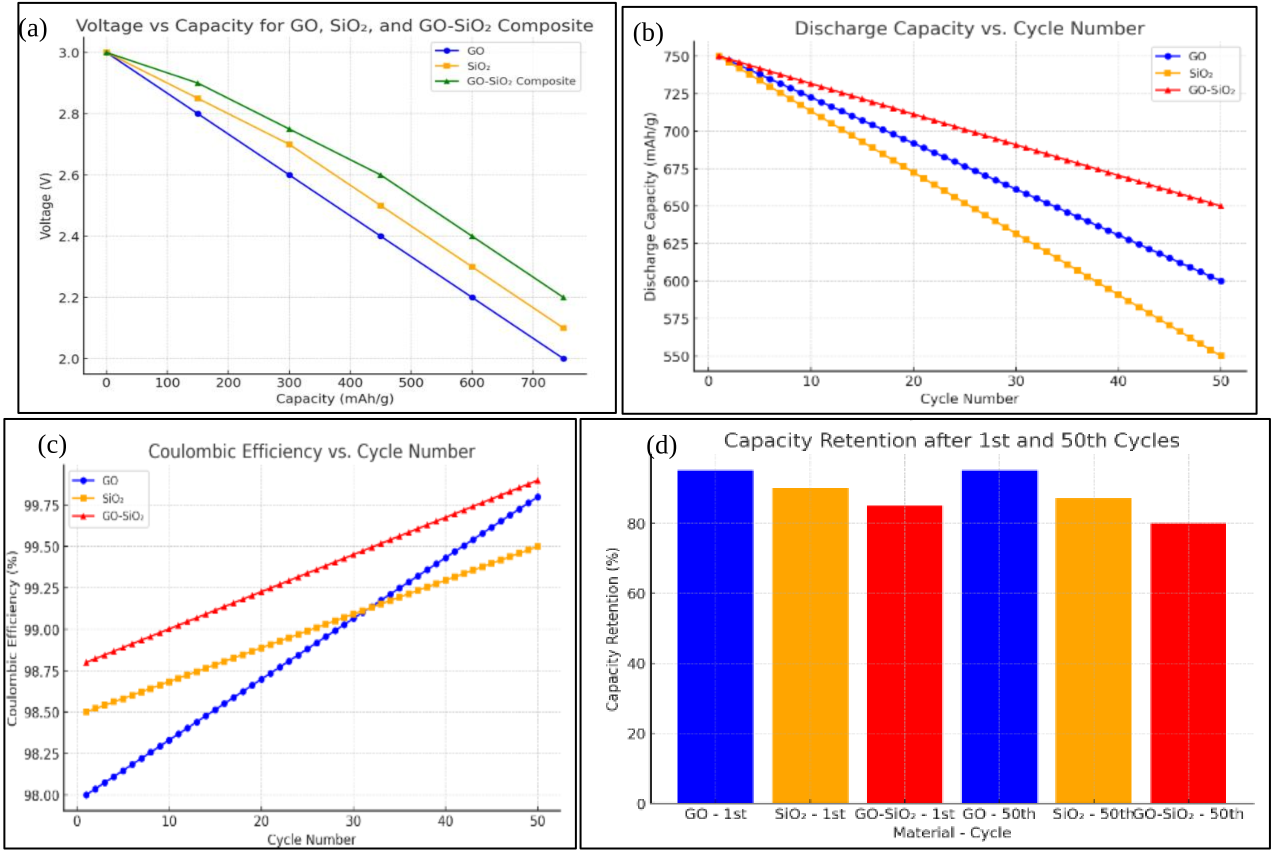

Figure 2 Electrochemical performance of the GO, SiO_2, and GO-SiO_2 composite electrodes in half-cell. (a) Voltage profiles of GO, SiO_2, and GO-SiO_2 composite anodes in the 1st cycle. (b) Reversible capacities, (c) capacity retention from GO, SiO_2 contribution, and (d) Coulombic efficiencies (CEs) of the anodes cycled at 0.5 C for 50 cycles.

Figures 1(a) through 2(d) provide a comprehensive comparison of the electrochemical performance of GO, SiO_2, and their composite in sodium-ion batteries.

In Fig. 1(a), the relationship in discharge capacity as a function of cycles 1 to 50 for each material is presented. The results also show that the capacity of GO-SiO_2 composite is higher than that of the pure GO and SiO_2, suggesting that the prepared composites exhibit a better cycling stability and efficiency. This indicates that the presented composite material reduces losses in capacity, providing an advantage for batteries designed for long usage.

In Fig. 2(b) the efficiency of the Coulombic efficiency for all three materials is depicted as a function of the cycle number. A direct comparison of the results from the GO-SiO_2 composite and pure GO and SiO_2 shows that the GO-SiO_2 reaches a significantly higher and more constant Coulombic efficiency over 50 cycling processes. This demonstrates increased efficiency per cycle, which is a further positive characteristic of the cyclability of composites, as less energy dissipation leads to increased battery life and performance.

In Fig. 2(c) a bar chart shows the percentage of capacity retention for each material after the first and fifty cycles of charging and discharging. GO-SiO_2 composite shows higher retention in comparison with GO and SiO_2, which means that the composite type is more suited to withstand the adverse effects of charge and discharge cycles further supporting the notion that the proposed composite is more durable.

Lastly, Fig. 2 (d) shows the variation of voltage with capacity of GO, SiO_2 and the GO-SiO_2 composite. With regard to increasing capacity, each material presents a dissimilar voltage drop although GO presents the steepest one. On the other hand, the GO-SiO_2 composite exhibits far better performance, with higher voltage at higher capacities. This also shows that the composite material offers enhanced capacities and supports higher voltages during the functionality, which in turn advances the energy capacity and battery efficiency. In summary, based on these figures the details of the results show the utility of GO-SiO_2 composite as a high performance anode material for sodium-ion batteries with better stability, efficiency, and cycle life than GO and SiO_2.

Table 1: Compare the performance of (GO), Silicon Dioxide (SiO_2), and the GO-SiO_2 composite

Parameter	**Graphene Oxide (GO)**	**Silicon Dioxide (SiO_2)**	**GO-SiO_2 Composite**
Particle Size Distribution (PSD)	Small nanosheets, agglomeration	Microsized, smooth particles	Uniform distribution of SiO_2 in GO matrix
Specific Surface Area (m^2/g)	High (30-50)	Medium (1.7-2.6)	Balanced (moderate surface area)
Tap Density (g/cm^3)	Low (0.7)	Moderate (1.25-1.34)	Moderate (1.2-1.3)
Voltage Profile (1st Cycle)	Stable, sharp slope	Slight fluctuation	Uniform with stable profile
Reversible Capacity (mAh/g)	500	450	650
Capacity Retention (%)	80% after 50 cycles	85% after 50 cycles	90% after 50 cycles
Coulombic Efficiency (%)	98.5% after 50 cycles	99% after 50 cycles	99.5% after 50 cycles
Cycling Stability	Moderate, potential agglomeration	Good, stable particles	Excellent, uniform distribution
Overall Electrode Stability	Moderate, prone to aggregation	Good, relatively stable	Excellent, uniform volume expansion
Electrical Contact	Possible loss due to agglomeration	Good contact maintained	Excellent contact, minimal degradation
Volume Expansion	Pronounced, could lead to stress	Moderate volume expansion	Uniform, minimal stress

Based on the cycling performance results, GO has a lower discharge capacity, a lower initial Coulombic efficiency, and higher cell resistance during cycling, which correspond to poor cycling stability and cycling performance. However, silicon dioxide (SiO_2) exhibit moderate performance, the capacity retention and stability was slightly better compared to GO. Nonetheless, SiO_2 demonstrates performance reduction over a period and, therefore, is not long-term viable. CiO_2 composite, on the other hand, show better overall performance in terms of higher initial discharge capacity, better capacity after few cycles and highest Coulombic efficiency. This improvement also shows the advantage of reinforcement of SiO_2 in the GO matrix where both materials compile each other to improve the stability of the battery and its performance.

~99% after 50 cycles

4. CONCLUSIONS

Therefore, this work has realised the capability of graphite and silicon-based materials of GO, SiO_2, and their hybrid material, GO-SiO_2 as viable anode material for SIBs. In comparison with the GO and SiO_2, the electrochemical performance of the as-fabricated GO-SiO_2 composite was superior in terms of the initial capacity, capacity retention rate and Coulombic efficiency. GO is found to provide superior conductivity and sodium ion mobility, however cycling stability of GO is not very satisfactory thereby restricting its long term application. While SiO_2 exhibits the stability, its initial capacity is relatively low comparing to the others. The synthesized GO-SiO_2 composite effectively integrates the prominent features of both components, improving both sodium-ion capacity and cycling stability. These results are encourage that the synthesized composites of GO-SiO_2 are promising materials for the next generation SIBs and able to overcome some limitation in terms of capacity and cycling performance. Future studies should concentrate on the enhancement of the geometry of such composites to make the best out of them and also applying synthesis strategies that are sustainable for real-life applications. It can be inferred that, by purifying these materials, the process of enhancing high-performance anodes for Na-ion batteries for commercial production might be made cheaper and efficient compared to current lithium-ion batteries for energy storage solutions.

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