

Facile Fabrication of Silicon-Manganese Composite Anode from Steel Slag and Electrochemical Investigation for Li-Ion Batteries

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ABSTRACT

Li-ion batteries (LIBs) are growing in modern energy storage systems for motor vehicles and portable devices. Unfortunately, the graphite anode material in typical batteries cannot support significant increases in energy density, because its specific capacity is limited. Si, with a very high theoretical capacity, gives a promising way to make high-energy-density batteries; even so, serious challenges like excessive volume expansion during charging result in low cycle life. The research focuses on the electrochemical investigation of a Si-Mn composite anode fabricated from industrial steel slag for 20 electrochemical cycles. The cell potential increases gradually and becomes stable after a few cycles. However, the cell exhibited stable discharge and charge current profile over 20 cycles. Additionally, the cell showed fluctuating coulombic efficiency (CE) initially, which became stable at ~65% after 19 cycles.

Keywords: Li-Ion Battery, Steel Slag, Anode, Composite, Cycling and Coulombic Efficiency

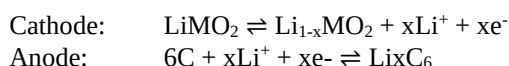


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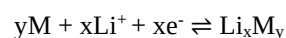
1. Introduction

LIBs are pivoting in the current forms of energy storage systems dominating powering systems in electric vehicles (EVs), portable gadgets, and renewable energy [1]. Lithium-ion cells operate on the basis of the reversible intercalation and deintercalation of the lithium ion on the cathode and the anode of a battery through an electrolyte [2]. A usual LIB consists of lithium metal oxides (e.g. LiCoO₂, LiFePO₄) as the cathode and graphite as the anode. Li⁺ ions flow between the cathode and the anode by electrolyte, and electrons circulate through the external circuit during charging. When the ions are discharged they recombine with the cathode, and the electrochemical stored energy is released. The general electrochemical reactions will be written as



To date, graphite anode, the most common one, is a limiting factor with a rather low theoretical capacity of 372 mAh g⁻¹ [3]. Graphite anodes have intrinsic drawbacks that influence performance as well as safety. Graphite is initially subjected to a 10-30% volume expansion during the lithiation reaction, resulting in structural degradation and fading of capacity during repeated cycles [4, 5]. When lithium deposition becomes uneven at either low temperatures, or in rapid-charging situations, dendrite growth can occur and may break through the separator, create internal short circuits, and in serious cases, lead to thermal runaway (TR) and even battery failure [6]. This safety risk is further worsened by decomposition of the solid electrolyte interphase (SEI). Moreover, slow diffusion of lithium in graphite limits charge transfer hence low rates of charge transfer and consequently limits the overall fast-

charging potential of lithium-ion batteries [7]. In the past forty years, many new anode candidate have been developed, such as intercalating type Mo₃Nb₂O₁₄ [8], GaNb₁₁O₉ [9], and HfNb₂₄O₆₂ [10], alloy-type Si [3], Sn [11], and Al [12] and conversion-type CoO [13], MoO₃ [14] and Fe₂O₃ [15]. Silicon (Si) whose theoretical capacity (~4200 mAh g⁻¹) is orders of magnitude larger has been suggested as a very promising alternative [16]. Unlike (de)intercalation mechanism of graphite, metalloids and metals of group IVA (Si, Ge, Sn, Sb) and group VA (P, As, Bi) alloy with LiM and binary alloys, M being the metalloids and metals [17]. The Li configuration mechanism can be expressed as:



Nevertheless, Si has very high-volume growth (70-300%) with lithiation and de-lithiation, which causes mechanical degradation, unstable SEI formation, and fast fading of the capacity [18]. To address these challenges, Si-Mn composites have attracted attention. Manganese acts as a structural stabilizer, buffering the volume changes of silicon and improving cycle life and capacity retention [4, 5]. Zuo and Yin [16] reported SiMn composite prepared through mechanical ball milling showed enhanced performance in cycling, where Mn acted as an inactive buffer to reduce silicon volume variation. The optimized sample (60 h milling, 300 °C annealing) provided 455 mAhg⁻¹ with 52% initial Coulombic efficiency, but agglomerated particles in the cycling decreased electrode contact. Additional improvement came in the form of incorporation of graphite in Si-Mn composites. Si and Mn (0.5-2 μm) particles were uniformly dispersed in the carbon matrix maintaining electrical connectivity and limiting silicon morphology transformations. The SiMn20 wt.% C composite that

annealed at 200 °C attained 463 mAhg⁻¹ and retained 387 mAhg⁻¹ with 40 cycles, which was better than Si-Mn, itself [21]. A SiMn/C compound anode containing inactive Mn₄Si₇ alloy exhibited superior electrochemical performance, retaining 82.3% capacity after 100 cycles and producing 880.6 mAhg⁻¹ at 13 Ag⁻¹. The Mn₄Si₇ phase is a structural stabilizer between nano-silicon particles, which enhances the integrity of electrodes and interfacial stability, thus facilitating better cycling and rate performance of silicon-based anodes. [19]

In addition to that, scientists have considered the potential cost-effective and sustainable sources of these materials. Steel slag, the side product of steelmaking, is also a source of silicon and manganese oxides, so it could be used as a raw material to make anodes. Traditionally, steel slag can be evaluated as industrial waste presenting the aesthetic of bacteria during waste valorization and creating a perspective of planet-friendly synthesis of battery material. Vanpeene and Heitz [22] were able to convert silicon slag into a high-capacity anode material and they show promising cycling performance after mechanical processing. This favours the applicability of industrial byproducts in the manufacturing of next-generation LIBs. Another advance in silicon-based anode is the incorporation of transition metal oxides such as Mn₂O₃ and Fe₂O₃ that increase conductivity and structural stability [23]. Nanostructuring, core/shell designs, and coatings with conductive carbon have also been demonstrated to reduce the impact of the volume expansion and enhance cycling behavior [24,25]. This study investigates the electrochemical behaviour of Si-Mn composites synthesized from steel slag, evaluating their suitability as low-cost, sustainable anode materials for LIBs. Thus, the paper is dedicated to the use of steel slag-based SiMn composites as the prospective anode material in LIBs in an effort to achieve both sustainability and high-electrochemical performance. This research aims to show that transformation of industrial byproducts into economically viable and long-life next-generation anodes is possible by evaluating their capacity, cycling stability and structural integrity.

2. Methodology

A Si-Mn composite was synthesized from the steel slag obtained from a local steel manufacturing facility. To encourage resource utilization sustainably, this slag that was naturally mixed with both silicon and manganese were selected to avoid sourcing of separate material. Raw slag was hand crushed by mortar and pestle and mechanically reduced through grinding to a smaller particle size and in some cases further reacted through ball milling to better the homogeneity and surface activation. To synthesize the Si-Mn composite from steel slag, the present oxides, primarily SiO₂ and MnO_x, must undergo mechanical activation and amalgamate during milling and heating. During ball milling, enhanced particle contact facilitates the partial reduction and amalgamation of silicon and manganese oxides, resulting in Si-Mn mixed phases. The technique additionally facilitates the reduction of particle size and enhances uniformity. This straightforward method of production minimizes the requirement for pure precursors and utilizes the inherent oxide content of slag, benefiting the environment and reducing costs. Regarding the confirmation of Si-Mn phases in the synthesized composite, their presence was conspicuously visible in the metallic sheen, and their presence was also assumed to be evident based on the

improvement in electrochemical performance. XRD or EDS characterization is recommended in future work to quantitatively confirm the exclusion of other oxide species, such as CaO or FeO, which are known constituents of steel slag. The obtained powder was combined with 15 wt% conductive carbon black and 15 wt% PVDF binder. A slurry was made by adding N-methyl-2-pyrrolidone (NMP). The mixture was stirred until homogeneous and deposited onto copper foil with the use of the doctor blade method and dried at vacuum oven at 105 °C to make it dry. Circular disks were punched in the dried foil and slightly pressed to increase interfacial contact and mechanical strength. Here, Fig. 1 summarizes the above-mentioned processes.

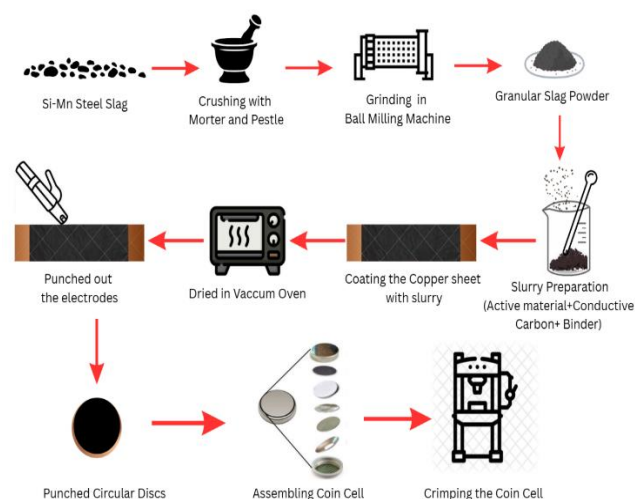


Fig. 1: Schematic representation of Si-Mn steel slag preparation process, electrode preparation and coin cell assembly.

The electrodes were pressed into CR2032-type coin cells in a full-cell configuration, which comprises of seven parts, were used to evaluate the electrode performance: a stainless-steel positive cap, LiCoO₂ as cathode material, polypropylene or polyethylene separator, electrolyte, anode material, spacer/spring and a stainless-steel negative cap. This design offers effective sealing, constant contact pressures and is commonly used to test lithium-ion battery electrodes in the laboratory scale. The electrolyte was a 1 M lithium hexafluorophosphate (LiPF₆) dissolved in a 1:1 volume blend of ethylene carbonate (EC) and diethyl carbonate (DEC). The cell assembly was done in an argon-filled glove box to eliminate wetness and oxygen and the cells were sealed with a coin cell crimping machine at a pressure of 80 psi. The electrochemical properties were subsequently quantified by galvanostatic charge-discharge (GCD) cycling indicating the voltage profile, CE, capacity retention, and so on and so forth, to determine the potentiality of the Si-Mn composite as a LIB anode.

A series of electrochemical cycling operations were carried on fabricated batteries composed of Si-Mn composite anode via LANDt and LAND 2001A Battery Testers. Based on this experimentation, we endeavored to characterize the electrochemical performance of these commercial batteries.

3. Results And Discussion

The voltage-time profile of the Si-Mn steel slag composite anode is presented in Fi. 2 which shows the battery voltage response on galvanostatic charge discharge cycling. It has a typical sawtooth shape, which denotes mode

of constant current operation. Each cycle is characterized by two different stages: the charging process is performed with the progressive increase of the voltage and corresponding insertion of lithium ions into the Si-Mn composite. The voltage goes down during the discharging cycle with the lithium ions leaving the anode. The initial peak cell potential was $\sim 1.75\text{V}$, which increase gradually up to $\sim 2.8\text{V}$ at 7th cycle. We also notice a little fluctuation after that, and the peak cell potentials were nearly stable on the following cycles. Initially, during charging, the incoming Li^+ from cathode forms a solid electrolyte interface (SEI) at anode/electrolyte interface. This consumes Li from the Li inventory of cathode active material. The formation of the SEI generally occurs at the 1st cycle of GCD. However, the volume fluctuation during GCD leads to breakdown of SEI followed by reformation of SEI. This initial formation-breakdown of SEI makes the cell unstable and hence, instability in cell potential occurred. The lack of sudden voltage changes or anomalies indicates that there is no serious voltage decay during the monitoring period (~ 40 minutes), which has implications for the future application of the material in LIBs.

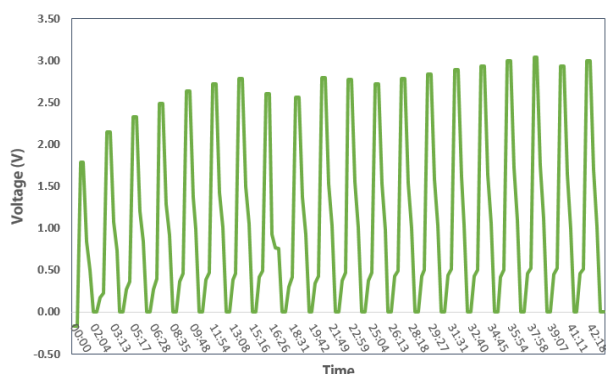


Fig. 2: Voltage profile for first 20 cycles

The current-time profile of the Si-Mn steel slag composite anode is shown in Fig. 3, which represents the current used during the test, which is held constant. Positive pulses of current reflect charging and negative ones reflect discharging. The current values are quite stable between cycles. The peak charge currents (positive current profile) were 5 mA over 20 cycles. However, the peak discharge currents (negative current profile) were 4 mA, which is less than charge current. The electrode material may not be sufficient to deliver as equal as charge current. Notably, the loss of Li inventory due to the formation of SEI leads to low discharge current. In addition, parasitic side reactions occurring at the interfaces also result in loss of Li inventory and low discharge current. This implies the occurrence of cell degradation gradually. This progressive deterioration of the discharge performance indicates the difficulty of the electrode stability in Si-Mn composites. These effects could be alleviated by improving surface alterations or incorporating conductive layers and improving long-term current response.

As shown in Fig. 4, the cycling performance of Si-Mn Steel slag anode was evaluated through 20 cycles. Coulombic Efficiency (CE) is defined as the ratio of discharge capacity to charge capacity of a cycle.

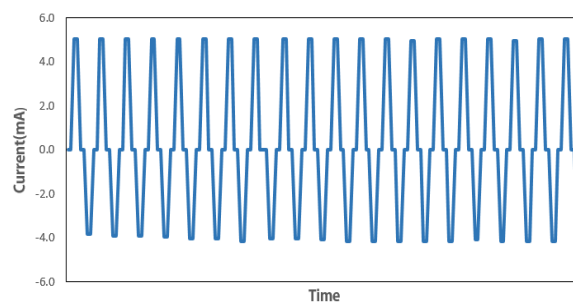


Fig. 3: Current profile for first 20 cycles.

The graph of the CE against cycle number shows that there is a considerable variation during the initiation cycles, but prominent peaks are achieved more than about 94% at a single 9-phase. In the 2nd, 6th, and 7th, sharp decreases below 60% were recorded, which reflected instability in the initial electrochemical behaviour. The SEI formation, incomplete lithiation, or the instability of the electrode/electrolyte interface is the reason for the initial low CE. As loss of Li inventory is occurring in each cycle either due to SEI formation of parasitic side reactions, the charge supply and discharge capacity reduce, and cell impedance increases in each cycle. Starting on cycle 12, the efficiency then stabilizes at 65-70% indicating stability of the CE. This low CE indicates irreversible capacity loss.

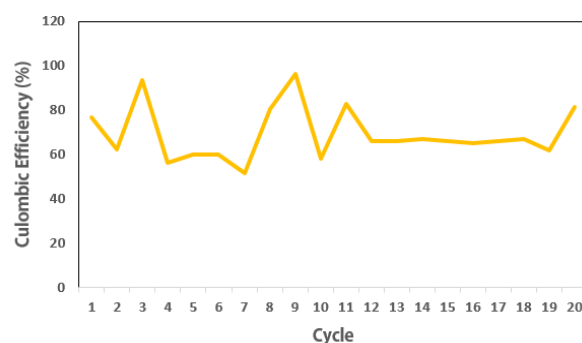


Fig. 4: Coulombic efficiency for the first 20 cycles.

Besides, in Fig. 5, it is shown that the total capacity is fairly low across the board, between 60 and 80 mAh, and shows somewhat more aggressive oscillations over the cycling window. Although these deviations are not as significant as the ones occurring in efficiency, they tend to coincide with such cycles that higher efficiency was registered (i.e. cycle 3, 10, and 20). The low and consistent capacity could indicate the scarcity of active sites in the slag structure or incomplete lithium (de)insertion, which is typical of complex industrial waste-based materials. The cycling data reveal that the Si-Mn steel anode slag is subjected to electrochemical and structural changes within the initial few cycles, thus creating inefficiencies and capacity variation. Nevertheless, the concurrent stability that occurred after the 12th cycle shows how the material can be used to form a part of the reversible lithium storage even in repeated cycles. The capacity is adequate but this behavior shows the potential to grow more.

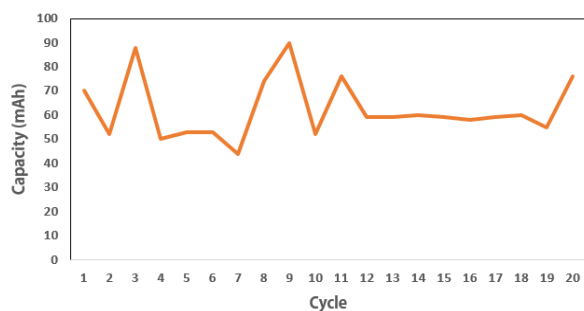


Fig. 5: Discharge capacity for first 20 cycles.

The voltage-capacity profile as shown in Fig. 6, can offer useful insights into both the (de)lithiation during electrochemical cycling. In this figure, the capacity (mAh) refers to the amount of charge that is stored or released, and the voltage (V) indicates the working voltage of the anode material during charge and discharge. Every curve in the profile is one full cycle charge-discharge.

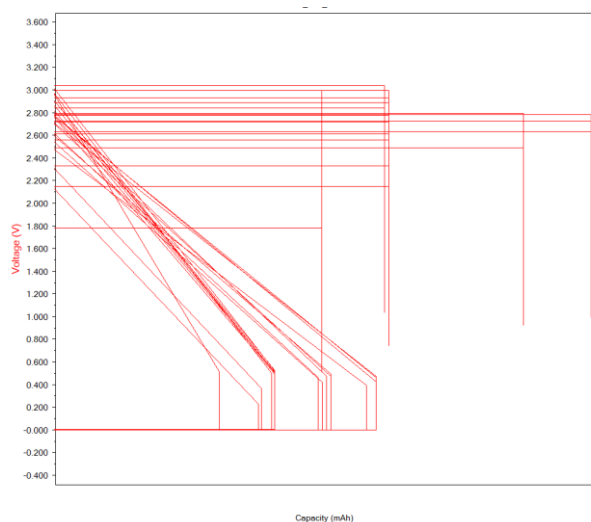


Fig. 6: Voltage-Capacity for first 20 cycles.

In the discharge curve, there is a slow decrease in the voltage range of about 2.8 to below 0.1 V, which corresponds to the lithiation process where the lithium ions are inserted into the structure of Si-Mn composite. On the other hand, the curves of charges possess an increasing trend, which is related to the process of delithiation, a departure of lithium ions out of the electrode compound. Interestingly, all the curves fail to show well-defined plateaus of voltage versus the lithiation charge, and instead, show purely sloping curves, which is typical of a multi-phase lithiation. This is common of silicon-based materials with complex, or amorphous structures, like those of industrial slag. The capacity is reduced over successive cycles as is evident by the narrowing of the curves along the x-axis. This trend indicates that there was active materials degradation which was probably due to volume expansion, SEI (solid electrolyte interphase) formation of mechanical degradation in the anode. Also, certain curves come to an abrupt end in later cycles suggesting premature termination of the curve because an upper cutoff in voltage, perhaps attributable to increased internal resistance or electrode fatigue, is being encountered.

The analysis of the electrochemical behavior of the synthesized Si-Mn composite depending on industrial steel slag in terms of a comparative evaluation with the relevant literature provides an emphasis on the superiority of the electrochemical behavior of the synthesized composite. The reference Si-Mn source claimed by Zuo and Yin had an initial discharge capacity of about 700 mAhg⁻¹, and it decreased to about 300 mAhg⁻¹ after 40 cycles. Coulombic efficiency increased very quickly until almost 100% after first few cycles, which is a manifestation of stable SEI formation and reversible lithium-ion transport. Similarly, another study via Vanpeene and Heitz [22] demonstrated the electrochemical performance of the derived Si slag as anode and obtained a moderate discharge capacity of around 900 mAh g⁻¹, after 20 cycles. In contrast, the Si-Mn composite made from slag in this research had a much greater average specific discharge capacity (1089.08 mAhg⁻¹) and values of between ~769 and 1572 mAhg⁻¹ during the initial 20 cycles. Even though the Coulombic efficiency varied between 60% and 100% with an average of 70%, this is due to the fact that as the SEI stabilized, the silicon-based phases were activated as the cycling proceeded. This increased strength could be attributed to the heterogeneous and partially amorphous microstructure of the slag-based composite, during which Mn-containing oxides and silicates act as buffering and conductive phases which reduce the volume expansion of silicon and prevent structural integrity. The current material has a greater lithium storage capacity, a high reversibility, and a sustainable fabrication pathway using cheap industrial waste than other reported slag or even the Si-based anodes. These findings indicate its great promise to be used as a clean and high-performance anode material in the next-generation lithium-ion batteries.

4. Conclusion

The electrochemical performance of Si-Mn composites fabricated from the steel slag as the anode material of LIBs was investigated. The superposition of voltage versus time and voltage versus capacity, current versus time, and cycling characteristic plots indicated partial electrochemical reversibility, moderate specific capacity, and improved stability with long cycle life of the Si-Mn slag-based anode. Although fluctuation of capacity was present in the early cycles, the material exhibited significant recovery and stabilization at later cycles. The Si-Mn composite exhibited promising cycling stability, suggesting that it will be a good alternative to the currently available anode material.

These findings support the feasibility of using steel slag—a low-cost and sustainable industrial by-product as a source of promising anode materials. Conclusively, the voltage-capacity characteristic of the Si-Mn steel slag anode shows a complex, but partially reversible, electrochemical process. Despite the gradual decrease in capacity, the stability in later cycles implies that structural integrity had been obtained within the material during cycling.

The promising electrochemical performance can still be enhanced in future by surface functionalization, coupling of carbon conductive coating, and reinforcement of the physical structure to improve mechanical stability and electronic conductivity. For an in-depth investigation of electro-chemo-mechanics, in situ and operando characterization techniques must be employed. Future research in nano-engineering and scalable processing methods should be studied to fully explore the potential of Si-Mn steel slag as a sustainable anode material of future LIBs.

5. Acknowledgement

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6. References

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