Improved electrochemical performance of SiO\textsubscript{2}-coated Li-rich layered oxides-Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2}

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\textbf{ABSTRACT}

Lithium-rich layered oxides (LLOs) such as Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} are suitable cathode materials for future lithium-ion batteries (LIBs). Despite some salient advantages, like low cost, ease of fabrication, high capacity, and higher operating voltage, these materials suffer from low cyclic stability and poor capacity retention. Several different techniques have been proposed to address the limitations associated with LLOs. Herein, we report the surface modification of Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} by utilizing cheap and readily available silica (SiO\textsubscript{2}) to improve its electrochemical performance. Towards this direction, Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} was synthesized utilizing a sol–gel process and coated with SiO\textsubscript{2} (SiO\textsubscript{2} = 1.0 wt\%, 1.5 wt\%, and 2.0 wt\%) employing dry ball milling technique. XRD, SEM, TEM, elemental mapping and XPS characterization techniques confirm the formation of phase pure materials and presence of SiO\textsubscript{2} coating layer on the surface of Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} particles. The electrochemical measurements indicate that the SiO\textsubscript{2}-coated Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} materials show improved electrochemical performance in terms of capacity retention and cyclability when compared to the uncoated material. This improvement in electrochemical performance can be related to the prevention of electrolyte decomposition when in direct contact with the surface of charged Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} cathode material. The SiO\textsubscript{2} coating thus prevents the unwanted side reactions between cathode material and the electrolyte. 1.0 wt\% SiO\textsubscript{2}-coated Li\textsubscript{1.2}Ni\textsubscript{0.13}Mn\textsubscript{0.54}Co\textsubscript{0.13}O\textsubscript{2} shows the best electrochemical performance in terms of rate capability and capacity retention.
1 Introduction

The energy storage requirements have been stringent throughout the years, and Li-ion batteries (LIBs) are an ideal solution that has been leading this field owing to their higher energy and power density [1–4]. With environmental concerns, there have been increasing interest in renewable energy sources [3]. The energy generated from various renewable energy sources must be stored into energy storage devices which could supply them instantly when needed [1]. In this regard, LIBs are considered the most attractive and viable option due to their higher energy and power density capabilities [2, 5]. LIBs are being used as power sources for most of the portable devices that we use in our daily life. However, to fulfill future demands for electric vehicles (EVs) and large scale energy storage system (ESS), the development of new materials with improved performance is essential [2, 5]. Since the commercialization of lithium-ion batteries by Sony in 1991, there has been no significant breakthrough in the development of new cathode materials [1, 6]. With more interest in electric vehicles, there is a severe need for new cathode materials with enhanced energy and power density, a stable and long cycle life, and with improved safety [7–11].

Lithium-rich layered oxides (LLOs) cathodes display a promising performance in terms of capacity and operating voltage and hence is considered as a potential cathode for future lithium-ion batteries. These materials have already gained much attention previously because of their considerably high discharge capacities (> 250 mAh g⁻¹) and higher operating voltages [12–18]. These materials are also very cost-effective and easy to produce [19, 20]. However, despite the tempting characteristics, these materials have a few drawbacks that need to be addressed before successful commercialization. These materials experience rapid capacity and voltage fading during successive cycles that have an adverse effect on their energy density. Moreover, these materials also experience poor rate capability and have serious safety concerns [18, 21–26].

To overcome these issues, various optimization techniques such as surface modification, doping of transition metals and morphology control have been widely reported [11, 18, 27]. Among them, the surface coating is widely accepted by the battery community for improving the performance of cathode materials for lithium-ion batteries [10, 11]. The surface coatings help to prevent the direct contact of electrolyte and the cathode material, thereby, reducing the unwanted side reactions by electrolyte oxidation, especially at higher operating voltages [28–34]. The type of coating and the coating thickness largely affects the overall performance of cathode materials. Thin and homogeneous coatings are ideal for the ultimate performance. However, if the coating is thick, it may impede the lithium-ion movement, which leads to an increase in charge transfer resistance at the cathode/electrolyte interface leading to inferior electrochemical performance [35, 36]. Several coating materials have been proposed and reported [37–39]. Among them, SiO₂ is readily available, cheap and environmentally friendly material [40–43]. However, it is challenging to develop a homogenous SiO₂ coating on the surface of particles since it requires high heat treatment temperatures and additional heat treatment step, which significantly increase the processing cost.

Here, we report the in situ coating process without any additional heat treatment step to form a homogeneous SiO₂ coating layer. The process itself is viable, scalable and cheap without employing any additional heat treatment step, making it as an ideal candidate for the coating material. Recently, there have been few reports on SiO₂ coating for cathode materials which show promising electrochemical results [11]. Herein, we synthesized and characterized SiO₂-coated Li₁₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%). The Li₁₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ (LLO) was prepared by the sol–gel synthesis process and coated with SiO₂ using dry ball milling approach. The phase purity of the synthesized materials was analyzed using X-ray diffraction (XRD) technique. The particle morphology was investigated using scanning and transmission electron microscopes (SEM and TEM). TEM was further used for elemental mapping of the synthesized materials. X-ray photoelectron spectroscopy (XPS) was used to identify the chemical states of different elements present in the cathode materials. Finally, the electrochemical measurements were conducted, and the performance of uncoated and SiO₂-coated Li₁₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%) materials was compared to elucidate the beneficial role of SiO₂ coatings.
2 Experimental

2.1 Materials preparation

The Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ was prepared using sol–gel synthesis process. The stoichiometric amounts of lithium acetate, manganese acetate, cobalt acetate, and nickel acetate (1.2:0.54:0.13:0.13) were added to 100 ml distilled water at 60 °C with continuous stirring. All the precursors were purchased from Sigma Aldrich. Later citric acid was added to the precursor solution in the ratio 1:2 (citric acid: metal ions) which acted as the chelating agent. Under constant stirring, the solution temperature was increased to 80 °C and left until a gel was formed. The gel was transferred to the oven at 120 °C to remove the traces of water from the gel. After complete drying, the gel was then ground into a fine powder, pressed into pellets, and decomposed in a muffle furnace at 450 °C for 6 h. The decomposed precursor material was again ground using an agate mortar and mixed homogenously. Finally, the precursor material was again pressed into pellets and calcined at 900 °C for 12 h in the muffle furnace to get the desired material.

The SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ (SiO$_2$ = 1.0, 1.5 and 2.0 wt%) materials were synthesized by a similar synthesis process as above stated. However, after decomposition of the precursor at 450 °C for 6, SiO$_2$ nanoparticles were added to it and ball milled for 24 h using zirconia balls. Later, this material was calcined at 900 °C for 12 h to achieve SiO$_2$-coated materials. Figure 1 shows the experimental process for the synthesis of the Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ cathode materials.

2.2 Structural, compositional, and thermal stability characterization

Powder X-ray diffraction analysis (PAN Analytical—Empyrean) with Cu-K$_\alpha$ radiation (1.5425 Å) was used to analyze the phase purity and study the crystal structure of the synthesized materials. The samples were scanned in the range 10 ≤ 2θ ≤ 90° with a scan step size of 0.01313°. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were used to investigate the particle morphology. TEM was further used for elemental mapping of the surfaces of the synthesized materials. X-ray photoelectron spectroscopy (XPS, Thermo-Scientific-Sigma Probe) was further used to confirm the presence of SiO$_2$ coating layer on the particle surface and to study the chemical states of different elements in synthesized materials. Furthermore, surface area and porosity of the developed materials were analyzed using BET (Quanta chrome 4200e) technique. Thermal stability of pristine and SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ materials was studied using DSC, 8500, PerkinElmer. For DSC measurement, the cells were charged to 4.7 V at 0.1 C and transferred to the argon-filled glovebox. The cells were opened, and the excessive electrolyte was removed from the electrode surface. The electrode was scratched from the current aluminum collector and transferred to the high-pressure stainless-steel pan. DSC measurements were performed from room temperature to 450 °C with a heating rate of 5 °C.

2.3 Electrode and cell fabrication

Electrode fabrication for electrochemical testing was done by forming a slurry of the active materials (uncoated and SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$), Super-P carbon, and PVDF binder in the ratio 80:10:10 respectively in the NMP solvent. The cathode slurry was mixed in a glass vial for around 12 h. Later, this slurry was coated on aluminum current collect using the doctor blade, keeping the thickness of the coated electrode around 25 μm. The cast electrode was then shifted to the oven for drying at 120 °C for 3 h. The electrodes were then calendared using a rolling press. Electrodes with a diameter of 14 mm were then punched from the calendared electrodes. These circular electrodes were shifted to a vacuum oven at 120 °C for 2 h to remove the trace of water. Finally, the electrodes were moved to an argon-filled glovebox for cell fabrication. For electrochemical testing, CR-2032 coin cells were fabricated using lithium metal as the anode, and 1 M LiPF$_6$ in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by v/v.) (Sigma Aldrich) was used an electrolyte. Moreover, Celgard 2325 was used as the separator. The electrochemical tests for these materials were conducted at room temperature (25 °C) using WonAtech (WBCS 3000L, Korea) battery cycler. All the galvanostatic charge/discharge measurement were conducted in the voltage window of 2.0–4.9 V.
3 Results and discussion

XRD spectra of uncoated and SiO₂-coated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%) materials are shown in Fig. 2. XRD spectra confirmed the synthesis of highly crystalline materials without the presence of any impurity phases. The synthesized materials are indexed to R-3m and C2/m space groups, as reported earlier [19, 44]. Furthermore, it can be noticed that there is no significant difference between the XRD spectra of uncoated and SiO₂-coated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ materials. Finally, due to the presence of a small amount of SiO₂, it is undetected using XRD analysis.

The FE-SEM images of the uncoated and SiO₂-coated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%) materials are displayed in Fig. 3. It is observed that all synthesized materials display a well-defined morphology with homogenous particle size distribution. It can also be observed that the particle size for the SiO₂-coated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%) materials is smaller when compared with the uncoated sample which can be due to the ball milling effect. The average particle size for uncoated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ is ~ 400–800 nm, whereas the average particle size for SiO₂-coated Li₁₂Ni₀.13Mn₀.54Co₀.13O₂ is ~ 150–350 nm. The particle size of the developed materials was calculated using ImageJ software.
reduction in particle size of the coated materials can be due to (i) dry ball milling effect and (ii) impediment of particle growth at high-temperature calcination owing to the presence of SiO₂ coating on the particle surface. The BET curves for the uncoated and SiO₂-coated Li₁.₂Ni₀.1₃Mn₀.₅₄Co₀.₁₃O₂ materials are shown in Fig. S-1. No significant difference can be found in BET isotherms for uncoated, and SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ materials. The surface area for uncoated material is 6.139 m²/g whereas the coated materials have 6.718 m²/g, 6.412 m²/g, and 6.120 m²/g for 1.0 wt%, 1.5 wt% and 2.0 wt% SiO₂, respectively.

High-resolution TEM and element mapped images for 1.5 wt% SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ are shown in Fig. 4. Figure 4a clearly shows the rock-like spherical morphology of the particles. The particle size of 1.5 wt% SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ samples is ~ 150–300 nm which is consistent with FE-SEM images in Fig. 3. TEM image of 1.5 wt% SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ material shown in Fig. 4b confirms the existence of the SiO₂ coating layer on the particles. Furthermore, TEM elemental mapping of SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ materials was also conducted, and the results for 1.5 wt% coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ are shown in Fig. 4c–h. The homogenous distribution of Ni, Mn, Co, O, and Si on the particle surfaces can be identified from elemental mapping images which further confirms the presence of Si on the particle surfaces. It is pertinent to note that SiO₂ is homogeneously coated on the surface of the particles even with small amounts used. Hence, both high-resolution TEM and elemental mapping images provide strong evidence for the existence of a homogeneous SiO₂ coating around the particles of Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂, which is expected to have a positive impact on its electrochemical properties.

XPS analysis was performed on uncoated and SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ to study the chemical states of transition metals in the synthesized materials and further to get evidence of SiO₂ layer on the Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ surface as shown in Fig. 5. The survey patterns for the uncoated and SiO₂-coated Li₁.₂Ni₀.₁₃Mn₀.₅₄Co₀.₁₃O₂ (SiO₂ = 1.0, 1.5 and 2.0 wt%) materials are shown in Fig. S-2. The high-resolution
XPS spectra for Si further confirmed the presence of SiO$_2$ coating layer. The XPS spectra were fitted using XPS peaks fit software to analyze the chemical states of the transition metals. The high-resolution spectra for Si (Fig. 5m–p) clearly show that no SiO$_2$ layer was present on uncoated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$, whereas, for the coated materials, the SiO$_2$ can be detected. The high-resolution XPS spectra for Ni, as shown in Fig. 5a–d display two peaks as Ni$_{2p_{1/2}}$ at $872.77 \pm 0.20$ eV and Ni$_{2p_{3/2}}$ at $854.82 \pm 0.10$ eV, which corresponds to Ni$^{2+}$ [18]. Moreover, as shown in Fig. 5e–h, Mn shows peaks for Mn$_{2p_{1/2}}$ at $654.42 \pm 0.28$ eV and Mn$_{2p_{3/2}}$ at $642.66 \pm 0.10$ eV, which is consistent with the presence of Mn$^{4+}$ [29, 45]. Finally, Co also displays two peaks as Co$_{2p_{1/2}}$ at $795.68 \pm 0.11$ eV and Co$_{2p_{3/2}}$ at $780.68 \pm 0.1$ eV, as shown in Fig. 5i–l, which corresponds to Co$^{3+}$. The binding energies for the transition metals are displayed in Table 1, which are consistent with previous reports [29, 45]. It can be noticed that with the increasing amount of SiO$_2$ as coating, there is a slight increase in the binding energies of Si, which may be due to stronger interactions of SiO$_2$ with Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ materials.

The galvanostatic charge/discharge curves of uncoated and SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$
(SiO$_2$ = 1.0, 1.5 and 2.0 wt%) materials are shown in Fig. 6. For the uncoated material, the discharge capacities are ~ 205 mAh g$^{-1}$ and 16 mAh g$^{-1}$ at 0.1 C and 2 C, respectively. Whereas SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ (SiO$_2$ = 1.0, 1.5 and 2.0 wt%) materials show similar initial discharge capacities but demonstrate better discharge capacity, especially at higher C-rates. For instance, the 1.0 wt% SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ material as shown in Fig. 6b, shows an initial discharge capacity of ~ 212 mAh g$^{-1}$ and ~ 91 mAh g$^{-1}$ at 0.1 C and 2 C, respectively, validating the improvement in the electrochemical performance of SiO$_2$-coated materials. Moreover, 1.5 and 2.0 wt% SiO$_2$-coated materials also display improved rate performance when compared to uncoated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ material.

Figure 7 compares the rate capability performance of uncoated and SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ materials.

### Table 1: Binding energies of metals in uncoated and SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$

| Material          | Mn 2p$_{3/2}$ | Mn 2p$_{1/2}$ | Ni 2p$_{3/2}$ | Ni 2p$_{1/2}$ | Co 2p$_{3/2}$ | Co 2p$_{1/2}$ | Si 2p |
|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|-------|
| 0.0 wt% SiO$_2$   | 642.66        | 654.42        | 854.81        | 872.77        | 780.68        | 795.68        | –     |
| 1.0 wt% SiO$_2$   | 642.57        | 654.15        | 854.82        | 872.70        | 780.61        | 795.61        | 102.72 |
| 1.5 wt% SiO$_2$   | 642.73        | 654.43        | 854.92        | 872.71        | 780.62        | 795.79        | 102.74 |
| 2.0 wt% SiO$_2$   | 642.72        | 654.42        | 854.92        | 872.97        | 780.79        | 795.79        | 102.78 |
| Ref. [29, 45]     | 642.7         | 654.10        | 855.00        | 872.30        | 780.80        | 795.20        | –     |
materials at various C-rates. Uncoated material shows rapid capacity fading, especially at higher C-rates. On the other hand, SiO2-coated materials display an improved rate capability performance. At low C-rates, almost all the materials show very similar discharge capacity; however, at higher C-rate, the coated materials display higher capacity and better rate performance. The uncoated materials show the discharge capacity of around 100 mAh g\(^{-1}\) and 16 mAh g\(^{-1}\) at 1 C and 2 C, respectively. Whereas, all SiO2-coated materials display higher discharge capacity at 1 C and 2 C. The improvement in capacity is quite prominent in the case of 1 wt% SiO2-coated Li\(_{1.2}\)Ni\(_{0.13}\)Mn\(_{0.54}\)Co\(_{0.13}\)O\(_2\) material. The 1 wt% SiO\(_2\)-coated Li\(_{1.2}\)Ni\(_{0.13}\)Mn\(_{0.54}\)Co\(_{0.13}\)O\(_2\) materials demonstrate the best rate capability performance and display capacity of \(~125\) mAh g\(^{-1}\) and \(~93\) mAh g\(^{-1}\) at 1 C and 2 C, respectively. Usually, during high voltage operations, the electrode in de-lithiated states are quite unstable and rapidly reacts with electrolytes which result in degradation of battery performance. These types of surface coating are known to prevent the direct contact of electrolyte and cathode materials which helps to reduce the unwanted side reaction between them. It can be further noticed from Fig. 6 that increasing the coating amount from 1 wt% to 1.5
wt% and 2.0 wt% leads to decreasing discharge capacities. The main reason for the decrease in initial discharge capacity can be related to increased interfacial resistance due to the presence of inactive coating layer. This has been well understood and reported in several previous studies [11, 40, 43, 46]. Table 2 lists the discharge capacities of uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 material at various C-rates.

Table 2 Discharge capacities of uncoated and uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 (SiO2 = 1.0, 1.5 and 2.0 wt%) materials at various C-rates

| Materials/C-rate | 0.1 C (mAh g\(^{-1}\)) | 0.2 C (mAh g\(^{-1}\)) | 0.5 C (mAh g\(^{-1}\)) | 1 C (mAh g\(^{-1}\)) | 2 C (mAh g\(^{-1}\)) |
|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 wt% SiO2     | 205                     | 182                     | 142                     | 97                      | 21                      |
| 1.0 wt% SiO2     | 214                     | 185                     | 152                     | 125                     | 93                      |
| 1.5 wt% SiO2     | 213                     | 189                     | 138                     | 114                     | 83                      |
| 2.0 wt% SiO2     | 203                     | 179                     | 144                     | 104                     | 50                      |

The cycling performance at 0.1 C for 50 cycles for uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 (SiO2 = 1.0, 1.5 and 2.0 wt%) materials is shown in Fig. 8. It is observed that all the materials show slow capacity fading till 50 cycles. However, the uncoated Li1.2Ni0.13Mn0.54Co0.13O2 material shows a relatively faster capacity fading when compared to SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 (SiO2 = 1.0, 1.5 and 2.0 wt%) materials. Figure 8b–e show the charge/discharge curves of uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials at different cycle numbers. It can be clearly seen that the synthesized material displays fast voltage degradation upon cycling, which is the inherent issue with this material. However, the SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials show relatively slower voltage and capacity degradation, as seen in Fig. 8b–e. This voltage and capacity decay is generally due to the unstable crystal structure; however, with SiO2 coating, the surface structure is protected, which prevents phase transformation upon cycling. The uncoated sample shows an initial discharge capacity of ~ 200 mAh g\(^{-1}\), which decreases to ~ 160 mAh g\(^{-1}\) after 50 cycles with the capacity retention of ~ 71%.

On the other hand, the SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials show improved capacity retention. It can be observed that 1.0 wt% SiO2-coated material displayed the best initial discharge capacity. However, with increasing the thickness of the coating layer, the initial discharge capacity is slightly decreased, which might be due to increased interfacial resistance. Overall, SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials exhibit improved cycling performance when compared with uncoated materials.

Figure 9 shows the thermal stability of uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials. It can be seen from the DSC results that all the materials are stable till 215 °C (on average). However, they show strong exothermic peaks beyond this temperature. Uncoated Li1.2Ni0.13Mn0.54Co0.13O2 shows a strong exothermic peak at around 217.84 °C, which corresponds to the reaction between the charged cathode and the electrolyte solution. It is interesting to note that the thermal stability behavior of SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 improved in terms of onset temperature and heat generation. The onset temperature for 1.0 wt% SiO2 material is almost similar to uncoated material. However, the amount of heat generation decreased to a considerable amount for 1.0 wt% SiO2 material. Moreover, the onset temperatures for 1.5 and 2.0 wt% SiO2 materials increased to around 245 °C. Nevertheless, it can be noticed that heat generation for 2.0 wt% material has increased. Higher onset temperature might have resulted in the severe condition, which results in more heat generation once the exothermic reaction between the charged electrode and electrolyte initiated. Table 3 compares the onset temperatures and heat generations of uncoated and SiO2-coated Li1.2Ni0.13Mn0.54Co0.13O2 materials. The onset temperatures and heat generation trends have also been shown in Fig. S-3.
4 Conclusions

The lithium-rich layered oxide (LLO) cathode was synthesized and coated with silica (SiO$_2$) to form SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ materials (SiO$_2$ = 1.0, 1.5 and 2.0 wt%). The XRD results suggest the synthesis of phase pure materials without the presence of any impurity phases. SEM/TEM and XPS analysis confirmed the synthesis of nanometric sized particles and the presence of SiO$_2$ layer on the surface of the particle. The electrochemical study shows that SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ materials demonstrate improved performance in terms of rate capability and cycling performance. Moreover, SiO$_2$-coated Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ displayed improved thermal stability behavior when compared to...
uncoated material. The improvement in electrochemical and thermal performance can be associated with the prevention of direct contact between cathode material and the electrolyte, which reduce the unwanted side reactions between them. However, the strategy of SiO$_2$ coating on Li$_{1.2}$Ni$_{0.13}$Mn$_{0.54}$Co$_{0.13}$O$_2$ is quite effective and may pave the way for commercial battery materials coatings if effectively engineered.

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**Compliance with ethical standards**

**Conflicts of interest** Not applicable

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