Supporting Information

Ion Conducting Li_2SiO_3-Coated Lithium-rich Layered Oxide Exhibiting High Rate Capability and Low Polarization

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Experimental

1. Synthesis

Synthesis of $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ sample**.** $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ sample was synthesized by a Co-precipitation (CP) method. Stoichiometric amounts of nickel (II) sulfate and manganese (III) sulfate were dissolved in deionized water. The $Na_2C_2O_4$ solution was added dropwise into the above solution under violently stirring. The mixed oxalate precursor was then filtered, washed, and dried overnight at 70°C.

Synthesis of $SiO_2@Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O$. A solvothermal process was carried out to coat SiO_2 on $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O$ samples. 1.2mmol $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ was dispersed into 10ml absolute ethanol, followed by addition of $Si(OC_2H_5)_4$ diluted in absolute ethanol. The mixture was maintained at 180°C for 5 hours. During the solvothermal process, the phase of

$Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ remain unchanged in addition to the loss of some H_2O. Then, the product of $SiO_2@Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O$ was washed with ethanol, and collected by centrifugation.

Synthesis of $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ compound. $SiO_2@Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O$ was dispersed in ethanol, and mixed with stoichiometric amounts of $LiOH{\cdot}H_2O$. The amounts of $LiOH{\cdot}H_2O$ is calculated by the following equation: $n_{LiOH{\cdot}H2O} = 1.3n_{(Ni+Mn)} + 2n_{Si}$

The mixture was first stirred under 80°C until it was dry, and then it was collected and calcinated at 800°C for 12 hours with a heat rate of $5°C{\cdot}min^{-1}$ to get $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$.

Three pivotal chemical reaction equations to presented the microstructural evolution of all the samples during the synthesis of $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ steps.

$$Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O \xrightarrow[\text{solvothermal}]{180°C} Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O + zH_2O \tag{1}$$

$$zH_2O + Si(OC_2H_5)_4 \longrightarrow SiO_2 + C_2H_5OH \tag{2}$$

$$SiO_2@Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}yH_2O + LiOH{\cdot}H_2O \xrightarrow{800°C} Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2 + CO_2 + H_2O \tag{3}$$

The molar ratio of Si:(Ni+Mn) is 3:100 during synthsis of $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ compound. So we can calculate that the molar ratio of Li_2SiO_3:$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ is 3:100 in the sample and the content of Li_2SiO_3 is 2.951%.

Synthesis of pristine $Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ compound. In order to exclude the influence of the solvothermal process, the $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ sample was also maintained at 180°C for 5 hours without addition of $Si(OC_2H_5)_4$. Then the $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$ sample was mixed with stoichiometric amounts of $LiOH{\bullet}H_2O$ and calcinated at 800°C for 12 hours with a heat rate of $5°C{\bullet}min^{-1}$ to get pristine $Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$.

2. characterizations

The crystal structures of the samples were characterized by X-ray diffractometer (Persee XD2) equipped with Cu-Kα radiation (α=1.5418). The FTIR spectra were measured on a Nicolet

Avatar 360 FTIR instrument by a transmission mode (Thermoelectro., USA). Particle morphologies of the prepared powders were observed by scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). Thermo gravimetric analyzer 2050 (TGA 2050) was applied on the metal oxalates precursors from room temperature to 600°C at a heating rate of 5°C /min under air flow.

3. Electrochemical Measurement

A two-electrode cell was used in the electrochemical characterization by galvanostatic cycling. The composite positive electrodes were prepared by a slurry coating procedure. The slurry was made by mixing 82wt% active materials, 10wt% carbon black, and 8wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone (NMP). The slurry was spread uniformly on an aluminum foil current collector and dried under vacuum at 120°C for about 12h. Then 2016-type coin cells were assembled in an Ar-filled glove box using Li foil as the counter electrode. The electrolyte was 1mol/L $LiPF_6$ in a 1:1mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and the separator was Celgard 2500. Galvanostatic charge-discharge cycling was performed between 2.0-4.8V (vs. Li/Li^+) using automatic galvanostat (NEWARE) at different current rates at room temperature. The electrochemical spectroscopy (EIS) was performed with an (PGSTAT 302N, Metrohm-Autolab) instrument using an amplitude of 5mV and a frequency range from 100 kHz to 0.1Hz.

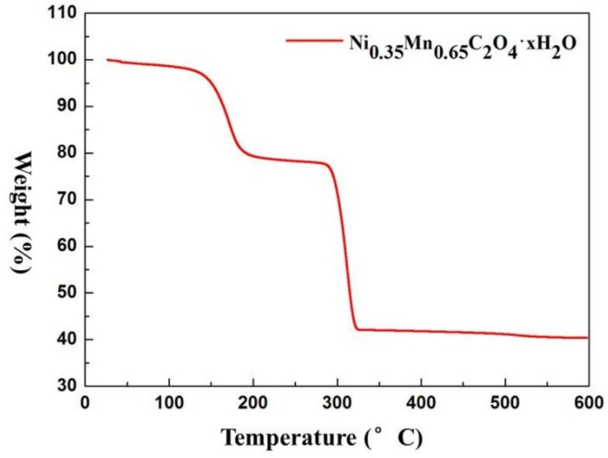

Figure SI 1. The TGA curves for $Ni_{0.35}Mn_{0.65}C_2O_4{\cdot}xH_2O$.

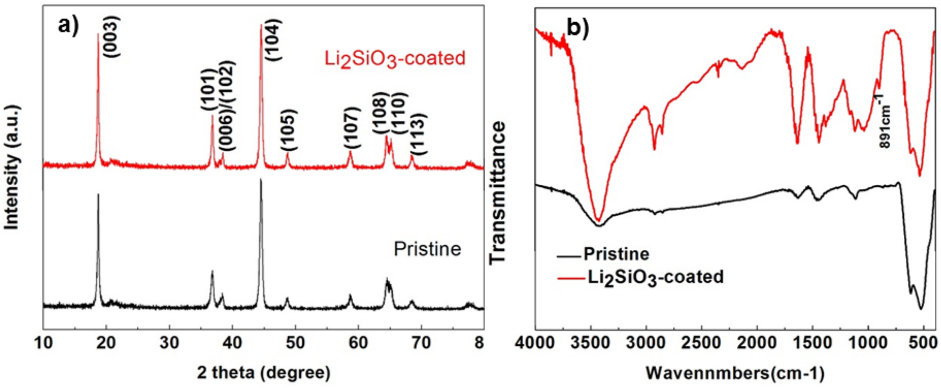

Figure SI 2. a) The XRD patterns of the pristine and Li_2SiO_3@$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ electrode. b) The FTIR spectra of the pristine and Li_2SiO_3@$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ samples.

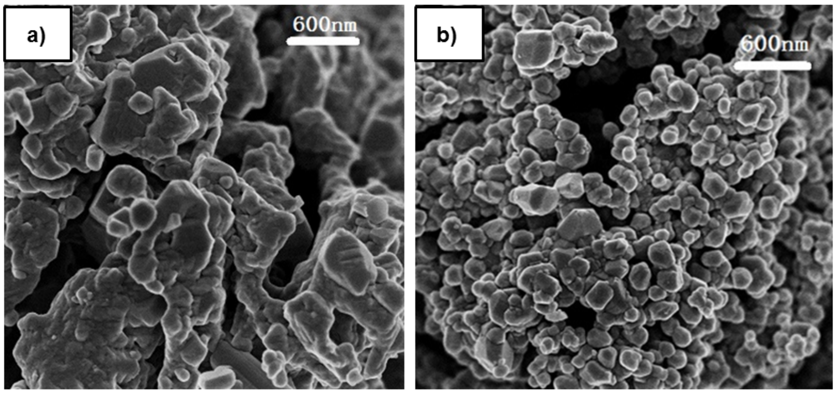

Figure SI 3. SEM images of the pristine and Li_2SiO_3@$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ samples.

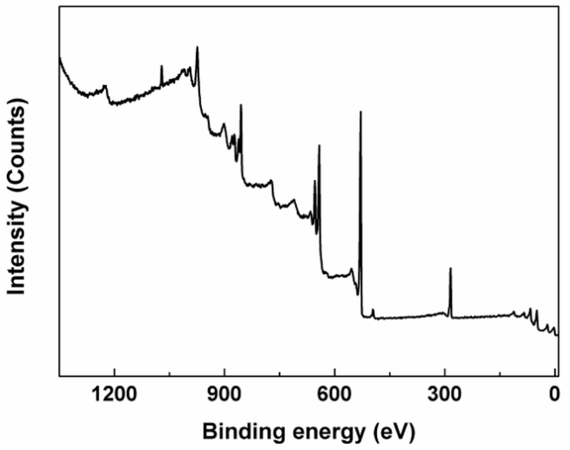

Figure SI 4. X-ray photoelectron spectrum of $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$.

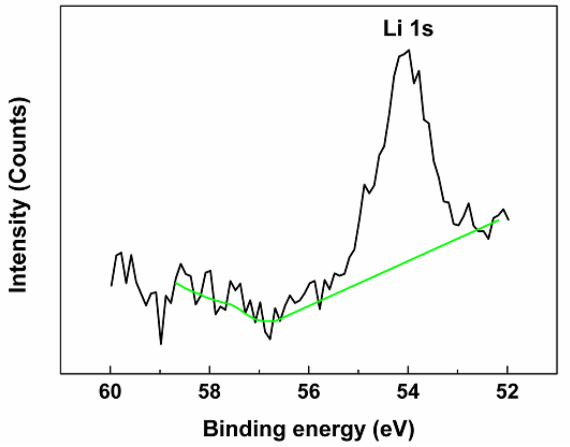

Figure SI 5. X-ray photoelectron spectroscopy (XPS) spectra of Li 1s for $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ powders.

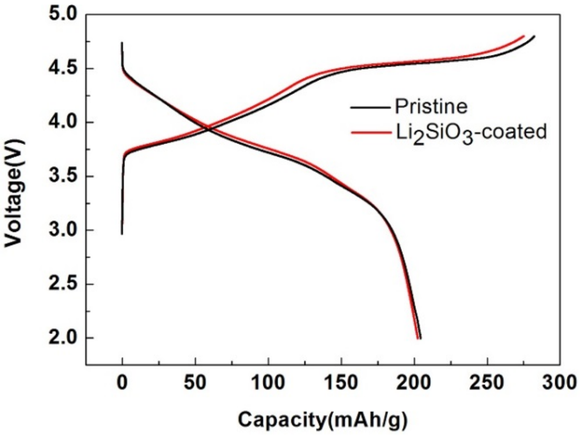

Figure SI 6. The first charge-discharge specific capacity vs. voltage curves for the $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ and pristine electrode.

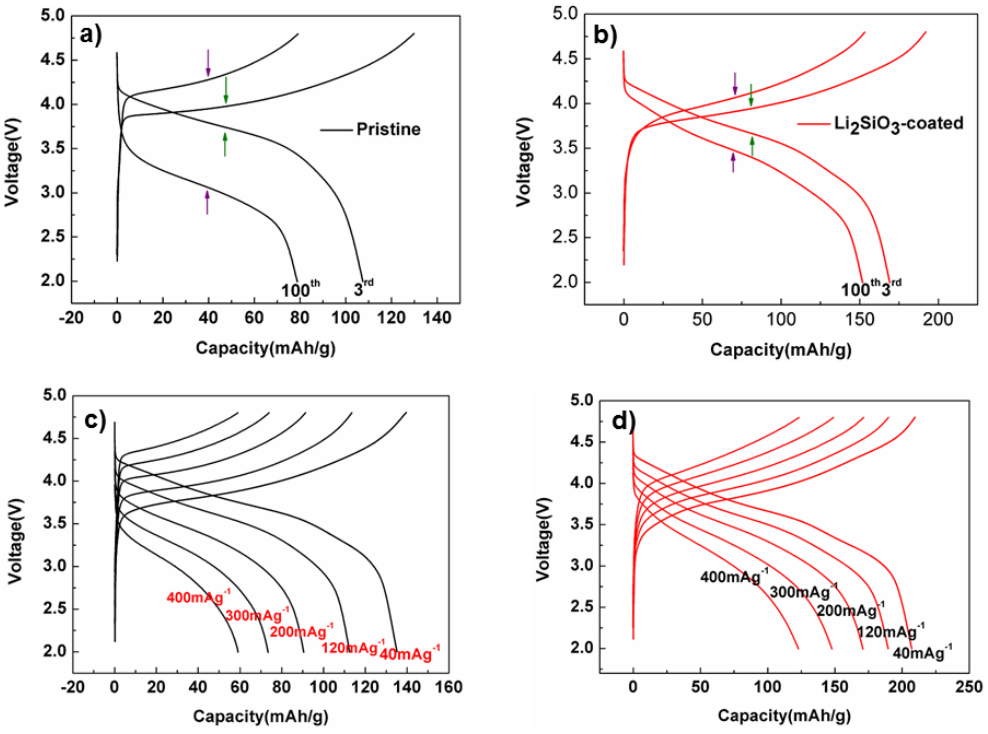

Figure SI 7. a, b) Specific capacity vs. voltage curves for the pristine and $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ electrode at 3rd, 50th and 100th cycle. The charge-discharge curves of the cells at various rates between 2.0 and 4.8V: c) pristine electrode, d) $Li_2SiO_3@Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ electrode.

Table SI 1. Discharge capacity of the coated and pristine samples at the current density of 100mAg^{-1}.

cycle	3rd	20th	50th	80th	100th
Pristine (mAhg^{-1})	107.6297	90.852	86.2082	82.9749	78.8837
Coated (mAhg^{-1})	169.2761	164.9555	164.0623	157.9252	152.0316

Table SI 2. Capacity retention of the coated and pristine samples at different charge-discharge current density.

Rate	100mAg^{-1}		400mAg^{-1}	1000mAg^{-1}
Sample	Coated	Pristine	Coated	Coated

Highest capacity (mAhg^{-1})	169	108	148	110
Final capacity (mAhg^{-1})	152	79	119	74
Capacity retention (%)	90	73	80.4	67.3

Table SI 3. The fitted solution resistances (R_s) and charge transfer resistances (R_{ct}) for the Nyquist plots of Li_2SiO_3@$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ and pristine samples.

Sample	R_S		R_{ct}	
	Value(Ω)	Error%	Value(Ω)	Error%
$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$	5.4662	3.647	380.96	0.848
Li_2SiO_3@$Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$	2.056	8.94	325.22	2.718