

Supplementary Information

Encapsulation of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ with thin inorganic electrolyte film to reduce gas evolution in the application of lithium ion batteries

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S. 1. Experimental details: measurement of the amount of gas generated

0.03 g of Li_2CO_3 or LiOH (99.9%, Sigma-Aldrich, vacuum-dried at 110°C for 24 h) was embedded in a pouch with 0.5 g of electrolyte solution (1 M LiPF_6 dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) mixed in a 3:3:4 volume ratio) or with each carbonate solvent. The pouch was evacuated (~ 0.1 Torr) and sealed. The volume of the pouch was measured using the liquid pycnometer method before and after high temperature (85°C) storage to measure the amount of gas generated. The whole process was conducted in a dry room in which the dew point was maintained at -50°C .

In order to measure the amount of gas generated by charged cathode, a 2016-type coin half-cell was fabricated and was charged to 4.45 V vs. Li/Li^+ (0.1C CC-CV). The cell was disassembled at the charged state, and the cathode electrode was separated. 10 pieces of the electrode containing a total of 0.5 g of charged NCM were embedded in a pouch with 1 g of electrolyte solution or with each solvent, and the amount of gas generated was measured using the same method as the measurement of the amount of gas generated by Li_2CO_3 or LiOH. It

had been previously confirmed that the error range of our volume measurement using specially designed pycnometer was ± 0.015 cc, which is small enough considering that volume change of pouch was far larger.

S. 2. Accuracy of the measurement volume measurement by the pycnometer method

We designed a pycnometer for the measurement of volume of pouches which contained charged cathodes and electrolyte solutions. By measuring the volume change of the pouch during the storage, amount of the gas generated could be estimated. The cap of the pycnometer was specially designed to be detachable so that the pouch whose size was 30 x 80 mm could be immersed in water.

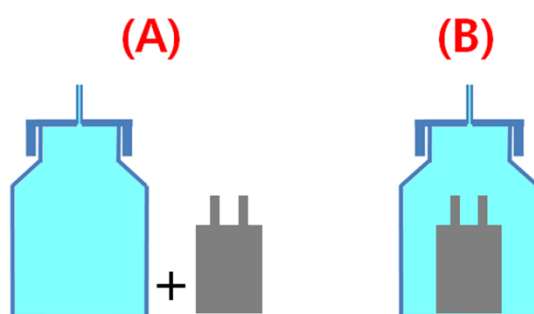


Fig. Liquid pycnometer method to measure the volume of pouch samples

Weight difference between (A) and (B) of the above figure is mass of the water equivalent to the volume of the pouch. We examined reliability of the method by measuring volume of a coin (100 won coin of Korea). The data presented in the following table showed that standard variation of the measurement is 0.015 cc. Actual error range of the volume measurement is expected to be smaller because we measured three times per sample and averaged the data.

Day	Number of trial	Temperature of water ($^{\circ}\text{C}$)	Mass (A)	Mass (B)	Volume of the coin (cc)
Day 1	#1	21.0	549.61	544.81	0.62
	#2		549.60	544.80	0.62
	#3	21.5	549.57	544.77	0.62
	#4		549.56	544.75	0.61

Day 2	#1	22.5	549.51	544.72	0.63
	#2		549.52	544.72	0.62
	#3	23.5	549.40	544.63	0.65
	#4		549.42	544.62	0.62
Day 3	#1	22.7	549.51	544.70	0.61
	#2		549.49	544.69	0.62
	#3	23.2	549.45	544.65	0.62
	#4		549.44	544.65	0.63

Table. Measurement of the volume of a coin to verify reliability of the method.

Although abnormal data rarely appeared as marked in red in the table, they could be filtered out by repeating the measurement several times in case.

S. 3. Experimental details: $Li_{3x}La_{2/3-x}TiO_3$ coating

The coating layer of the cathode material was formed using a mass-producible sol-gel process. Acetylacetone (99.0%, Junsei) and diethylenetriamine (99.0%, Sigma-Aldrich) were added to 2-methoxyethanol (99.0%, Samchun), and the solution was stirred for 10 min. $LiNO_3$ (99.0%, Sigma-Aldrich), $La(NO_3)_3 \cdot 6H_2O$ (99.0%, Sigma-Aldrich), and titanium isopropoxide ($Ti\{OCH(CH_3)_2\}_4$, 98%, Samchun) were dissolved in the solution. Commercial NCM523 (Samsung SDI, Co.) was added into the solution. After the slurry was stirred for 30 min, it was dried at 120°C and then heated at 600°C for 2 h. Al_2O_3 -coated NCM was also prepared using a sol-gel process for comparison. (Details of the process are given in the supplementary data.)

The solution used for the LLTO coating was prepared as follows: Acetylacetone (AcAc, 99.0%, Junsei) and diethylenetriamine (DETA, 99.0%, Sigma-Aldrich) were mixed with 2-methoxyethanol (2-ME, 99.0%, Samchun), and the solution was stirred for 10 min. $LiNO_3$ (99.0%, Sigma-Aldrich), $La(NO_3)_3 \cdot 6H_2O$ (99.0%, Sigma-Aldrich), and titanium isopropoxide (99.0%, Samchun) were added, and the resulting solution was stirred for 30 min. The molar ratios DETA:(Li+La) and AcAc:(Li+La+Ti) were maintained at 1:1. The concentration of LLTO in the solution was 10 wt%; therefore, the ratio of the NCM powder to the coating solution was 2:1 for producing a 5-wt% LLTO coating. The solution composition (x) was

varied such that $x = 0, 0.0625, 0.125, \text{ and } 0.25$ to find the optimal coating condition. The amount of each precursor required to produce a 5-wt% LLTO coating on 30 g of NCM is presented in the following Table:

	$x = 0$	$x = 0.0625$	$x = 0.125$	$x = 0.25$
LiNO ₃ (g)	0	0.107	0.223	0.488
La(NO ₃) ₃ ·6H ₂ O (g)	2.298	2.167	2.025	1.703
AcAc (g)	1.328	1.486	1.657	2.047
DETA (g)	0.547	0.677	0.817	1.136
Ti(OPr) ₄ (g)	2.262	2.354	2.455	2.683
2-ME (g)	8.565	8.209	7.823	6.944
Total (g)	15.000	15.000	15.000	15.000

Table. Amount of each precursor required for coating 30 g of NCM with 5 wt% Li_{3x}La_{2/3-x}TiO₃.

Commercial NCM523 (Samsung SDI, Co.) was added to the solution. The slurry was stirred for 30 min and dried at 120°C. The dried powder was then heated in air at 600°C for 2 h.

The coating solution without mixing with NCM was dried and fired at 500 and 600°C. White powder could be obtained and the phase was analyzed by XRD. The diffraction pattern of the powder fired at 600°C showed that LLTO phase is synthesized with this condition, but intensity of the peaks was very weak indicating low crystallinity. The powder synthesized at 500°C seems to be amorphous in that the diffraction pattern is composed of a few broad bands. The XRD pattern of LLTO-coated NCM523 was also examined but the LLTO peak was not observed clearly probably because of small coating amount and low crystallinity of the LLTO.

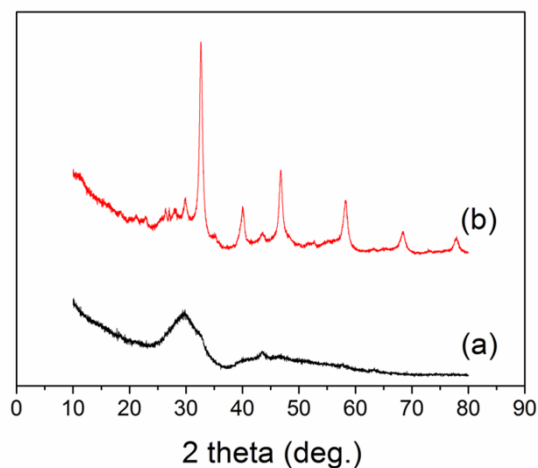


Fig. XRD pattern of LLTO powder obtained firing of the coating solution at (a) 500°C and (b) 600°C.

S. 4. Experimental details: Al₂O₃ coating

AcAc and ethanol were mixed and then stirred for 10 min. Aluminum butoxide (98.0%, Acros) was added, and the solution was again stirred for 30 min. The molar ratio of Al to AcAc was 1:1, and the Al₂O₃ concentration in the solution was 2 wt%; thus, the ratio of the NCM powder to the solution was 2:1 for producing a 1 wt% Al₂O₃ coating on NCM. After the slurry was stirred for 30 min, it was dried and heated under the same conditions as for LLTO.

S. 5. Experimental details: measurement of rate performance and cyclic capacity retention

The rate performance of each cathode material was measured by fabricating a 2016-type coin half-cell and by charging/discharging the cell 3 times at 0.2, 0.5, 1, and 2 C-rates in the range 3.0–4.45 V (vs. Li/Li⁺). 2016-type coin full-cells were also fabricated, and the longevity was measured by repeatedly charging/discharging them in the range 3.0–4.35 V (considering difference of operation voltage between Li metal and graphite anode) at 45°C at 1 C-rate. The full-cell was designed so that the capacity of negative electrode was 20% higher than that of the positive one.

The electrode of cathode materials was prepared by coating the slurry on an Al foil. The

slurry was prepared by mixing 96 wt% of NCM, 2 wt% of carbon black, and 2 wt% of polyvinylidene fluoride dissolved in N-methylpyrrolidone. The cathode material was loaded 0.015~0.020 g/cm². The discharge capacity showed somewhat fast decrease in our experiment comparing with other reports, probably because the cells were cycled at the elevated temperature of 45 °C, mixing amount of carbon black is relatively small (2 wt%), and loading level of cathode material per area was large.