Experiments

Sample preparation

All the samples were synthesized by high-temperature solid state reaction. The raw materials including Mn_2O_3 and Na_2CO_3 (8% excess for volatilizing during high-temperature calcination) were mixed well in the planetary ball mill. Then add a certain molar ratio of Bi_2O_3（All reagents were Analytical-reagent-grade）thoroughly ground in the agate bowl with the previous mixture. The final mixture was annealed at 750 °C for 20 h in air followed by natural cooling process. Finally, the synthesized samples were immediately transferred to a glove-box in Ar-atmosphere. After the material synthesized and stored in same condition, the sample is soaked in water for 12 hours and dried in the oven overnight to test the stability.

Material Characterizations

The crystal structure was obtained by (XRD, Rint 1000, Rigaku, Japan) Cu (Kα) radiation source in the $10° < 2\theta < 70°$ range. The particle morphologies were observed by scanning electron microscopy (SEM TESCAN VEGA3) instrument. The as-prepared sample was characterized by high-resolution transmission electron microscope (TEM, JEOL JEM-2100 microscopy) for crystal structure information. The X-ray photo-electron spectroscopy (XPS) data were characterized by XPS, ESCALAB 250Xi, Al Ka for determine the valence states of the elements in as-prepared material.

Electrochemical Characterizations

The electrochemical performance of all the samples were obtained with coin cells (CR2025). The cathode was fabricated by mixing 80 wt% of active materials, 10 wt% of acetylene black (AB) and 10 wt% of polyvinylidene fluoride (PVDF) with the blending to form uniform slurry using NMP as a dispersing agent. Then, the slurry was pasted onto on a current collector Al-foil and dried at 120 ℃ for 12 h in a vacuum oven. All the cells were assembled in an Ar-filled glove box with H_2O and O_2 contents less than 0.1 and 10 ppm, respectively. For all Na half-cells, metallic Na discs were used as

the counter electrode. Glass fibers (GF/D Whatman) were used in the half-cell as separators. The electrolyte consists of 1 M $NaClO_4$ dissolved in a solution of ethylene carbonate/diethyl carbonate (EC/PC, 1:1, v/v) with the additive 5 vol% fluoroethylene carbonate (FEC) by volume. The coin cells were galvanostatically charged and discharged in the voltage range of 2.0-4.1V at various current rates (1C=100mA g^{-1}) by battery test system (NEWARE).

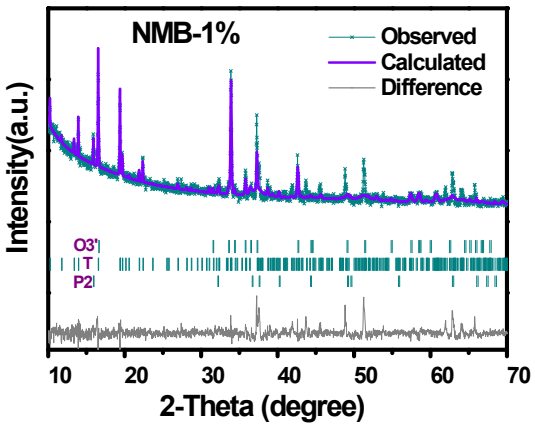

Figure S1. The Rietveld refinement of the as-synthesized samples NMB-1%.

Table S1. Refined crystallographic sites of prepared samples NMB-1%.

Phase	*Atom*	*site*	*x*	*y*	*z*	U_{iso}	*Occupancy*
Pbam	Mn_1	4g	0.031400	0.306600	0.000000	0.00014	1.0000
	Mn_2	4h	0.361800	0.090300	0.500000	0.00097	1.0000
	Mn_3	2c	0.000000	0.500000	0.000000	0.00021	1.0000
	Mn_4	4h	0.357200	0.306100	0.500000	0.00008	1.0000
	Mn_5	4g	0.014200	0.108100	0.000000	0.00011	1.0000
	Na_1	4g	0.197699	0.210225	0.000000	0.00088	0.9951
	Na_2	4h	0.207240	0.414701	0.500000	0.00088	0.5467
	Na_3	4g	0.132747	0.000005	0.000000	0.00006	0.5414

	Bi_1	4g	0.197699	0.210225	0.000000	0.00049	0.0069
	Bi_2	4h	0.207240	0.414701	0.500000	0.00088	0.0156
	Bi_3	4g	0.132747	0.000005	0.000000	0.00006	0.0138
	Mn_1	2a	0.000000	0.000000	0.000000	0.00076	1.0000
	Na_e	2d	0.000000	0.000000	0.250000	0.80000	0.2905
$P6_3/mmc$	Na_f	2b	0.333300	0.666700	0.750000	0.00055	0.4100
	Bi_e	2d	0.000000	0.000000	0.250000	0.00015	0.80000
	Bi_f	2b	0.333300	0.666700	0.750000	0.00018	0.00055
	Mn_1	2/m	0.000000	0.000000	0.000000	0.00880	1.0000
$C2/m$	Na_1	2/m	0.000000	0.500000	0.500000	0.00043	0.9979
	Bi_1	2/m	0.000000	0.500000	0.500000	0.00043	0.0021
		***Rp* (%)**	**8.00%**		**χ^2**	**2.988**	
		***Rwp* (%)**	**11.40%**				

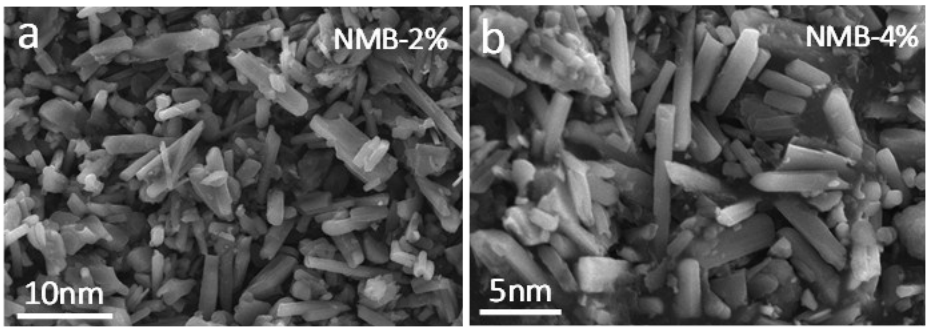

Figure S2. (a-b) SEM images of NMB-2% and NMB-4% samples.

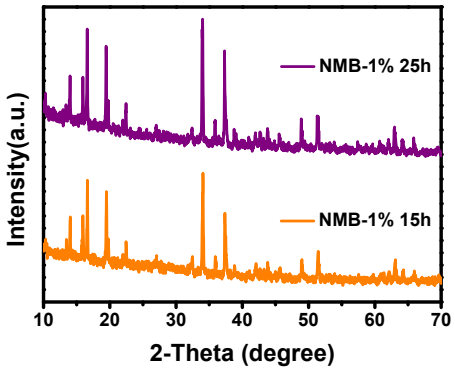

Figure S3. The XRD patterns of samples NMB-1% 15h and NMB-1% 25h in different annealing time.

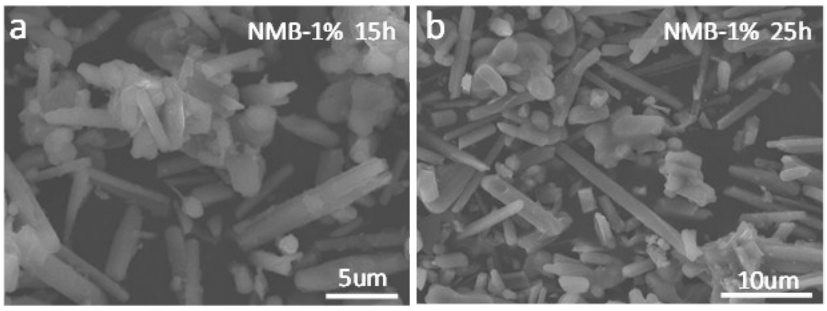

Figure S4. The SEM images of samples NMB-1% 15h and NMB-1% 25h in different annealing time.

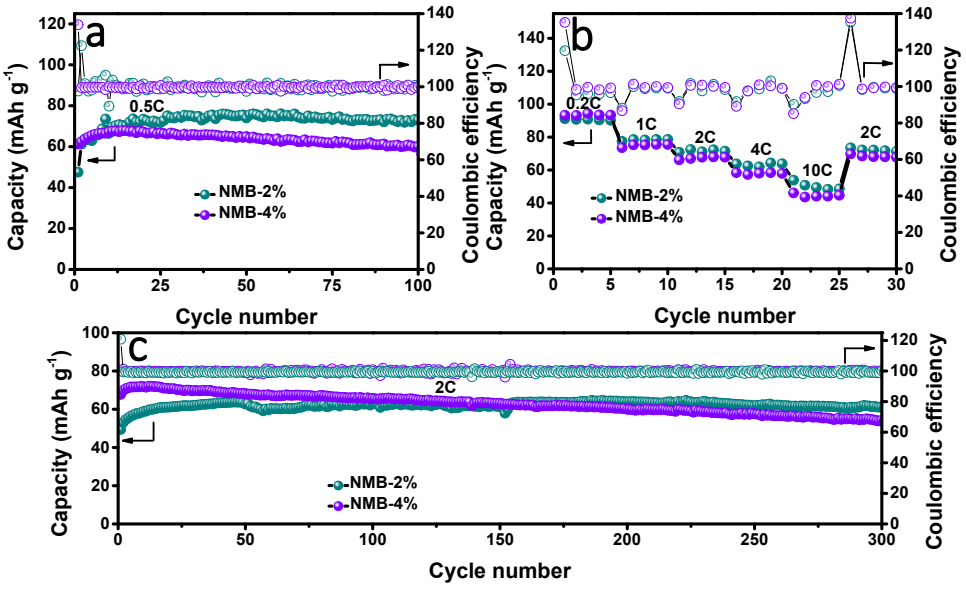

Figure S5. (a) Electrochemical cycle properties of NMB-2% and NMB-4% at 0.5C. (b) Rate performance of as-prepared samples NMB-2% and NMB-4% at rate of 0.2-10C. (c) Rate cycle performance of NMB-2% and NMB-4% at 2C.

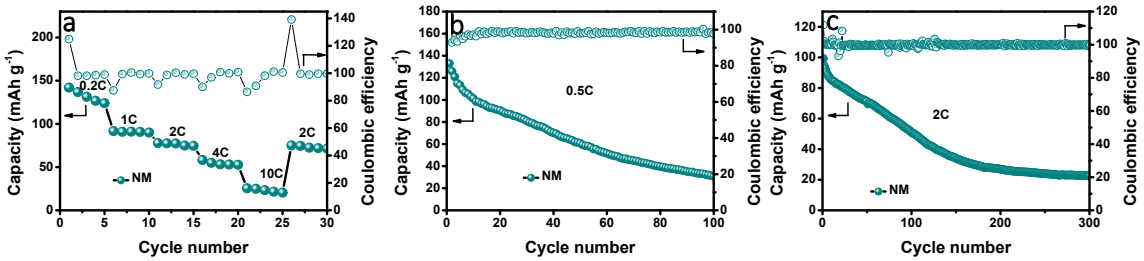

Figure S6. (a) Rate performance of as-prepared samples NM at rate of 0.2-10C. (b) Electrochemical cycle properties of samples NM at 0.5C. (c) Rate cycle performance of NM at 2C.

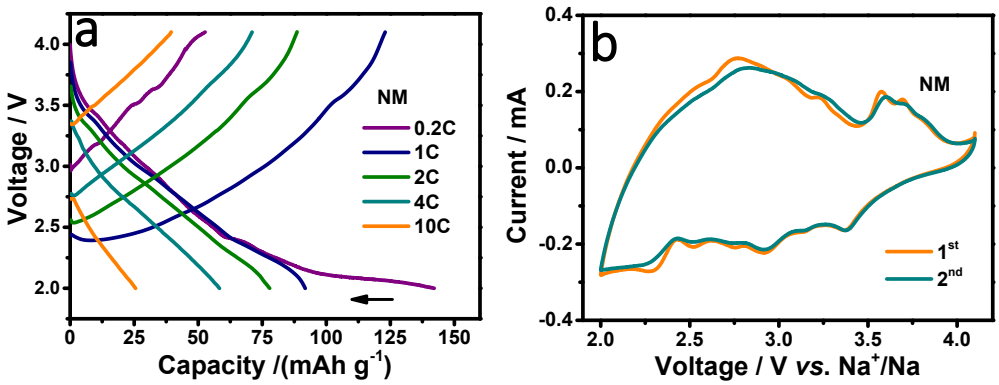

Figure S7. (a) Charge-discharge curves of as-synthesized NM at rate of 0.2-10C. (b) CV curves of NM sample at the scan rate 0.2mV/s.

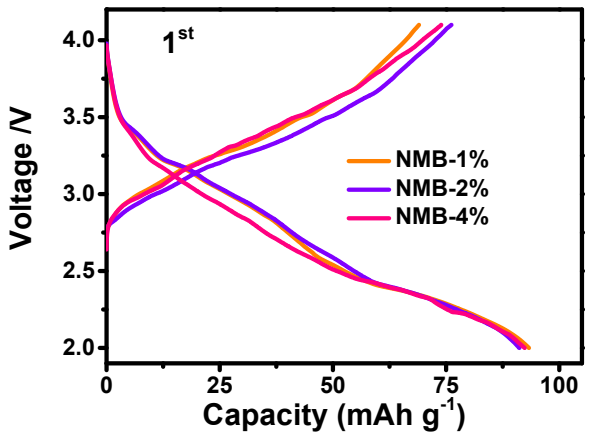

Figure S8. The 1st charge-discharge curves of as-prepared samples NMB-1%, NMB-2% and NMB-4% at 0.2C.