ISSN 1990-7931, Russian Journal of Physical Chemistry B, 2021, Vol. 15, Suppl. 1, pp. S140–S148. © Pleiades Publishing, Ltd., 2021.

CHEMICAL PHYSICS OF NANO-MATERIALS

Increasing the Performance of Cathode Material in Alkaline (Li, Na and K) Ion Battersis: Synthesis and Characterization

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Received January 15, 2021; revised June 22, 2021; accepted July 20, 2021

Abstract—The purpose of this study is to find a ternary solid solution of nickel, magnesium, manganese in the alkaline-based cathode material (Na, Li) replacement with $LiCoO_2$ that is too much expensive and toxic. Samples from the proposed {[(1–*x*–*y*) $LiNi_{0.7}Co_{0.3}$ (Al and Mg doped)] O_2} system were synthesized using the sol-gel method. Stoichiometric weights of the $LiNO_3$, Mg $(NO_3)_2{\cdot}6H_2O$, Mn $(Ac)_2{\cdot}4H_2O$, $Co(Ac)_2{\cdot}4H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ as starting materials of lithium, magnesium, manganese , cobalt and nickel, in 28 samples of {[(1–*x*–*y*) $LiNi_{0.7}Co_{0.3}$ (Al and Mg doped)] O_2}, respectively. We exhibited "$Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$" is the best composition for cathode material. Obviously, the used weight of cobalt in these samples is lower compared with $LiCoO_2$ that is an advantage in view point of cost in this study. With the same method we used (1–*x*–*y*) $LiNi_{0.7}Co_{0.2}Mg_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composites and five samples have been found with the best conditions in viewpoints of capacity and cyclability. Among these samples with $Li_{1.333}Ni_{0.1}Mg_{0.017}Co_{0.551}Mn_{0.333}O_2$ structure is the best sample of those 28 compositions including Mg doped position. Charge-discharge characteristics of the mentioned cathode materials were investigated by performing cycle tests in the range of 2.4–4.6 V. Our results confirmed, although these kind systems can help for removing the disadvantage of cobalt which mainly is its cost and toxic, the performance of these kind systems are similar to $LiCoO_2$ or $NaCoO_2$ cathode materials.

Keywords: Sodium ion battery, Lithium Ion battery, $LiCoO_2$, $NaCoO_2$, sol-gel method, Mg doped, Al doped

DOI: 10.1134/S1990793121090049

1. INTRODACTION

Transition elements of cathode materials including manganese, nickel cobalt (NMC), are especial metals for lithium ion batteries (LIBs) due to their potentials for operating in high voltages and large energy storing in a small space. Although the Ni in NMC and NCA (nickel, cobalt and aluminum) gives a high capacity for storing energies, it is also passive and unstable, with a propensity towards destructive reactions with the electrolyte. As it can be seen in the (Table 1) there are both advantages and disadvantages factors for NMC of LIBs [1–5]. A major disadvantage of cobalt is its cost and toxic and typically it is around two times more costly to manufacture than nickel. This is one important factor when considering its use in mass produced consumer items which any extra cost is a basic issue. Safety factor is also a matter of crucial importance to the lithium batteries which this problem appears in big size batteries as compared to the small size batteries i.e. batteries for electric vehicle would have more risk of catching fire as compared to batteries for cell phones. When mixed solid solution is used as cathode material, the explosion of batteries can be control, especially with doping of other elements such as Mg and Al. Moreover (1–*x*–*y*) $LiNi_{0.7}Co_{0.3}O_2$ doped with Al and Mg are environment friendly as compared to isolated cathode such as $LiCoO_2$ [4, 5].

The purpose of this study is to find a ternary solid solution of Li-based cathode material in NMC that is advantageous replacement for $LiCoO_2$ which is expensive and toxic. Therefore a combination of ternary composition diagram including (1–*x*–*y*) $LiNi_{0.7}Co_{0.3}O_2$, xLi_2MnO_3 and $yLiCoO_2$ have been considered. NMC LIBs were the most interest among the scientist to replace with $LiCoO_2$ which firstly reported by Rossen et al. in 1992 [6] for composition of $LiNi_{0.5}Mn_{0.5}O_2$.

Similar the work of Rossen [6], a study was reported in 1998 by Saphr et al. [7] in view point of electrochemical behavior which indicate Ni as an active ion and Mn were present in "+2" and "+4" oxidation rather the "+3". They exhibited in temperature of 750 there are a large falling capacity after 25 cycle from 150 $mAhg^{-1}$ to 125 mAh/g after 25 cycles and to 75 mAh/g after 50 cycles. Nickel, which forms between +2 and +4 valences positions is active mate-

Table 1. Characteristics of commercial Li-ion battery cathode materials [5]

Material	Potential versus Li/Li^+	Capacity, mAh/g	Energy, Wh/kg	Advantage	Disadvantage
$LiCoO_2$	3.9	140	546	Low	High
NCA (Nickel, Cobalt, Aluminum)	3.8	180–200	680–760	Slow reaction with electrolyte High capacity, high voltage Excellent high rate performance	High coast of Ni and Co
NMC (Nickel, Cobalt, Manganese)	3.8	160–170	610–650	High capacity, high operating voltage Slow reaction with electrolyte Moderate safety (oxygen release)	High coast of Ni and Co

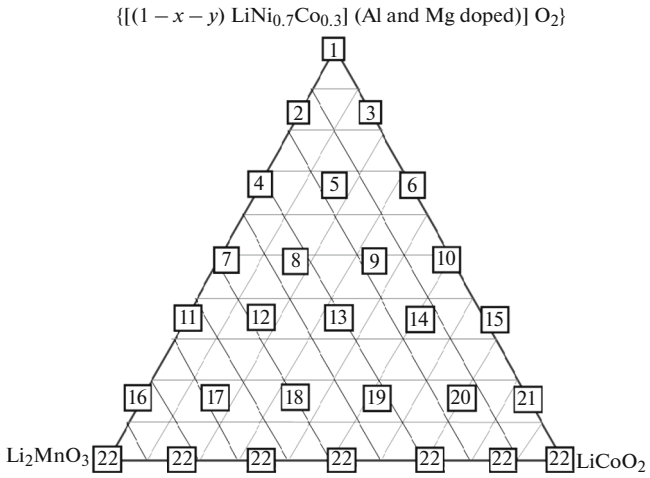
rial in this cathode composition, meanwhile manganese is +4, which remain without Jahn-Teller distortion with the +3 valance(Mn^{+3}). Makimura and coworkers [8] presented an initial discharging around 150.5 mAh/g for 30 cycles at 4.35 V and again in 2003 [9] their results exhibited 200 $mAhg^{-1}$ of rechargeable capacity of $LiNi_{1/2}Mn_{1/2}O_2$ among the voltages of 2.5–4.5 V after 30 cycles [9].

Obviously, mixing proper mole fractions of various transition elements [8, 9] to get the advantageous efficiency of each led to the discovery of these kind materials. Therefore these materials are derived from Li $(Ni_{(1-X-Y)}Mn_xCo_y)O_2$ categorize that were first published in 1999 and 2000 by Liu and Yoshio respectively [10, 11]. They exhibited that the enhancement of cobalt would stabilize the composition blocks the Ni from entering the lithium layers. Meanwhile nickel and manganese would provide the structural stabilities and high capacities respectively. As too much of cobalt causes decreasing capacities and large amount of Nickel and manganese making problems in cation mixing and spinel structures, therefore mixing of these elements must be optimized with suitable mole fraction.

Makimura and coworkers in 2001 synthesize the layered compound of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [12] and exhibited that this cathode has about 205 mAh/g reversible discharge capacity in the range of 2.6–4.5 V including large rate capabilities and thermal stabilities.

For appropriate stoichiometry of Li $(Ni_xCo_{(1-2x)}Mn_x)O_2$, $x = 1/3$, the medium oxidation numbers must be +3 such as Mn^{+4} , Co^{+3}, and Ni^{+2}, with electrochemical flow in the ranges between 2.5 up to 4.4 V vs. Li/Li^+ (through two electron transfer reaction between Co^{+3}/Co^{+4} and Ni^{+2}/Ni^{+4}) [13]. In addition concerning of further electrochemical phenomenon some more studies of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ [14], $Li(Ni_{0.8}Co_{0.2})O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes [15] have been shown. Although the rate capability of this material is smaller than that of $LiCoO_2$, thermal stabilities are much better.

In this work we focused on various composition of Binary and ternary solid solutions containing Li_2MnO_3, $LicoO_2$ and {[(1–*x*–*y*)$LiNi_{0.7}Co_{0.3}$ (Al and Mg doped)]O_2} (Scheme 1). Currently, Li_2MnO_3 has been distinguished for its suitable capacity, better safety, without toxic and inexpensive than $LiCoO_2$ [16].



Scheme 1. Binary and Ternary diagram of {[(1–*x*–*y*)$LiNi_{0.7}Co_{0.3}$ (Al and Mg doped)] O_2}.

Li_2MnO_3 which can be demonstrated as $Li[Li_{1/3}Mn_{2/3}]O_2$ has a similar structure as $LiCoO_2$, but there is super-lattice ordering of Li^+ and Mn^{4+} in transition metal layers. Li_2MnO_3 has a layered rock like shape which is consist of lithium and manganese ions in alternating (1 : 2 ratio respectively) positions and the layers are separated via a cubic oxygen layer. As manganese is present in +4 oxidation number, it is impossible to be further oxidization in low voltages therefore Li_2MnO_3 might be electrochemically inactive, whereas this material in higher voltages i.e. >4.4 V will extract the lithium ions (in the form of Li_2O) through behind of MnO_2 layers. Meanwhile the mentioned mechanism is unilateral and not reversible therefore only one Li+ ion can return during discharging towards $LiMnO_2$ structure which is an active material. The extra lithium atom which refracts within charging attaches to the higher capacities. Using of cathodes with Li_2MnO_3 is important due to simplify the intercalation mechanism and also providing structural stabilities during this intercalation [17].

Solid solutions were basically elected in terms of obtaining a cathode composition with superior efficiency of cyclability, capacity and structural stabilities also with costs low. By a few works the solid solutions have been applied as cathode material including both binary and ternary systems [18, 19]. Solid solutions containing Li_2MnO_3 were found suitable for two major sake, one the extraction of two Li+ ions at voltages >4.4 V which gives the extra amount of initial charge capacities and second the MnO_2 ingredient that on removal of lithium gives well structural stability in that composition.

It is notable that the initial crystal structures of the cathode material not only specifies the initial characteristic capacity, but also imply to the stability. The consistency of de-lithiated cathode materials is substantial for any increasing of the cycle life. During the lithium-ion extracting, nickel and cobalt will be oxidized from +3 to +4 valance positions, so the crystal cell volume will be change. Al substitution in cobalt structure is a suitable doped metal for improving the stability and electrochemical performance. Aluminum remains in the +3 valence position, and has no any contribution to its capacity only helps to reduce the crystal volume changing and keeping the structure stable after a few cycling.

Therefore in the system of $(1-x-y)LiNi_{0.7}Co_{0.2}Al_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composite (Table 2), the high nickel content usually gives higher initial specific capacities while cobalt and aluminum improve the structural stabilities and life cycle. Not only, Mg-doping improves the capacity retention [20] well but also, Mg-doping promotes the diffusion of Li^+ in $(1-x-y)LiNi_{0.6}Co_{0.3}Mg_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composition. Moreover, Mg-doping represses the phase transitions that usually occur in $LiNiO_2$ during cycling and improves the charge-discharge reversibility of related composition.

EXPERIMENTAL SECTION

The composites were synthesized using the sol-gel method due to simple chemical reaction with a low temperature and a high degree of homogeneity. Stoichiometric weights of the $LiNO_3$, $Mg(NO_3)_2{\cdot}6H_2O$, $Mn(Ac)_2{\cdot}4H_2O$, $Co(Ac)_2{\cdot}4H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ as starting materials of lithium, magnesium, manganese, cobalt and nickel, in 28 samples of $\{[(1-x-y)LiNi_{0.7}Co_{0.3}]$ (Al & Mg doped)$]O_2\}$, respectively. These mixtures were first dissolved in 50 ml of DI H_2O and then equivalence-molar weights of citric acid were added (the amount of citric acid was equal to the total molar of Co, Ni, and Mg). The whole mixtures were heated through water bath at 90°C and during the heating process, a clear, pink solution without any precipitation formed. At last, the clear solution was slowly dried and turned into gel. This solution was continuously stirred for about 25 min for the formation of a homogeneous mixture of gel and then is kept under a hot-plate for 12–14 h around 100°C so that all the distilled water gets evaporated. Usually, acetate requires two heating temperatures (low and high) for the formation of a correct phase. The beaker containing the gel is then kept in a furnace and is heated to 450°C (air atmospheric pressure) for 3–5 h. the first heating is at a low temperature. Basically what happens during this stage is that all the acetates present would get burned off, but the desired phase is not formed. The heat-treated products were ground in an agate mortar to obtain powders and then the powder was calcined at 800–850°C for 10–12 h. It is notable that the 2nd heating is done at so higher temperatures because of the wide range of materials present in the composition and also more importantly to ensure the formation of a proper phase for the crystalline structure then the material collected from the furnace is stored at a dry place until it is made into a cathode. For fabrication of cathodes, the prepared products were fist mixed with acetylene black and poly-vinylidene fluoride in N-methyl-pyrrolidone (NMP). For all systems the Glove-Box model of kk-011AD (serial no: kk-1760) has been used.

ELECTROCHEMICAL MEASHUREMENTS

Anode Materials and Electrolytes

Anode materials (94 wt %) were mixed with PVDF (5 wt %, Solef type 6020), Super S (1%, Timcal) and NMP (N-methyl-pyrrolidone, ISP) to form slurries, and then smeared on Cu foil using a doctor blade coater, vacuum dried overnight at 130°C and roll pressed to obtain electrodes. The electrodes were punched into 13.0 mm (ID) disk electrodes and assembled into CR2032 coin-type cells with a Li

Table 2. 28 different composition points according to using the lever rule, stoichiometric weights and mole-fractions of the triangle diagram

Sample	Composition	Al doped	Mg doped
1	$LiNi_{0.7}Co_{0.3}O_2$	$LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$	$LiNi_{0.6}Mg_{0.1}Co_{0.3}O_2$
2	$Li_{1.167}Ni_{0.583}Co_{0.25}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.583}Co_{0.167}Al_{0.083}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.5}Mg_{0.083}Co_{0.25}Mn_{0.167}O_2$
3	$LiNi_{0.583}Co_{0.417}O_2$	$LiNi_{0.583}Co_{0.334}Al_{0.083}O_2$	$LiNi_{0.5}Mg_{0.083}Co_{0.42}O_2$
4	$Li_{1.333}Ni_{0.467}Co_{0.203}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.467}Co_{0.133}Al_{0.067}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.4}Mg_{0.067}Co_{0.2}Mn_{0.333}O_2$
5	$Li_{1.167}Ni_{0.467}Co_{0.366}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.467}Co_{0.299}Al_{0.067}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.4}Mg_{0.067}Co_{0.366}Mn_{0.167}O_2$
6	$LiNi_{0.467}Co_{0.533}O_2$	$LiNi_{0.467}Co_{0.466}Al_{0.067}O_2$	$LiNi_{0.4}Mg_{0.067}Co_{0.533}O_2$
7	$Li_{1.5}Ni_{0.35}Co_{0.15}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.35}Co_{0.1}Al_{0.05}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.3}Mg_{0.05}Co_{0.15}Mn_{0.5}O_2$
8	$Li_{1.333}Ni_{0.35}Co_{0.317}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.35}Co_{0.267}Al_{0.05}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.3}Mg_{0.05}Co_{0.317}Mn_{0.333}O_2$
9	$Li_{1.167}Ni_{0.35}Co_{0.483}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.35}Co_{0.433}Al_{0.05}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.3}Mg_{0.05}Co_{0.483}Mn_{0.167}O_2$
10	$Li\ Ni_{0.35}Co_{0.6}O_2$	$LiNi_{0.35}Co_{0.6}Al_{0.05}O_2$	$LiNi_{0.3}Mg_{0.05}Co_{0.65}O_2$
11	$Li_{1.667}Ni_{0.233}Co_{0.1}Mn_{0.667}O_2$	$Li_{1.667}Ni_{0.233}Co_{0.067}Al_{0.033}Mn_{0.667}O_2$	$Li_{1.667}Ni_{0.2}Mg_{0.033}Co_{0.1}Mn_{0.667}O_2$
12	$Li_{1.5}Ni_{0.233}Co_{0.267}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.233}Co_{0.234}Al_{0.033}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.2}Mg_{0.033}Co_{0.267}Mn_{0.5}O_2$
13	$Li_{1.333}Ni_{0.233}Co_{0.434}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.233}Co_{0.4}Al_{0.033}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.2}Mg_{0.033}Co_{0.434}Mn_{0.333}O_2$
14	$Li_{1.167}Ni_{0.233}Co_{0.6}Mn_{0.167}O_2$	$Li_{0.167}Ni_{0.233}Co_{0.567}Al_{0.033}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.2}Mg_{0.033}Co_{0.6}Mn_{0.167}O_2$
15	$LiNi_{0.233}Co_{0.767}O_2$	$LiNi_{0.233}Co_{0.734}Al_{0.033}O_2$	$LiNi_{0.2}Mg_{0.033}Co_{0.767}O_2$
16	$Li_{1.835}Ni_{0.116}Co_{0.049}Mn_{0.835}O_2$	$Li_{1.833}Ni_{0.117}Co_{0.033}Al_{0.017}Mn_{0.833}O_2$	$Li_{1.835}Ni_{0.1}Mg_{0.017}Co_{0.049}Mn_{0.835}O_2$
17	$Li_{1.667}Ni_{0.116}Co_{0.217}Mn_{0.667}O_2$	$Li_{1.667}Ni_{0.117}Co_{0.199}Al_{0.017}Mn_{0.667}O_2$	$Li_{1.667}Ni_{0.1}Mg_{0.017}Co_{0.217}Mn_{0.667}O_2$
18	$Li_{1.5}\ Ni_{0.116}Co_{0.384}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.117}Co_{0.366}Al_{0.017}Mn_{0.5}O_2$	$Li_{1.5}Ni_{0.1}Mg_{0.017}Co_{0.384}Mn_{0.5}O_2$
19	$Li_{1.333}Ni_{0.116}Co_{0.551}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.117}Co_{0.533}Al_{0.017}Mn_{0.333}O_2$	$Li_{1.333}Ni_{0.1}Mg_{0.017}Co_{0.551}Mn_{0.333}O_2$
20	$Li_{1.167}Ni_{0.116}Co_{0.717}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$	$Li_{1.167}Ni_{0.1}Mg_{0.017}Co_{0.717}Mn_{0.167}O_2$
21	$LiNi_{0.116}Co_{0.884}O_2$	$LiNi_{0.117}Co_{0.866}Al_{0.017}O_2$	$LiNi_{0.1}Mg_{0.017}Co_{0.884}O_2$
22	Li_2MnO_2	Li_2MnO_2	Li_2MnO_2
23	$Li_{1.833}Co_{0.167}Mn_{0.833}O_2$	$Li_{1.833}Co_{0.167}Mn_{0.833}O_2$	$Li_{1.833}Co_{0.167}Mn_{0.833}O_2$
24	$Li_{1.667}Co_{0.333}Mn_{0.667}O_2$	$Li_{1.667}Co_{0.333}Mn_{0.667}O_2$	$Li_{1.667}Co_{0.333}Mn_{0.667}O_2$
25	$Li_{1.5}Co_{0.5}Mn_{0.5}O_2$	$Li_{1.5}Co_{0.5}Mn_{0.5}O_2$	$Li_{1.5}Co_{0.5}Mn_{0.5}O_2$
26	$Li_{1.333}\ Co_{0.667}Mn_{0.333}O_2$	$Li_{1.333}Co_{0.667}Mn_{0.333}O_2$	$Li_{1.333}Co_{0.667}Mn_{0.333}O_2$
27	$Li_{1.167}Co_{0.833}Mn_{0.167}O_2$	$Li_{1.167}Co_{0.833}Mn_{0.167}O_2$	$Li_{1.167}Co_{0.833}Mn_{0.167}O_2$
28	$LiCoO_2$	$LiCoO_2$	$LiCoO_2$

counter electrode, $LiPF_6$ (1.5 M) dissolved in EC/DEC electrolyte, and separator in an argon-filled glove box. The cycling performance of the coin cells was examined using a Maccor 4200 multichannel battery tester at 20°C. The cells were charged at a constant current (CC) density of 0.5 mA cm^{-2} (0.25 C rate) to 0.005 V, which was followed by charging in constant voltage (CV) mode with cutoff current of 0.02 C and then discharged at 0.25 C to 1.5 V for two cycles, prior to the cycling test. The cells were then cycled between cutoff voltages of 0.001 and 1.5 V by charging in constant current-constant voltage (CC–CV) mode at 0.25 C, as described above, and then discharging sequentially (1 charge/discharge per cycle) at various C-rates (0.25, 0.5, 1, 2, and 5 C). The cells were cycled between cutoff voltages of 0.001 and 1.5 V by charging in CC–CV mode at various C-rates (i.e., 0.25, 0.5, 1, 2, and 5 C) to 0.001 V with a 0.02 C cutoff current followed by consecutively discharging (CC at 0.25 C to 1.5 V).

RESULTS AND DISCUSSION

This investigation is used for finding the best cathode material compositions including $\{[(1-x-y)\ LiNi_{0.7}Co_{0.3}$ (Al and Mg doped)] $O_2\}$, xLi_2MnO_3, $yLiCoO_2$ systems with high initial discharge capacity, grate cyclability and inexpensive cost compared to current lithium-ion cathode materials. Therefore, initially, 28 different composition points according to using the lever rule,

Table 3. Summary capacity and cyclability for 28 samples, of the system $[(1-x-y)LiNi_{0.7}Co_{0.2}Al_{0.1}]O_2$

Sample	Blend	Li_2MnO_3	$LiCoO_2$	$LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$	Capacity, mAh/g	Cyclability
1	Pure	0	0	1	82.5	51
2	Binary	0.167	0	0.833	102.3	46
3	Binary	0	0.167	0.833	112.2	49
4	Binary	0.333	0	0.667	115.5	52
5	Ternary	0.167	0.167	0.667	150.5	60
6	Binary	0	0.333	0.667	78.5	80
7	Binary	0.500	0	0.500	165.5	82
8	Ternary	0.333	0.167	0.500	167.2	61
9	Ternary	0.167	0.333	0.500	153.1	81
10	Binary	0	0.500	0.500	159.2	79
11	Binary	0.667	0	0.333	114.7	99
12	Ternary	0.500	0.167	0.333	153.1	93
13	Ternary	0.333	0.333	0.333	180.1	78
14	Ternary	0.167	0.500	0.333	173.2	80
15	Binary	0	0.667	0.333	110.6	91
16	Binary	0.833	0	0.167	181.3	75
17	Ternary	0.667	0.167	0.167	141.5	95
18	Ternary	0.500	0.333	0.167	220.2	99
19	Ternary	0.333	0.5	0.167	139.3	92
20	Ternary	0.167	0.667	0.167	248.1	95
21	Binary	0	0.833	0.167	189.5	92
22	Pure	1	0	0	61.5	91
23	Binary	0.833	0.167	0	143.5	90
24	Binary	0.667	0.333	0	175.2	90
25	Binary	0.500	0.500	0	201.2	90
26	Binary	0.333	0.667	0	199.5	46
27	Binary	0.167	0.833	0	245.5	96
28	Pure	0	1	0	240.2	90

stoichiometric weights and mole-fractions were chosen in order to find an optimized material with good electrochemical performance. These 28 points were extracted through the triangle phase diagram of the defined system (Scheme 1 and Tables 2, 3) and synthesis through sol-gel method.

Ni, Al and Mg amount are decreased towards down direction of triangle, meanwhile the compositions of 22, 24 have zero Ni and Al percentage. High Mn value is found at sample 22 and its content decreases at the opposite end points of the triangle. Cobalt percentage is found in a wide region in the triangle and also decreases near $Li(Li_{0.33}Mn_{0.66})O_2$. It is predicted which capacities and cyclability of the compositions are directly related to the amount of Mn, Co, Ni, Mg and Al. It is notable, specific capacity is determined as the amount of energies which can be reserve in volume or mass (Ah), while the rate capability (which are related to their design and varies considerably between different manufactures), can be determined as the rate at which the cell is being charged.

Therefore the C-rate is the capacity of the battery divided by the hourly charging rate. The discharge capacity curves of this work have been compared with 18650-type "$C/LiCoO_2$ Sony battery" result which is modified by Ehrlich [21]. Since $LiCoO_2$ cathode has an initial discharge capacity around 145 mAh/g [22], therefore any materials of these compositions with initial capacities more than this amount (of course with a suitable cyclability) might be considered. The samples were tested via a cycler (Arbin BT 2000 battery testing system), between 2.4 and 4.6 V with low C-rate of C/12. The initial results indicate of a wide range and irregular of cyclability and capacities. The initial discharge capacities varied from 102 to 248 mAh/g. Both capacity and cyclability increase from $LiNi_{0.7}Co_{0.3}Al_{0.1}O_2$ towards the binary composition of Li_2MnO_3 and $LiCoO_2$.

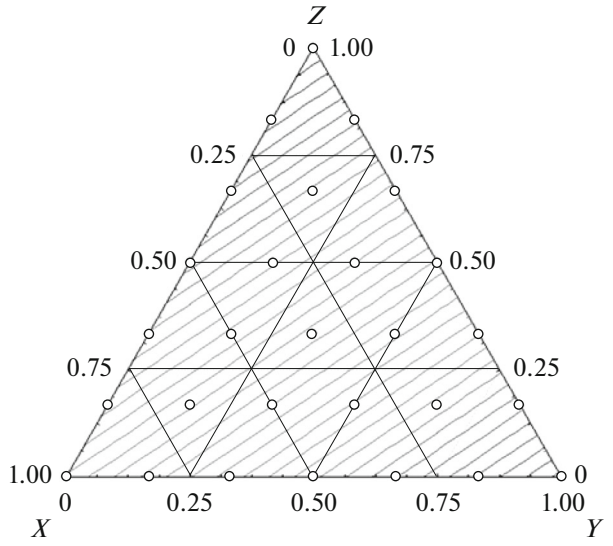


Fig. 1. Ternary of capacity versus X, Y and Z with relationship equation as: {Capacity = $152.55X + 229.48Y + 92.03Z$ (X, Y, Z, are Li_2MnO_3, Li_2CoO_2 and $LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$ respectively)}, for 28 samples of $(1-x-y)$ $LiNi_{0.7}Co_{0.2}Al_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composites.

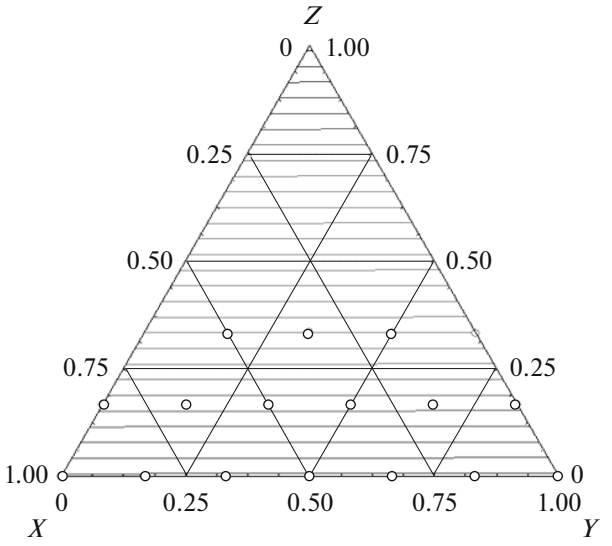


Fig. 2. Ternary of cyclability versus X, Y and Z with relationship equation as: {Cyclability = $88.68X + 88.84Y + 21.36Z$ (X, Y, Z, are Li_2MnO_3, Li_2CoO_2 and $LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$ respectively)}, for 28 samples of $(1-x-y)$ $LiNi_{0.7}Co_{0.2}Al_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composites.

Although sample 20 shows high capacity of 248.1 $mAhg^{-1}$, it contains of a suitable cyclability too. The sample 25 and 18 exhibit a good capacity of 201.2 and 220.2 mAh/g, respectively with high cyclability, meanwhile due to Mn^{4+} ion the sample 22 has a low capacity. Although these kinds of data are not sufficient for determining a suitable cathode material in view point of capacity and cyclability amount, the statistical analysis can be useful for finding the region of the best item from the data of the 28 compositions. Therefor any testing with both capacity and cyclability relation in view point of the triangle regions is needed. In this work the SATISTICA software has been used for analyzing the data which X, Y, Z, are Li_2MnO_3, $LiCoO_2$ and $LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$ respectively (Table 3 and Figs. 1, 2).

By this work various compositions are used for exploring the novel cathode materials with two-dimensional layered structure through the ternary composition's diagram among Iso-structural material.

Although Li_2MnO_3 or Li $[Li_{1/3}Mn_{2/3}]$ O_2 has a structure similar to $LiCoO_2$, there is super-lattice ordering of Mn^{4+} and Li^+ in transition layers. $LiNi_{0.7}Co_{0.2}Al_{0.1}O_2$ can be demonstrated as solid solution between $LiCoO_2$ and $LiNiO_2$ with Al doped in Co site, is a promising cathode material because of its improved stabilities and electrochemical performances.

Through an analyzing among these compositions, three samples were chosen and subsequently synthesized, characterized and tested consequently with high precisionist. Via initial discharge capacity and some extra results numbers 20, 27 and 28 are indicated as the best cathode material among those structures (Figs. 3, 4; Tables 2, 3). As the number 28 is pure material ($LiCoO_2$) and number 27 ($Li_{1.167}Co_{0.833}Mn_{0.167}O_2$) is binary, therefore the best ternary sample with number

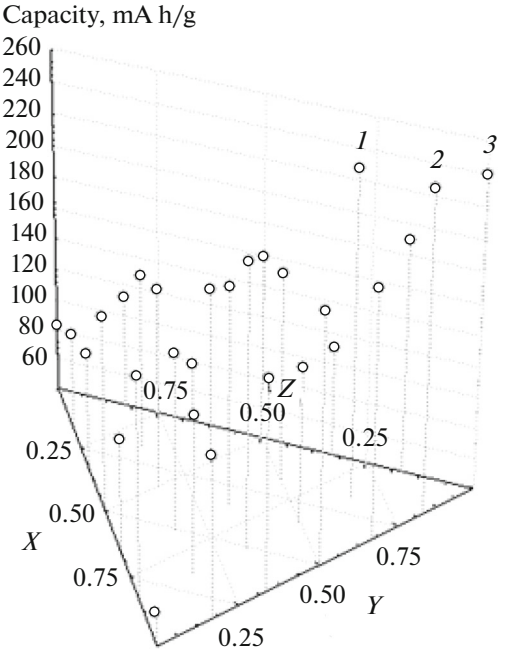


Fig. 3. Three samples with high precisionist of capacities: (*1*) $Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$, (*2*) $Li_{1.167}Co_{0.833}Mn_{0.167}O_2$, (*3*) $LiCoO_2$ (3).

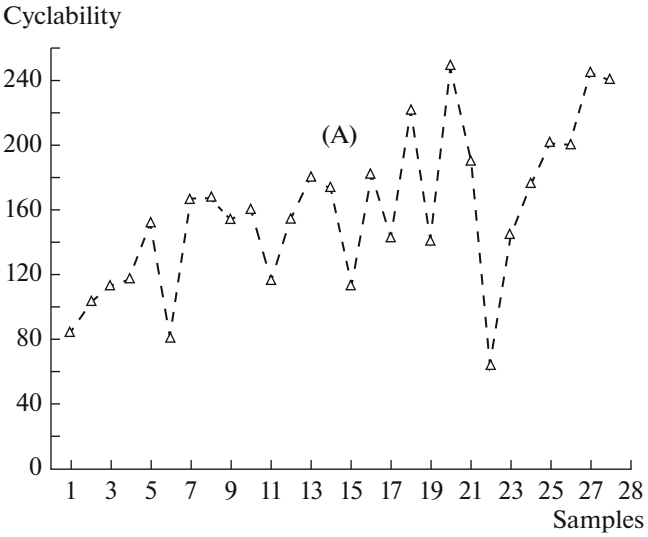


Fig. 4. Multiple variables, combinations of several composites; (A)—capacities.

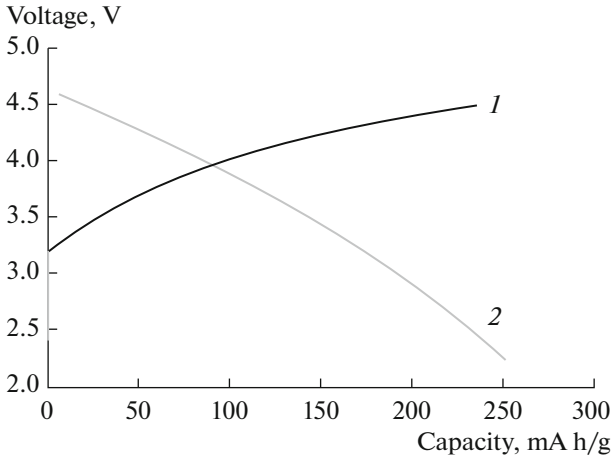


Fig. 5. Charge and discharge capacity of $Li_{1.333}Ni_{0.1}Mg_{0.017}Co_{0.551}Mn_{0.333}O_2$: (*1*) charge, (*2*) discharge.

20 "$Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$" is suggested as the best composition for cathode material by this work. Obviously, the used weight of cobalt in these samples is lower compared with $LiCoO_2$ that is an advantage in view point of cost in this study.

The repeat of sample 20 was made into T-Cells and subjected to electrochemical testing using the original conditions and the cycling was accomplished between 2.4–4.6 V with constant C-rate of C/12 at room temperature (Fig. 5).

The repeat sample exhibits better charge and discharge capacities (discharge capacity of 150 $mAhg^{-1}$) than the original sample. This improvement in the capacities is attributed to the synthesis conditions. With the same method we used $(1-x-y)$ $LiNi_{0.7}Co_{0.2}Mg_{0.1}$, xLi_2MnO_3, $yLiCoO_2$ composites and five samples (Fig. 6) have been found with the best conditions in viewpoints of capacity and cyclability (sample C_1–C_5) and SEM of these five samples are shown in Fig. 7. Among these samples C_3 is pure and C_1, C_2, C_4 are binary compositions, therefore the C_5 composition with $Li_{1.333}Ni_{0.1}Mg_{0.017}Co_{0.551}Mn_{0.333}O_2$ structure is the best composition for Mg doped position. The repeat of sample 19 was made into T-Cells and subjected to electrochemical testing using the original conditions and the cycling was accomplished between 2.4–4.6 V with constant C-rate of C/12 at room temperature. The repeat sample exhibits better charge and discharge capacities (discharge capacity of 155 $mAhg^{-1}$) in this work. In addition, this work is useful for any further investigation in lithium ion channels [23], manganese nano-composite [24] and also sodium ion batteries(NIBs) or any extended and mixed alkaline ion batteries (Li, Na, K, Rb and Cs) with such theoretical studies of the effect of doping [25].

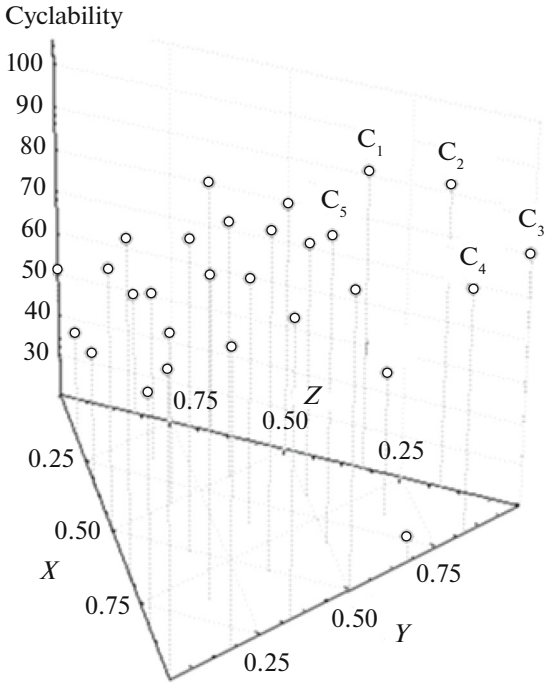


Fig. 6. Five samples with high precisionist of cyclability: C_1—sample 15, C_2—sample 21, C_3—sample 28, C_4—sample 27, C_5—sample 20.

CONCLUSIONS

$\{[(1-x-y)LiNi_{0.7}Co_{0.3}]$ (Al and Mg doped)$]$ $O_2\}$ systems of cathodes with submicron particles have been successfully synthesized by a sol–gel method. The structural and electrochemical properties have been systemically investigated to examine the effects of charge/discharge capacities and also capacity retention. The results show that all the prepared

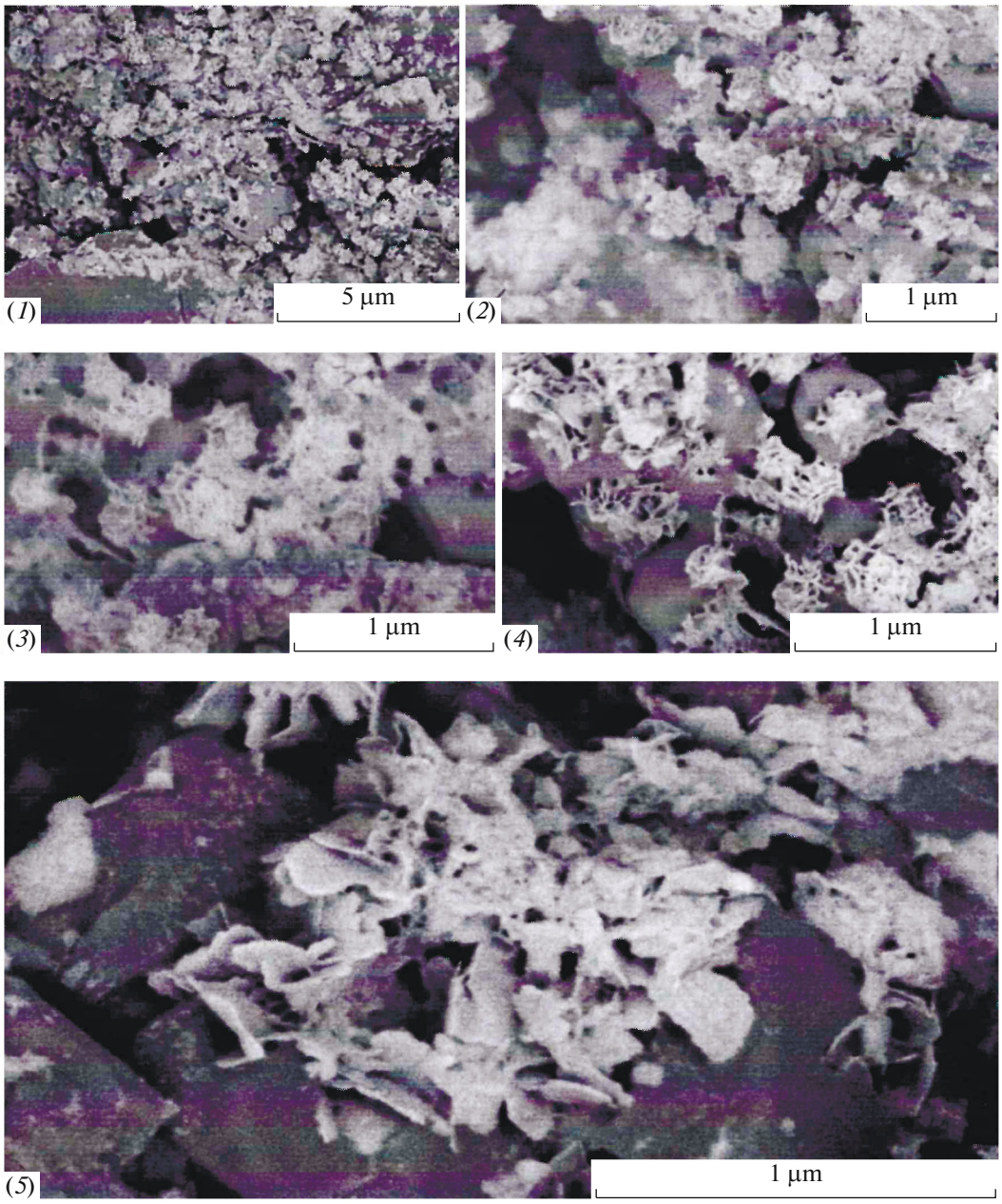


Fig. 7. The SEM of five cathode materials, for five samples including: (*1*) $LiNi_{0.233}Co_{0.734}Al_{0.033}O_2$, (*2*) $LiNi_{0.117}Co_{0.866}Al_{0.017}O_2$, (*3*) $LiCoO_2$, (*4*) $Li_{1.167}Co_{0.833}Mn_{0.167}O_2$, (*5*) $Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$.

"$Li_{1.167}Ni_{0.117}Co_{0.699}Al_{0.017}Mn_{0.167}O_2$" type layered structure regardless of the nickel content and Al doped improve the capacity retention significantly. Moreover, for magnesium doped instead of Al doped it could be suppressed the phase transitions that usually occur in $LiNiO_2$ during cycling and improves the charge-discharge reversibility of another composition with $Na_{1.333}Ni_{0.1}Mg_{0.017}Co_{0.551}Mn_{0.333}O_2$ structure. The percentage of nickel and cobalt exhibit a good performance. Although these kind systems can help for removing the disadvantage of cobalt which mainly is its cost and toxic, the performance of these kind systems is similar to $LiCoO_2$ or even $NaCoO_2$ cathode materials. Therefore fabrication of alkaline-ion batteries using a few more transition elements such as Mn, Al and Mg are suggested for any further research.

REFERENCES

1. Lithium Ion Batteries Outlook and Alternative Energy Vehicle (HEVs, PHEVs) Technologies, Markets, Competitors and Opportunities: 2010–2012 Analysis and Forecasts Market Research (Rockville, MD, 2010).

2. M. Yoshio, R. J. Brodd, and A. Kozawa, Lithium-Ion Batteries, Science and Technologies (Springer, New York, 2009).
3. B. Scrosati and J. Garche, J. Power Sources **195**, 2419 (2010).
4. C. Daniel and J. O. Besenhard, Handbook of Battery Materials, 2nd ed. (Wiley-VCH, Weinheim, 2011).
5. R. A. Meyers, Encyclopedia of Sustainability Science and Technology (Springer, New York, 2012)
6. E. Rossen, C. D. W. Jones, and J. R. Dahn, Solid State Ionics **57**, 311 (1992).
7. M. E. Spahr, P. Novák, B. Schnyder, et al., J. Electrochem. Soc. **145**, 1113 (1998).
8. T. Ohzuku and Y. Makimura, Chem. Lett. **30**, 744 (2001).
9. Y. Makimura and T. Ohzuku, J. Power Sources **119–121,** 156 (2003).
10. Z. Liu, A. Yu, and J. Y. Lee, J. Power Sources, **81–82**, 416 (1999).
11. M. Yoshio, H. Noguchi, J.-I. Itoh, et al., J. Power Sources **90**, 176 (2000).
12. T. Ohzuku and Y. Makimura, Chem. Lett. **30**, 642 (2001).
13. I. Belharouak, Y.-K. Sun, J. Liu, and K. Amine, J. Power Sources **123**, 247 (2003).
14. J. K. Ngala, N. A. Chernova, M. Ma, et al., J. Mater. Chem. **14**, 214 (2004).
15. W.-S. Yoon, K. Y. Chung, J. McBreen, and X.-Q. Yang, Electrochem. Commun. **8**, 1257 (2006).
16. B. Ammundsen, J. Paulsen, I. Davidson, and R.-S. Liu, Electrochem. Soc. **149**, A431 (2002).
17. M. M.Thackeray, C. S. Johnson, J. T. Vaughey, N. Li†, and S. A. Hackney, J. Mater. Chem. **15**, 2257 (2005).
18. L. Zhang, H. Noguchi, and M. Yoshio, J. Power Sources **110**, 57 (2002).
19. S. S. Shin, Y. K. Sun, and K. Amine, J. Power Sources **112**, 634 (2002).
20. Hailang Zhang, Adv. Mater. Sci. Eng. **746341**, 7 (2014).
21. G. M. Ehrlich and D. Linden, Handbook of Lithium-Ion Batteries (McGraw-Hill, New York, 2002).
22. Z.-G. Yang, J.-L. Zhang, M. C. W. Kintner-Meyer, et al., Chem. Rev. **111**, 3577 (2011).
23. A. E. Galashev, O. R. Rakhmanova, K. P. Katin, M. M. Maslov, and Yu. P. Zaikov, Russ. J. Phys. Chem. B **14**, 1055 (2020).
24. A. A. Kashmeri, F. Nawaz, M. Yousaf, A. Shameem, M. Shabir Mahr, J. Iqbal, M. Shafique and M. A. Javed, Russ. J. Phys. Chem. B **14**, 552 (2020).
25. F. K. Fotooh and M. Atashparvar, Russ. J. Phys. Chem. B **13**, 1 (2019).