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Li-containing Oxide Nanopowders Prepared by the Plasma Chemical Synthesis

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Plasma chemical synthesis is used to obtain lithium – transition metal (Co, Mn, Ni) oxide powders, which can be applied as cathode materials for Li-ion secondary batteries. Evaporation of raw powder mixtures (Li_2CO_3+Co or (Mn_2O_3+MnO_2) or Ni) in air or nitrogen RF-IC plasma flow, subsequent quenching with air and condensation of products results in formation of nanopowders with SSA of 14 – 24 m^2/g. Prepared powders are investigated by XRD, BET, DTA methods and wet chemical analysis. In dependence on corresponding raw powder mixture composition, plasma forming gas and consumption of quenching gas $LiCoO_2$, $LiMn_2O_4$, Li_2MnO_3, $Li_2Ni_8O_{10}$ compounds and admixture phases of Co_3O_4, NiO and in all cases $LiNO_3 \cdot nH_2O$ are formed in nanopowders. To avoid from humidity and formation of lithium nitrate additional heating of powders is needed. After heating at 600 – 1000 °C pure lithium cobaltate $LiCoO_2$ (initial molar ratio Li/Co = 1.0) and spinel $LiMn_2O_4$ (initial molar ratio Li/Mn = 0.5) with good crystallinity and average particle size of 66 – 105 nm are prepared.

Keywords: plasma chemical synthesis, nanopowders, Li-containing oxides, lithium cobaltate, lithium manganese spinel.

1. INTRODUCTION

Li-ion secondary batteries became a power source for portable electronic equipment due to their high energy capacity and long service life. The materials for lithium-ion batteries include cathode materials ($LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, a. o.), anode materials (coke and graphite), and electrolyte materials (lithium salts, organic solvents and additives).

$LiCoO_2$ is the most common Li storage material for Li rechargeable batteries, used widely in electronic devices such as laptop computers. The high cost and toxicity of commertially used $LiCoO_2$ cathode have prompted extensive searches for alternatives. There is an increasing demand for manganese based mixed oxides which can effectively replace the presently used $LiCoO_2$ as cathode in Li-ion batteries. $LiMn_2O_4$ is one of the most promising cathode materials because of natural abundance of manganese in the crust and its low toxicity to environment. Lithium ion can almost reversibly intercalate into or deintercalate from spinel oxide $LiMn_2O_4$ [1]. The possible use of $LiNiO_2$ similar to $LiCoO_2$ as a positive electrode material in rechargeable lithium batteries was recognized 20 years ago. Using low cost raw material (Ni), it is expected to be cost competitive with the manganese based systems usually mentioned as low cost on the total cell $/Wh basis [2].

Cathode materials can be prepared, including in form of nanosized powders, by high temperature solid-state reactions, mild and common hydrothermal synthesis ($LiCoO_2$ particles with average size 70 – 200 nm) [3], sol-gel [4 – 6] (the average particle size of $LiCoO_2$ is 300 nm [5] but the average crystallite size of $LiMn_2O_4$ spinel is about 40 nm [6]), micro-emulsion and mechano-chemical assisted methods, Pechini synthesis, spray-drying technique and others. Submicrometer particle size and high surface area of cathode materials result in good electrochemical properties for high discharge rate. The initial capacity of oxide materials is improved due to the smaller particle size and good homogeneity, which improves the Li^+ diffusion in the cathode [4].

In this work the preliminary studies of Li-containing nanosized oxide powders preparation by plasma chemical synthesis, some physical properties and as well phase and chemical composition of synthesized nanopowders are presented.

2. EXPERIMENTAL

Lithium – transition metal (Co, Mn or Ni) oxide powders are produced by evaporation of coarse powder mixtures of commercially available chemical element and compounds (Li_2CO_3, Co, Mn_2O_3, MnO_2, Ni with particle size < 160 μm) and subsequent condensation of products in radio frequency inductively coupled (RF-IC) plasma flow on semi-industrial experimental installation. The elaborated experimental apparatuses consist of radio frequency (1.76 MHz) oscillator with maximum power of 60 kW, quartz discharge tube with induction coil, raw powder and gas supply systems, water cooled stainless steel reactor and heat exchangers, and cloth filter for collecting powders [7].

Along with evaporation during plasma chemical synthesis in a very short time such chemical reactions, as lithium carbonate decomposition, oxidation of Co or Ni, interaction of oxides, formation of lithium nitrate, are proceeded. To provide the oxidation and to regulate the growth of product particles additionally cold air as quenching gas is introduced into vapour flow through a special ring unit. The average particle size of produced powders depends on concentration of particles in the gas flow and growth time of products, that is determined by plasma velocity, formation and melting temperature of compounds as well as the cooling rate of particles.

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Air or nitrogen is used as plasma forming gases. Air also is used as carrier and quenching gas. Raw powder mixtures are introduced into plasma tail radially through 4 tubes by the powder feeder, working by the principle of pneumatic transport. The mass consumption of raw powder mixtures is 9 – 16 g/min. The average mass temperature of the plasma flow in the powder introduction plane is of 5000 – 5500 K.

Synthesized and heated powders are characterized by powder X-ray diffraction (XRD) and conventional wet-chemical analyses. Diffractometer DRON-3 with Cu-K_α radiation (Ni filter) is used. Nitrogen amount in as-synthesized powders is determined by Devarda's method. Lithium amount is determined by flame photometry, cobalt and manganese by complexometric titration with Titriplex III. The specific surface area (SSA) of powder products is measured by Brunauer–Emmett–Teller (BET) argon adsorption-desorption method [8]. The average particle size (d_{av}) of oxide powders is calculated from SSA and available in literature density.

Heating of products up to 1000 °C in air is performed both during differential-thermal analysis (DTA) on derivatograph Q-1500 of the Paulik–Paulik–Erdey system at heating rate of 10 °C/min and in the electrical camera furnace.

3. RESULTS AND DISCUSSION

3.1. Li – Co – O system

Evaporation of raw powder mixtures Li_2CO_3 + Co with molar ratios Li/Co = 1.0; 0.76; 0.53 and 0.40 in air plasma flow and mixture with molar ratio Li/Co = 1.0 in nitrogen plasma flow results in obtaining of black fine powders with SSA correspondingly of 14 – 21 m^2/g and of 15 – 19 m^2/g depending on consumption of quenching gas and initial components ratio.

Rhombohedral (hexagonal) lithium cobaltate $LiCoO_2$ is the main phase at ratios Li/Co = 1.0 and 0.76, but at ratios Li/Co = 0.53 and 0.40 along with cobaltate cubic cobalt oxide Co_3O_4 is observed by XRD analysis. At all Li/Co ratios by-product of lithium nitrate hydrate $LiNO_3 \cdot nH_2O$ is presented in the as-synthesized powders. Content of fixed nitrogen in powder samples at initial ratio Li/Co = 1.0 is 2.2 – 2.4 wt.% when air is used as plasma forming gas and 0.5 – 1.75 wt.% when nitrogen plasma is used. Formation of such by-phase is explained by thermodynamic properties of plasma flows and/or humidity of used air gas and environment.

First of all, samples of as-prepared $LiCoO_2$ powders are heated during DTA (Fig. 1). There are the mass losses of samples prepared in air plasma flow up to 18 wt.% mainly because of dehydration (to temperatures of 125 – 140 °C) and lithium nitrate thermal decomposition (up to 600 °C). After temperatures of 600 – 620 °C mass losses in samples are negligible. These processes are accompanied with endothermic minimums on DTA curve (for example, at 130 °C and 230 – 240 °C). Small endothermic minimum at ~ 800 °C (Fig. 1) is associated obviously with $LiCoO_2$ particle re-crystallization and increasing in sizes. Powder samples prepared in nitrogen plasma flow have the same character of DTA and TG curves, only the mass losses are two-three times lower (up to 5 wt.%) and denitration process is proceeded in temperature range of 385 – 700 °C.

Some characteristics of heat-treated powders with initial molar ratio Li/Co = 1.0 and 0.76 are shown in Table 1. The $LiCoO_2$ cathode materials with good voltage properties are characterized by very high values of I_{003}/I_{104} peak ratios in the X-ray diffraction pattern [9] (theoretically ratio is equal to 2.857). In Table 1 it is shown, that I_{003}/I_{104} ratio for as-prepared $LiCoO_2$ powders noticeably increases after heating up to 600 and 1000 ºC.

Heat-treated samples with initial ratio Li/Co = 1.0 exhibit a X-ray difraction pattern with all characteristic peaks for rhombohedral lithium cobaltate $LiCoO_2$ only. At ratio Li/Co = 0.76 along with lithium cobaltate peaks characteristic peaks for cobalt oxide Co_3O_4 with low intensity are presented on X-ray diagram, but at ratio Li/Co = 0.40 quantity of Co_3O_4 still more is increased.

Chemical composition of prepared nanosized $LiCoO_2$ powders including after heat treatment in dependence on initial Li/Co ratio is shown in Table 2. Chemical composition of heat-treated powders with nominal ratio Li/Co = 1.0 is close to stoichiometric of lithium cobaltate $LiCoO_2$.

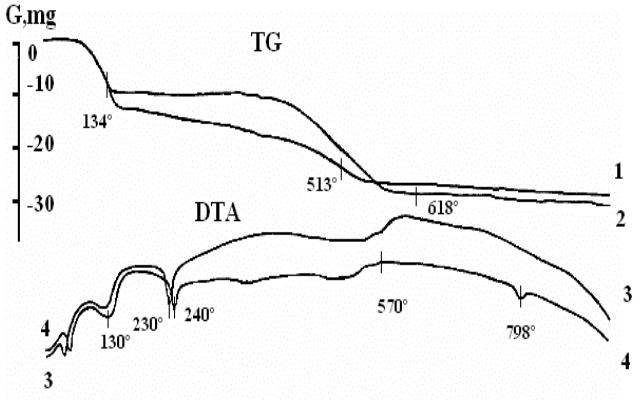

Fig. 1. Thermogravimetric (TG) (1, 2) and differential-thermal (DTA) (3, 4) curves for powder samples with initial molar ratio Li/Co = 1.0 prepared in air plasma flow: 1, 4 – sample 1.2 (Table 1) with initial mass 150 mg; 2, 3 – sample 2.1 (Table 1) with initial mass 200 mg. G axis – mass losses

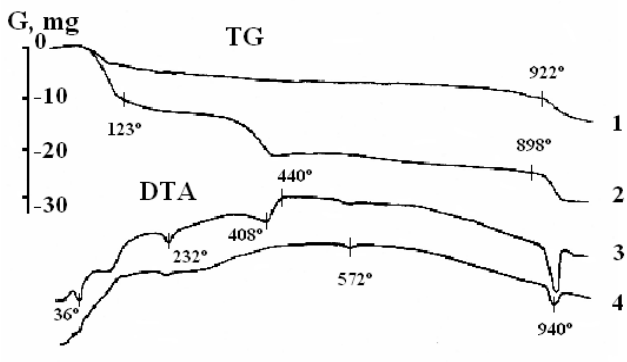

Fig. 2. Thermogravimetric (TG) (1, 2) and differential-thermal (DTA) (3, 4) curves for as-prepared in air plasma flow powder samples with initial molar ratio Li/Mn = 0.5 (1, 4) and 1.0 (2, 3). Initial masses of samples – 150 mg. G axis – mass losses

Table 1. Characteristics of heat-treated $LiCoO_2$ nanosized powders

No. of sample	Initial Li/Co molar ratio	Plasma forming gas	Maximal temperature, ºC	Overall mass losses, wt.%	Specific surface area (SSA), m^2/g	Average particle size (d_{av}), nm	I_{003}/I_{104} ratios:	
							before heating	after heating
1.1	1.00	air	600	17.5	18.1	65.6	1.29	1.46
1.2	1.00	air	1000	18.3	12.3	96.6	1.29	1.99
2.1	1.00	air	1000	14.4	18.0	66.0	1.20	1.35
3.1	0.76	air	1000	11.6	11.7	101.5	1.40	1.70
4.1	1.00	nitrogen	1000	4.9	11.3	105.1	1.26	2.90

Table 2. Chemical composition of nanosized $LiCoO_2$ powders

No. of sample	Nature of powder	Plasma forming gas	Initial Li/Co ratio	Content of elements, wt.%				Determined Li/Co	Chemical formula
				Li	Co	N	O (balance)		
1	as-prepared	air	1.0	5.80	49.7	2.3	42.20	0.991	$Li_{0.98}CoO_{2.10}$
1.2	heat-treated	air	1.0	6.84	59.3	–	33.86	0.980	
2	as-prepared	air	1.0	6.05	50.0	2.4	41.55	1.028	$Li_{0.98}CoO_{2.31}$
2.1	heat-treated	air	1.0	6.62	57.4	–	35.98	0.980	
3	as-prepared	air	0.76	4.90	56.1	1.7	37.30	0.742	$Li_{0.78}CoO_{1.94}$
3.1	heat-treated	air	0.76	5.64	61.8	–	32.56	0.775	
4	as-prepared	nitrogen	1.0	7.00	55.7	0.5	36.80	1.067	$LiCo_{0.94}O_{2.00}$
4.1	heat-treated	nitrogen	1.0	7.35	58.7	–	33.95	1.063	

Table 3. Characteristics of heat-treated lithium manganese oxide nanosized powders

No. of sample	Plasma forming gas	Initial Li/Mn molar ratio	Mass losses (wt.%):		SSA, m^2/g	d_{av}, nm	Phase composition
			in range 15 – 500 °C	overall			
1.1	air	1.0	6.4	13.3	15.4	95.3	$LiMn_2O_4 + Li_2MnO_3$
1.2	air	1.0	13.3	20.9	17.3	84.8	$LiMn_2O_4 + Li_2MnO_3$
2.2	air	0.5	4.6	9.7	16.0	87.6	$LiMn_2O_4$
3.2	nitrogen	0.5	2.5	8.1	16.3	86.0	$LiMn_2O_4$
4.1	nitrogen	1.0	1.8	6.5	12.8	114.6	$LiMn_2O_4 + Li_2MnO_3$
4.2	nitrogen	1.0	4.5	10.7	15.5	94.7	$LiMn_2O_4 + Li_2MnO_3$

Table 4. Chemical composition of heat-treated lithium manganese oxide nanosized powders

No. of sample	Plasma forming gas	Initial Li/Mn molar ratio	Content of elements, wt.%			Determined Li/Mn molar ratio	Chemical formula
			Li	Mn	O (balance)		
1.1	air	1.0	6.90	54.60	38.50	1.001	
1.2	air	1.0	7.00	53.50	39.50	1.036	
2.1	air	0.5	3.40	61.80	34.80	0.436	$LiMn_{2.3}O_{4.44}$
2.2	air	0.5	3.95	60.70	35.35	0.515	$LiMn_{1.94}O_{3.88}$
3.2	nitrogen	0.5	4.25	61.20	34.55	0.550	$LiMn_{1.82}O_{3.54}$
4.2	nitrogen	1.0	7.70	56.95	35.35	1.070	

3.2. Li – Mn – O system

Evaporation of raw powder mixtures $Li_2CO_3 + Mn_2O_3 + MnO_2$ with molar ratio Li/Mn=2.0; 1.0 and 0.5 in air and nitrogen plasma flows results in obtaining of fine powders with SSA correspondingly of 15 – 21 m^2/g and 17 – 23 m^2/g depending on cooling rate of particles and initial molar ratio Li/Mn. At ratio Li/Mn=0.5 the main phase in as-synthesized powders is cubic $LiMn_2O_4$ spinel ($MgAl_2O_4$ type). Only some traces of monoclinic Li_2MnO_3 (at decreased consumption of quenching gas) and Li nitrate hydrate are presented on XRD diagrams. At ratio Li/Mn=1.0 $LiMn_2O_4$ and Li_2MnO_3 along with $LiNO_3 \cdot nH_2O$ are formed. Orange-coloured deposits of Li_2MnO_3 powder clearly are observed in upper section of reactor near the introduction ring. At ratio Li/Mn = 2.0 (nitrogen plasma) Li_2MnO_3 is the main phase

in the products with admixtures of $LiNO_3 \cdot nH_2O$ and perhaps Li-deficient spinel $Li_{1-x}Mn_2O_4$. Content of fixed nitrogen in the products obtained in air and nitrogen plasma flow is respectively 1.6 – 2.7 wt.% and 0.4 – 1.7 wt.%.

After heating of powder samples up to 1000 °C during DTA (Fig. 2) $LiMn_2O_4$ and Li_2MnO_3 are observed at initial ratio Li/Mn = 1.0, and $LiMn_2O_4$ only at ratio Li/Mn = 0.5 (trace amount of Li_2MnO_3 is observed in the sample prepared in air plasma flow). Characteristics and chemical composition of heat-treated lithium manganese oxide nanopowders are shown respectively in Tables 3 and 4. Mass losses of samples in temperature range of 15 – 500 °C are 5 – 13 wt.% for the powders prepared in air plasma and 2 – 4.5 wt.% for the powders prepared in nitrogen plasma. According to the chemical analysis the samples obtained in nitrogen plasma flow are enriched of lithium.

Dehydration of powders proceeds up to 123 – 150 °C and nitrate decomposition – at temperatures up to 417 – 440 °C (small endothermic minimums at temperatures of 232 °C and 408 °C) (Fig. 2). Endothermic minimums on DTA curves and mass losses at temperatures 900 – 950 °C evidently are explained by surplus oxygen evolution and spinel $LiMn_2O_4$ (at nominal ratio Li/Mn = 0.5) or Li_2MnO_3 and $LiMn_2O_4$ (at nominal ratio Li/Mn = 1.0) formation and re-crystallization in the powder samples.

3.3. Li – Ni – O system

Synthesized from initial raw powder mixture Li_2CO_3+Ni in air plasma flow (molar ratio Li/Ni = 1.0) and in nitrogen plasma (ratios Li/Ni = 1.0; 0.5; 0.25) products have SSA correspondingly of 18 – 20 m^2/g and 15 – 24 m^2/g and complicated phase composition. The main phase in as-synthesized powder samples evidently is rhombohedral (hexagonal) nickel oxide NiO and the main admixture phase, especially in air plasma flow, is lithium nitrate hydrate $LiNO_3 \cdot nH_2O$. The only lithium nickel oxide $Li_2Ni_8O_{10}$ is formed in air plasma only with low content in products.

After heating up to 1000 °C (during DTA) of powder sample with ratio Li/Ni = 1.0 prepared in air plasma flow hexagonal $Li_2Ni_8O_{10}$, rhombohedral (hexagonal) $LiNiO_2$ and to all appearances remaining NiO are observed by XRD analysis. Mass losses of this sample are 19.4 wt.% in temperature interval of 16 – 570 °C and overall – 29.7 wt.%, but SSA is 13.8 m^2/g and average particle size – approximately 75 nm.

On the other hand, phase composition of heat-treated sample with ratio Li/Ni = 1.0 prepared in nitrogen plasma consists of $Li_2Ni_8O_{10}$ only and remaining NiO. During heating SSA of powder is decreased sharply up to 3.6 m^2/g (average particle size ~275 nm) and mass losses are 3 wt.% at 16 – 570 °C, but overall – 7 wt. %.

4. CONCLUSIONS

Evaporation of raw powder mixtures Li_2CO_3+Co, $Li_2CO_3 + Mn_2O_3 + MnO_2$ and Li_2CO_3 + Ni in high temperature (5000 – 5500 K) air or nitrogen radio frequency inductively coupled plasma flow, subsequent quenching with air and condensation of products results in formation of Li-containing oxide nanopowders with SSA of 14 – 24 m^2/g.

At initial molar ratios Li/Co = 1.0 and 0.76 nanopowders of lithium cobaltate $LiCoO_2$ is obtained.

At molar ratio Li/Mn = 0.5 nanopowders of lithium manganese spinel $LiMn_2O_4$ is obtained. At ratio Li/Mn = 1.0 nanopowder mixture of $LiMn_2O_4$ and lithium manganese oxide Li_2MnO_3 is prepared. But at ratio Li/Mn = 2.0 only Li_2MnO_3 is formed.

At initial molar ratios Li/Ni = 1.0; 0.5 and 0.25 preferably nickel oxide NiO is obtained. Only at ratio Li/Ni = 1.0 in air plasma flow small quantities of lithium nickel oxide $Li_2Ni_8O_{10}$ are observed in as-synthesized products.

Along with Li-containing oxide nanopowders the admixture phase of lithium nitrate hydrate $LiNO_3 \cdot nH_2O$ is formed in obtained products in part of 5 – 19 wt.% in air plasma and of 2 – 9.5 wt.% in nitrogen plasma flow.

Additional heat treatment of as-prepared powders up to 1000 °C leads to obtaining of pure $LiCoO_2$ (at ratio Li/Co = 1.0) and $LiMn_2O_4$ (at ratio Li/Mn = 0.5) with good crystallinity and average particle size in range of 66 – 101 nm. Mixtures of $LiMn_2O_4$ and Li_2MnO_3 (average particle size of 85 – 95 nm) at ratio Li/Mn = 1.0 and of $Li_2Ni_8O_{10}$, $LiNiO_2$ and remaining NiO at ratio Li/Ni = 1.0 are formed.

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