Supplementary Materials

Average oxidation degree of cobalt (Co^{Z+}, $z = 4 - x$) in the samples of the Na_xCoO_2 layered sodium cobaltite was determined iodometrically, dissolving of weighed powder of Na_xCoO_2 in the concentrated hydrochloric acid (HCl) at presents of KI potassium iodide in an inert atmosphere of nitrogen and then titrating the evolving iodine with sodium thiosulfate according to the reactions of (*S*1, *S*2)

$$x\ Co^{3+} + (1-x)\ Co^{4+} + 2I^- \rightarrow I_2 + Co^{2+}; \quad (S1)$$

$$I_2 + S_2O_3^{-} \rightarrow S_4O_6^{2-} + 2I^- \quad (S2)$$

Taking into account the titration results the sodium content (x_{Na}) in Na_xCoO_2 was calculated with equation of (*S*3)

$$x_{Na} = (2m - 90.932CV)/(m + 22.98977CV) \quad (S3)$$

where m – mass of powder of Na_xCoO_2 taken for the chemical analysis, g; C – concentration of solution of $Na_2S_2O_3$, consumed for titration of I_2, which was formed due to the oxidation of I^- ions by Co^{3+} and Co^{4+} ions (reaction S1), mol/l; V – volume of $Na_2S_2O_3$ solution, l.

Sodium content in the obtained ceramic materials (x_{Na}) was also determined using results of reverse potentiometric titration, which let us to determine exact the cobalt ions content in the average oxidation degree according to the reactions of (*S*4, *S*5)

$$x\ Co^{3+} + (1-x)\ Co^{4+} + (2-x)\ \bar{e} \rightarrow x\ Co^{2+}; \quad (S4)$$

$$Co^{2+} + [Fe(CN)_6]^{3-} \rightarrow Co^{3+} + [Fe(CN)_6]^{4-}, \quad (S5)$$

To perform the experiment, weighed powder of $Na_xCo_{0.90}M_{0.10}O_2$ complex oxide was dissolved in the concentrated hydrochloric acid (HCl),then to the obtained solution the camouflage citrate-ammonium buffer solution and 25% NH_3 solution (to get pH = 10), as well as fixed volume of fixanale solution of $K_3[Fe(CN)_6]$ (0.05 mol/l) were added. The resulting solution was titrated by fixanale solution of $CoSO_4$ (0.05 mol/l) by means of TitroLine easy (SI Analytics SCHOTT). On the base of titration results the sodium content (x_{Na}) in $Na_xCo_{0.90}M_{0.10}O_2$ was calculated using equation of (*S*6)

$$x_{Na} = [m/(22.98977(0{,}05 \cdot V_1 - 0.05 \cdot V_2)] - [M(Co_{0.90}M_{0.10}O_2)/22.98977] \quad (S6)$$

where m – mass of powder of $Na_xCo_{0.90}M_{0.10}O_2$, g; V_1 – volume of $K_3[Fe(CN)_6]$ solution, l; V_2 – volume of $CoSO_4$ solution, l.

Table *S*1. Chemical composition of ceramic samples of layered cobaltite of $Na_{0.55}CoO_2$ and $Na_{0.55}Co_{0.90}M_{0.10}O_2$ (M = Cr, Ni, Zn, W) solid solution

Состав	Элемент	keV	mas.%	Error%
$Na_{0.55}CoO_2$	O–K	0.525	62.45	0.40
	Na–*K*	1.041	24.86	0.98
	Co–*K*	6.924	12.70	0.44
$Na_{0.55}Co_{0.90}Cr_{0.10}O_2$	O–K	0.525	51.80	0.19
	Na–*K*	1.041	34.76	0.37
	Co–*K*	6.924	11.63	0.19
	Cr–*K*	5.411	1.82	0.12
$Na_{0.55}Co_{0.90}Ni_{0.10}O_2$	O–K	0.525	41.35	0.15
	Na–*K*	1.041	22.52	0.37
	Co–*K*	6.924	31.44	0.15
	Ni–*K*	7.471	4.69	0.18
$Na_{0.55}Co_{0.90}Zn_{0.10}O_2$	O–K	0.525	38.61	0.16
	Na–*K*	1.041	25.05	0.44
	Co–*K*	6.924	31.53	0.15
	Zn–*K*	8.630	4.82	0.33
$Na_{0.55}Co_{0.90}W_{0.10}O_2$	O–K	0.525	46.52	0.17
	Na–*K*	1.041	17.97	0.30
	Co–*K*	6.924	24.86	0.14
	W–*L*	8.390	10.65	0.71