Development of a cathode material based on the $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrode system for lithium ion batteries

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Abstract

The cathode material is the main factor determining the capacity, power and cost of lithium-ion cells (LIC). The particle size and surface area of the cathode material determine the resistance of solid-phase diffusion and the charge transfer reactions on the positive electrode in a lithium-ion cell. Thus, to create a battery capable of operating at high currents, it is necessary to reduce the size of crystals of the active material. Studies were aimed at improving the electrochemical characteristics of LIC of the Li/MnO_2 system by modifying the MnO_2 electrode with lanthanum, which favors the formation of additional vacancies for moving lithium ions in the structure of the cathode material and provides an increase in the discharge current density and discharge time, as well as improves the electrode cycleability. To solve the problem on the way to successful commercialization of spinel cathodes, the problem of dissolution of a small amount of manganese ions from the spinel surface followed by their transfer to the anode, which in turn deactivated the anode surface (the anode underwent corrosion damage), was solved. The proposed mechanism for the dissolution of manganese ions includes disproportionation by the scheme: $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$. Choosing an anode that is corrosion resistant to the electrolyte during cycling was another important task. To inhibit the corrosion of the anode, lanthanum ions were incorporated into the anode because a LiAl anode by itself actively interacts with the electrolyte, which results in electrode embrittlement and hence shortens the battery life time. The intermetallic compounds chosen by us based on the LaLiAl anode favored the inhibition of corrosion in the aprotic electrolyte solution during the cycling process and stability of the electrode morphology. The effect of cathodic polarization and temperature of lanthanum salicylate solution on the kinetics of formation of a thin-film $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrode is also considered in this study. Using the degree of recovery method, the compositions of the Li_xMnO_2 , $\text{La}_y\text{Mn}_{1-y}\text{O}_2$, and $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrode phases formed were determined. The currentless chronopotentiometry method was used to determine the stability of the resulting chemical compounds of lanthanum in the MnO_2 electrode structure. Based on the cyclic chronovoltammetry results, good reversibility of the $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\sigma}(\text{C}_{60})_n$ electrode was established. The results of galvanostatic cycling indicate that the discharge capacity of the electrodes increases in the series: $\text{Li}_x\text{MnO}_2 > \text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2 > \text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\sigma}(\text{C}_{60})_n$.

Key words: fullerene, lanthanum, electrochemical modification, intercalation, lithiation, manganese dioxide, lithium.

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Introduction

Incorporation of carbon-based additives (graphite, carbon black and other varieties of carbon materials) into the composition of the active material of metal-oxide electrodes for ensuring the required electronic conductivity characteristic of active materials of positive electrodes of all rechargeable chemical power cells (CPS).

As shown in studies performed in the past decades [1, 2], graphite and various types of carbon compounds of layered or 3D (spherical) structure possess electrochemical activity and can affect the mechanism and kinetics of processes both at the interface and in the bulk of the electrode solid phase during cycling in a given mode. This allows us to consider a MnO_2 electrode as a multielectrode electrochemical system whose properties are determined by changes in the structure, composition and properties of active materials and opens up wide opportunities for improving the existing technologies and developing new, more cost-effective and environmentally friendly ones for synthesizing active materials for CPS and for lithium-ion cells in particular.

Compounds of the type Li_xC_6 are known for lithium, and in particular, compounds with the composition LiC_{24} and LiC_{12} , the formation of which in the surface electrode layers ensures the accumulation of the LiC_6 compound in deeper layers. Graphites with spherical structures, *i.e.*, fullerenes, are of profound interest in this respect [4, 5]. Incorporation of C_{60} fullerene [6–8] into a compressed Li_xC_6 electrode [6–8] is accompanied by a synergistic effect due to an increase in the lithium intercalation constant. The sphericity of fullerenes and completeness of their elementary structural unit in comparison with the infinite atom clusters in graphite and diamond ensures the formation of stronger chemical bonds and explains the unique ability of fullerenes to accumulate significant amounts of intercalation products of metal cations within their internal space, and also allows new compounds with new properties to be synthesized [9].

The purpose of this work was to obtain a new cathode material with the $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2(\text{C}_{60})_n$ composition based on a manganese dioxide electrode by electrochemical modification by cathodic intercalation of lanthanum and lithium salts in aprotic organic solutions.

Experimental

The following objects were studied: 1) manganese dioxide electrodes containing MnO_2 (90%), furnace technical conductive carbon P 267 E TU 38.11574-86 (5%), fluoroplastic suspension F-4D in the form of plates with a working surface area of 2.0 cm^2 (5%); 2) electrodes with the above composition modified by cathodic treatment in a DMF solution of lanthanum salicylate ($\text{La}(\text{OH}-\text{C}_6\text{H}_4-\text{COO})_3$); 3) electrodes with composition (2) additionally modified in 0.8 M lithium perchlorate (LiClO_4) solution in a mixture of propylene carbonate (PC) with dimethoxyethane (DME) (1:1) by cathodic treatment in potentiostatic mode. The range of potentials studied was from -2.0 to -2.9 V. The time of

MnO₂ treatment was: 30 minutes in the lanthanum salicylate solution and 1 hour in the lithium salt solution. The temperature range studied was from +40 to –20°C. The electrodes synthesized in the indicated temperature range were then subjected to cathodic treatment in 0.8 M LiClO₄ in a PC + DME mixture (1:1) at $E_c = -2.9$ V and a temperature of 20°C. Before each experiment, the surface of the MnO₂ electrode was cleaned with alcohol and air-dried for 5 minutes. A La_yMn_{1-y}O₂(C₆₀)_n electrode was prepared by cathodic treatment (CT) of MnO₂ in a dimethylformamide solution of lanthanum salicylate (0.5 mol/l) containing C₆₀ (28 g/l) at $E_c = -2.9$ V, $t_{CT} = 0.5$ h. The MnO₂ and the corresponding La_yMn_{1-y}O₂ and La_yMn_{1-y}O₂(C₆₀)_n electrodes were rinsed with a 0.8 M LiClO₄ solution in the PC + DME (1:1) mixture before lithiation. Cathodic treatment was carried out for 1 hour at $E = -2.9$ V. As the auxiliary electrode material ($S = 1$ cm²), 100 μm thick aluminum foil was used (99.99%, A99 brand, GOST 11069-74), which was treated by the cathodic implantation method at a potential of $E = -2.9$ V for 0.5 hours in a solution of the lanthanum salt in order to provide the required chemical resistance of the LiAl anode material. The potential of Li_xMnO₂ and Ln_yMn_{1-y}O₂ was monitored against the non-aqueous silver/silver chloride electrode (SSCE) in 0.8 M LiClO₄ in a PC + DME mixture (1:1 v/v) saturated with LiCl or LnCl₃, respectively. The potential of the Li/Li⁺ electrode *versus* SSCE is –2.85 V.

To determine the diffusion-kinetic characteristics of modified electrodes, the initial parts of the i, t -curves corresponding to the stage of formation of a solid solution of the ions intercalating into the electrode material were replotted in $i - \sqrt{t}$, $i - 1/\sqrt{t}$ coordinates, and the intercalation constant k_{int} was determined from the slope as the $\Delta i / \Delta(1/\sqrt{t})$ ratio and accordingly the product $c\sqrt{D}$ was then calculated. By extrapolating the $i, \sqrt{t}$ plots to the ordinate axis (i), the value $i(0)$ which corresponds to the rate of the stage of the actual act of electrochemical intercalation was determined. Cycling in potentiodynamic mode was carried out in the potential range from –1.0 to –4.0 V. In addition, a mixed technique was used: lithium intercalation was carried out at $E_c = -2.9$ V for 1 hour, and then the Li_xLa_yMn_{1-y}O₂ electrodes were discharged in galvanostatic mode at a constant current density of 0.05 mA/cm² to $E = 0$ V.

The composition of the resulting phases Li_xMnO₂, La_yMn_{1-y}O₂, Li_xLa_yMn_{1-y}O₂, as well as La_yMn_{1-y}O₂(C₆₀)_n and Li_xLa_yMn_{1-y}O₂(C₆₀)_n electrodes was studied using currentless chronopotentiometry and by calculating the equilibrium potential E_{eq} of the phases formed during polarization in pulsed galvanostatic mode.

Results and Discussion

In the potential range studied, the i, t -curves show the minimum current density (Figure 1) of about 10–30 mA/cm² in the first 5–30 s.

Figure 1. Potentiostatic curves (initial parts) of $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ on treatment of a MnO_2 electrode in 0.5 M solution of lanthanum salicylate in DMF at different potentials and a temperature of 20°C.

At longer polarization (about 400–600 s), yet another current delay was detected, which indicates that two processes occur.

According to [10], these can involve the processes of ion charge exchange $\text{La}^{3+} \rightarrow \text{La}^{2+}$ (1) followed by intercalation of Ln^{2+} cations into the manganese sublattice: $y\text{La}^{2+} + 2\text{ye}^- + \text{MnO}_2 \rightarrow \text{La}_y\text{Mn}_{1-y}\text{O}_2$ (2). The first process (1) is determined by the diffusion rate, while the second process (2) of La^{2+} intercalation into the MnO_2 electrode structure is more hindered due to an increase in the energy of distribution of lanthanum cations in the structure of the $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ layer being formed.

The transition from one E region to the second one is accompanied by a stepwise increase in $i(0)$ and k_{int} (Table 1). The discovered phenomenon (Table 1) is an evidence of structural changes in the composition of the MnO_2 electrode. The $\text{La}^{3+} \rightarrow \text{La}^{2+}$ transition process is associated with filling of the intergranular space with lanthanum ions La^{2+} . At potentials more negative than -2.6 V, lanthanum is intercalated into the depth of a grain, with arrangement of lanthanum ions in defects of the manganese crystal lattice, which is accompanied by a decrease in manganese valence in MnO_2 structure from +4 to +3. This was confirmed by the shape of currentless chronopotentiograms (Figure 2).

As the potential is shifted in the negative direction, the steady state is established much more slowly and the minimum on the i,t -curves becomes more blurred. The area around the minimum is where the electrode structure is saturated with intercalated particles. It is characteristic that there are two regions in the potential region studied: 1) from -2.4 to -2.5 V and 2) from -2.0 to -2.3 V, within which the values of $i(0)$ and k_{int} are almost independent of the potential (Table 1).

Table 1. Dependence of the kinetic characteristics of $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ on the potential of lanthanum incorporation into the MnO_2 electrode.

Kinetic process parameters	Polarization potential, $-E$, V									
	–2.9	–2.8	–2.7	–2.6	–2.5	–2.4	–2.3	–2.2	–2.1	–2.0
$k = \Delta i / \Delta(1/\sqrt{t})$, $\text{mA cm}^{-2} \text{s}^{1/2}$	33.3 ± 0.02	28.6 ± 0.02	33.3 ± 0.01	32.1 ± 0.02	33.8 ± 0.03	25.0 ± 0.02	29.0 ± 0.01	33.3 ± 0.02	31.5 ± 0.03	31.8 ± 0.02
$C\sqrt{D}$, $\text{mol cm}^{-2} \text{s}^{-0.5} \cdot 10^{-5}$	20.3 ± 0.02	17.4 ± 0.02	20.3 ± 0.03	19.6 ± 0.02	20.6 ± 0.01	15.3 ± 0.02	17.43 ± 0.03	20.3 ± 0.02	19.2 ± 0.01	19.4 ± 0.02
$i(0)$, mA/cm^2	65.0	54.0	55.0	64.0	56.0	46.0	72.0	74.0	70.0	69.0
$i(0)$ mean, mA/cm^2	60 ± 5					72 ± 2

Figure 2. Currentless chronopotentiograms of a $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrode.

The effect of the solution temperature in the range from $+40$ to -20°C (Table 2) is ambiguous and is related to the degree of disordering in the structure of the phase that is formed at the MnO_2 electrode/solution (La^{3+}) interface that hinders the diffusion of La^{3+} ions into the electrode and results in a decrease in the concentration of La^{3+} ions involved in the act of electrochemical implantation, and hence, in an $i(0)$ decrease. At temperatures above 10°C , the structure is stabilized and the $(k, i(0))$ characteristics increase.

Table 2. Dependence of the kinetic characteristics of La^{3+} intercalation into a MnO_2 electrode on the temperature ($E = -2.9$ V).

Kinetic process parameters	Solution temperature, $^\circ\text{C}$						
	–20	–10	0	10	20	30	40
$k = \Delta i / \Delta(1/\sqrt{t})$, $\text{mA cm}^{-2} \text{s}^{1/2}$	156.0 ± 0.02	148.0 ± 0.03	83.0 ± 0.01	126.0 ± 0.02	222.0 ± 0.03	233.0 ± 0.02	141.0 ± 0.03
$C\sqrt{D}$, $\text{mol cm}^{-2} \text{s}^{-0.5} \cdot 10^{-5}$	94.0 ± 0.03	88.0 ± 0.02	50.0 ± 0.03	106.0 ± 0.01	133.0 ± 0.02	140.0 ± 0.03	84.6 ± 0.01
$i(0)$, mA/cm^2	32.0	29.0	18.0	41.0	40.0	36.0	32.0

Figure 3. Currentless chronopotentiograms of $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrodes in 0.5 M lanthanum salicylate solution in the temperature range studied.

At the initial stage of polarization, incorporation of lithium ions (and hence lanthanum ions) is accompanied by the formation of a solid solution of Li^+ (La^{3+}) ions in the electrode matrix (Figures 2, 3) at the initial stage, *i.e.*, it occurs without distortion of the crystal lattice of the cathode material. The formation of a new phase manifests itself as the appearance of potential delays on the $Q-E_d$ and $\lg Q-E_d$ curves in the ranges of ~ -0.2 and ~ -0.4 V due to a change in the Mn(III)/Mn(IV) ratio in the cationic sublattice of partially reduced MnO_2 caused by the intercalation of Li^+ (La^{3+}) ions. The E_d-x dependences, which characterize the discharge process of Li_xMnO_2 , $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ and $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$ electrodes, are presented in Table 3. The potentials of the interstitial phases formed are reproduced well enough both in the case of cathodic (charging) and anodic (discharging) current directions, which allows us to speak of a high corrosion resistance of the cathode material and of the electrode reversibility: $x\text{Li}^+ + \text{MnO}_2 + e^- = \text{Li}_x\text{MnO}_2$ and $\text{La}^{3+} + \text{MnO}_2 + ye^- \leftrightarrow \text{La}_y\text{Mn}_{1-y}\text{O}_2$, respectively.

Based on the data obtained, it can be stated that intercalation of lithium ions occurs with a simultaneous decrease in the Mn degree of oxidation in the LiMnO_2 matrix electrode by the reaction $\text{Mn}^{4+} + e^- \rightarrow \text{Mn}^{3+}$, while lanthanum cations that are intercalated in insignificant amounts into the MnO_2 cationic sublattice reduce the total manganese valence in MnO_2 and activate the process of lithium intercalation. The degree of intercalation of lithium cations increases upon transition from $\text{Li}_{(x=1)}\text{MnO}_2$ to $\text{Li}_{(x=1.06)}\text{La}_{0.01}\text{MnO}_2$ due to partial replacement of manganese in the MnO_2 structure with formation of a non-stoichiometric compound $\text{La}_{0.01}\text{Mn}_{1.99}\text{O}_4$ and creation of more optimal conditions for lithium intercalation, since the radius of the lanthanum ion ($r_{\text{La}^{3+}} = 0.1061$ nm) is smaller than the radius of the manganese ion ($r_{\text{Mn}^{3+}} = 0.1306$ nm).

Table 3. Composition of the Li_xMnO_2 , $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ and $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$ phases formed, calculated from the equilibrium potentials E_{eq} of these phases in pulsed galvanostatic polarization mode.

Discharge time, s	E_{eq} for Li_xMnO_2 , V	E_{eq} for $\text{La}_y\text{Mn}_{1-y}\text{O}_2$, V	E_{eq} for $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$, V	x for Li_xMnO_2	x for $\text{La}_y\text{Mn}_{1-y}\text{O}_2$	x for $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$
600	0.7	0.38	0.42	0.026	0.0004	0.266
1800	0.34	0.28	0.17	0.078	0.0012	0.533
2400	0.28	0.26	0.128	0.104	0.0016	0.799
3000	0.24	0.24	0.066	0.130	0.002	0.894
4800	0.18	0.18		0.208	0.0032	
7200	0.1	0.16		0.313	0.0048	
8400	0.08	0.13		0.365	0.01	

According to spectral studies [10], when C_{60} , like other higher fullerenes, is adsorbed on MnO_2 , it “absorbs” two Mn atoms due to the interaction of an unpaired electron delocalized over the fullerene “cell” with a common nuclear spin of the Mn_2^{n+} pair, in which the valence state of manganese ions is close to 2+. The additional hyperfine structure indicates an incomplete compensation of the spin magnetic moments of 4f electrons transferred to the fullerene “frame”. In this case, the formation of both endo- and exohedral complexes of the Me– C_{60} system (ligand) is possible, which is due to the properties of the fullerene ligand, such as polyhedral structure, steric bulkiness, the presence of a large number of coordination sites, and a significant electron acceptor ability.

The data obtained on the effect of the composition of the modified MnO_2 electrode on its open circuit potential and upon polarization in a working solution are in good agreement, as concerns the increase in the capacity for lithium, with the results of Li_xMnO_2 , $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$, $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\sigma}(\text{C}_{60})_n$ cycling in galvanostatic mode (Table 4).

Table 4. Values of specific charge/discharge capacity as a function of the cycle number in galvanostatic mode ($i_{\text{dis}} = 0.05 \text{ mA/cm}^2$); the final discharge potential is $E_{\text{dis}} = -(0.2 \pm 0.1) \text{ V}$.

Electrode	Cycle number N	Specific discharge capacity Q_{dis} , mAh/g	Specific charging capacity Q_{c} , mAh/g	Capacity efficiency, %
Li_xMnO_2	1	218.7	240.0	91.1
	50	39.3	240.0	16.4
	100	20.0	240.0	8.3
$\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_2$	1	173.0	240.0	72.1
	50	70.5	240.0	29.4
	100	28.6	240.0	11.9
	50	78.3	240.0	32.6
	100	32	240.0	13.8

Conclusions

In the potential ranges from -2.4 to -2.5 V and from -2.0 to -2.3 V, the values of $i(0)$ and k_{int} are almost independent of potential (Table 1). The transition from one E region to the second one is accompanied by a stepwise increase in $i(0)$ and k_{int} , which suggests that structural changes occur in the MnO_2 electrode. The $\text{La}^{3+} \rightarrow \text{La}^{2+}$ transition process is associated with filling of the intergranular space with lanthanum ions La^{2+} . At potentials more negative than -2.6 V, lanthanum is intercalated into the depth of grains with arrangement of lanthanum ions in defects of the manganese crystal lattice, which is accompanied by a decrease in manganese valence in the MnO_2 structure from $+4$ to $+3$, *i.e.*, the degree of manganese reduction increases.

According to our studies on the effect of solution temperature on the kinetics of lanthanum intercalation into a MnO_2 electrode, the effect of solution temperature in the range from $+40$ to -20°C (Table 2) on the kinetic characteristics of the process is ambiguous and depends on the degree of disordering in the structure of the phase formed at the MnO_2 electrode/solution (La^{3+}) interface, which hinders the diffusion of La^{3+} ions into the electrode and results in a decrease in the concentration of La^{3+} ions involved in the act of electrochemical intercalation and hence a decrease in $i(0)$ value. At temperatures above 10°C , the structure is stabilized and the (k , $i(0)$) characteristics increase.

Manganite $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ was obtained by cathodic intercalation of lanthanum into a manganese dioxide electrode in potentiostatic mode. It increases the corrosion resistance of the cathode material and provides higher capacitive characteristics in comparison with the original MnO_2 : the amount of intercalated lithium increases significantly on transition from LiMnO_2 to $\text{Li}_{1.06}\text{La}_{0.01}\text{MnO}_2$.

Comparative analysis of the electrical characteristics of electrodes obtained by electrochemical modification of MnO_2 with lanthanum and fullerene C_{60} with literature data shows the efficiency of using the cathodic intercalation method in order to simplify the synthesis, save energy costs, and the possibility of industrial implementation.

References

1. A.Yu. Tsivadze, T.L. and A.M. Skundin, *Prot. Met. Phys. Chem. Surf.*, 2013, **49**, no. 2, 145 (in Russian). doi: [10.7868/S0044185613020083](https://doi.org/10.7868/S0044185613020083)
2. T.L. Kulova, *Elektrokhimiya*, 2009, **49**, no. 1, 3 (in Russian).
3. I.A. Kedrinskiy, *Lithium-ion cells*, Krasnoyarsk, 2002 (in Russian).
4. *A method to manufacture a MnO_2 electrode for chemical power cells*, RF Patent 2145455, published in 2000 (in Russian).
5. *A chemical power cell of MnO_2 -Li system*, RF Patent 2195051, published in 2002 (in Russian).
6. L.D. Yushina and A.Y. Tarasov, *Elektrokhimiya*, 1977, **13**, no. 10, 1600 (in Russian).
7. L.N. Olshanskaya, S.S. Popova, T.V. Pominova and E.N. Astafieva, *Elektrokhimiya*, 2002, **38**, no. 4, 406 (in Russian).

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8. S.S. Popova, E.N. Astaf'eva, A.V. Denisov, N.S. Kuyunko and S.D. Kushch, *Elektrokhimicheskaya energetika*, 2003, **3**, no. 1, 26 (in Russian).
 9. D. Guerard and A. Herold, *Carbon*, 1975, **13**, no. 14, 334.
 10. E.S. Guseva and S.S. Popova, *Fizika i khimiya obrabotki materialov*, 2014, no. 6, 75–79 (in Russian).