Kinetics and mechanism of distribution of lanthanum ions in MnO₂ structure in the presence of fluoride ions

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Abstract

The study focused on improving the electrical characteristics of a MnO₂ electrode by cathodic incorporation of lanthanum from an aprotic organic solution of a salt containing fluoride ions made it possible to identify the extent of participation of each component in the formation of new Li_xLa_yMnO_{2-δ}F_δ phases with a structure that facilitated the process of subsequent intercalation–deintercalation of lithium and its accumulation in the cathode material, and to develop technology recommendations for the modification process conducted in potentiostatic mode: 0.5 mol/L lanthanum sulfanilate solution in a mixture of propylene carbonate with dimethoxyethane, PC+DME (1:1), which contained LiF (14 g/L); the potential was $E_c = 2.9$ V (relative to SCE); the time was 30 min. Subsequent lithium intercalation–deintercalation was carried out in 0.8 M solution of LiClO₄ in the PC+DME (1:1) mixture at the same potential. The presence of lanthanum cations that were incorporated into the structure of the LiAl anode prevented the inhibition of anodic dissolution (corrosion) during the charge-discharge process. Lanthanum cations contributed to the elevated inhibition of anodic processes and increased the number of cycles resulting from the electrode cycling [1, 2].

Key words: *fluoride ions, lanthanum, electrochemical modification, intercalation, lithiation, manganese dioxide, lithium, anode corrosion resistance.*

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Introduction

Due to the unique ability of fluorine to react almost with all chemical elements, its compounds occur widely in nature and are commonly used in engineering, in the development of new materials and technologies for various purposes, including electrochemical cells. The fluoride ion that possesses a high donor capacity is a component of many complexing agents. The stabilization of fluorides by complexation is a common phenomenon [3, 4]. In oxofluorides of the Me₂O₃–MeF₃ system, the anions are distributed separately from each other and nonuniformly, the cation framework is noticeably deformed, and a mutual effect of cations and anions takes place: the O²⁻ anions do not break up with the cationic tetrahedra despite their distortion and a considerable Me–O distance. On the contrary, the F⁻ anions occupy the cationic tetrahedra only in the vicinity

of the “tetrahedral” part of the structure and then leave them, either merging into the octahedral fragments and stay near one of the facets, or pass to the edge thus forming a predominant bond with two cations of $\text{Me}_n\text{O}_{n-1}\text{F}_{n+2}$ type.

Complex compounds of transient metal oxides with fluoride ions are characterized by stability and resistance to reduction processes. The ability of complex transient metal salts with lithium fluorides to dissolve in aprotic organic media and conduct electrical current combined with their electrochemical stability under the conditions of current source recharging creates prerequisites for their successful use in the development of fluorine-containing oxide cathodes. Special attention should be paid to the fact that the solutions of LiMeFx in aprotic media exhibit properties unique to this type of conductor, namely a negative temperature coefficient of electric conductivity, two-extremum isotherms of equivalent electric conductivity, and synergistic effects.

The work of detachment of even just one electron is high, and it requires much more energy to remove the eighth electron than that for the detachment of the first to seventh electrons. Therefore, fluorine has the maximum electron affinity. Fluorine never exists as a cation (F^+) in compounds. The high electron affinity of fluorine is determined by its small atomic and ionic radii. The energy required to form a F^+ ion is 419 kcal/g-atom, that is much higher than that needed for a hydrogen cation H^+ (364 kcal/g-atom) and much lower than that for other halogens. In an effort to pass into the state of F^- fluoride ion with a radius of 1.33 Å and the electron affinity of 81.3 kcal/g-atom, fluorine is able to remove electrons from all other elements; it fails to react directly only with oxygen and nitrogen. The energy needed to form O_2F_2 can be obtained either from an electric discharge or from another chemical process associated with oxide formation [3–7].

The aim of the work is to modify the composition, structure, and properties of the material industrially manufactured for the production of MnO_2 cathodes by cathodic incorporation of fluoride ions in aprotic organic solutions of lanthanum salts.

Experimental

The objects of the study included: 1) a manganese dioxide electrode composed of 90% MnO_2 , furnace electrically conductive carbon black P 276 E TU 38.11574-86–5%, a fluoroplastic suspension of brand F-4D–5% in the form of plates with a working surface area of 2.0 cm²; 2) electrodes of the indicated composition modified using cathodic treatment in a dimethylformamide solution of lanthanum salicylate ($\text{La}(\text{OH}-\text{C}_6\text{H}_4-\text{COO})_3$); 3) an electrode with composition (2) that was modified further in 0.8 M LiClO_4 solution in a 1:1 mixture of propylene carbonate (PC) with dimethoxyethane (DME) by cathodic treatment in potentiostatic mode. The potentials under study ranged from –2.0 to –2.9 V. The MnO_2 treatment lasted for 30 min in the solution of lanthanum salicylate and 1 h in the lithium salt solution. The investigations were performed within a temperature range from +40 to –20°C. The electrodes synthesized in this temperature range were subjected to cathodic treatment in 0.8 M LiClO_4 solution in the PC+DME (1:1) mixture at

$E_c = -2.9$ V and a temperature of 20°C. The surface of a MnO_2 electrode was cleaned with alcohol and dried in the air for 5 min prior to each experiment. The $\text{La}_y\text{Mn}_{1-y}\text{O}_2\text{F}_\delta$ electrode was prepared by cathodic treatment of MnO_2 in a dimethylformamide (DMF) solution of lanthanum salicylate (0.5 mol/L) containing LiF (14 g/L) at $E_c = -2.9$ V, $t_{cp} = 0.5$ h. Before lithiation, the MnO_2 electrodes, $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ and $\text{La}_y\text{Mn}_{1-y}\text{O}_2\text{F}_\delta$ were rinsed in 0.8 M LiClO_4 solution in the PC+DME (1:1) mixture. The cathodic treatment was carried out for 1 h at $E = -2.9$ V. A 100 μm thick foil of high purity aluminum (99.99%) (A99, GOST 11069-74) was used as an auxiliary electrode ($S = 1 \text{ cm}^2$), which was treated using the cathodic intercalation method in a lanthanum salt solution to provide the required chemical resistance of the LiAl anode at a potential of $E = -2.9$ V for a period of 0.5 h. The potentials of Li_xMnO_2 and $\text{Ln}_y\text{Mn}_{1-y}\text{O}_2$ were monitored with the use of non-aqueous silver chloride electrode (SCE) in 0.8 M LiClO_4 in the PC+DME (1:1 v/v) mixture saturated with LiCl or LnCl_3 , respectively. The potential of the Li/Li⁺ electrode was found to be -2.85 V against the SCE.

Discussion

Among non-metal fluorides, graphite fluoride $(\text{CF})_x$ is of particular interest since it is rather extensively used in batteries as a cathode material, it C–F bonds, and belongs both to organic and inorganic fluorine compounds. Numerous reports are available in literature on modification of the structure of active cathode materials with fluorine anions by physicochemical and mechanical methods. The beneficial effect of the presence of fluoride ions in the structure of an oxide cathodic material was proved. The saturation of manganese dioxide with cations of rare-earth elements (REE) from aprotic organic solutions of REE salts in the presence of lithium fluoride significantly increases the electrical characteristics of the cathode. Unfortunately, the mechanism of activation effect of interactions between fluoride ions on the behavior and structure of the MnO_2 cathode has received almost no attention. The available information is scarce. It is known that the rates of both anodic and cathodic reactions increase on introduction of F^- ions into an electrolyte, which is caused by the entrance of F^- ions ($r = 1.36 \text{ \AA}$) into the anionic sublattice of an oxide and substitution of a fraction of oxygen ions ($r = 1.40 \text{ \AA}$) in the oxide. This affects the electronic and ionic conductivity properties of a MnO_2 electrode and the electrode reaction rates. Mass spectrometric studies detected F^- ions in the structure of a MnO_2 electrode at a depth of 250 $\text{\AA}$ and more. The motion of F^- ions within the anionic sublattice disturb the stoichiometry, and, as a consequence, change the electrical characteristics of the cathode. An important goal of this work is to study the potential improvement of electrochemical properties of a manganese dioxide electrode by cathodic intercalation in a lanthanum salt solution in DMF saturated with fluoride ions in the form of LiF.

As follows from the potentiostatic curves recorded for the MnO_2 electrode (Figure 1) in a lanthanum salicylate solution in DMF containing LiF as a fluorine-containing salt

additive, the rate of lanthanum intercalation into the MnO_2 electrode was largely determined by the concentration of the LiF additive into the solution. The potentiostatic measurements showed that at a specified constant potential value (Figure 1), the rate of the process depended both on the duration of polarization and on the amount of LiF added to the working electrolyte solution. With the increase in the amount of LiF from 1.75 to 3.4 g/L, the current density at the electrode grows almost four-fold at the very beginning when the diffusion law $i=f(\sqrt{t})$ is obeyed, and almost five-fold under steady-state conditions. In this case, the step-like shape of the $i-t$ curves is more pronounced. The process rate, which is determined by the diffusion parameters of the process, attains a maximum value when the concentration of the additive is 14 g/L (saturated solution) (see Table 1).

Figure 1. Potentiostatic curves of MnO_2 electrode at $E_c = -2.9$ V in 0.5 M lanthanum salt solution in DMF with the LiF additive, g/L: 1–14; 2–7; 3–3.5; 4–1.75.

Table 1. Effect of the LiF additive concentration in 0.5 M lanthanum salicylate solution in DMF at $E_c = -2.9$ V (at 25°C) on the diffusion-kinetic characteristics of the electrochemical formation of the $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\sigma}\text{F}_\sigma$ phase on a MnO_2 electrode.

Concentration of LiF additive, g/L	Kinetic parameters of the process		
	$K_{\text{int}}, \text{mA} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2}$	$C_{\text{Li}} \sqrt{D_{\text{Li}}}, \text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2} \cdot 10^{-5}$	$i(0), \text{mA/cm}^2$
14	51.47 ± 2	31.5 ± 2	40.5
7	22.9 ± 2	14.0 ± 2	18
3.5	14.86 ± 2	9.08 ± 2	12.5
1.75	10.8 ± 2	6.60 ± 2	10

The modification process was carried out at $E_c = -2.9$ V. Therefore, one cannot ignore the fact that both La^{3+} and Li^+ cations are involved in the process.

The results of X-ray powder diffraction analysis (Figure 2) and scanning electron microscopy (Table 2) provide an evidence of the formation of intercalation phases in the structure of a MnO_2 electrode in the course of cathodic polarization in an aprotic solution of lanthanum salicylate containing the LiF additive. The intercalation of fluorine into the oxygen sublattice of MnO_2 results in the redistribution of the atomic composition of components in the $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ system. X-Ray powder diffraction analysis (Figure 2) revealed the $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$, MnO_2 , Mn_3O_4 , and LiF phases in the structure of the $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrode studied. This inevitably leads to variations in the currentless potential, $E_{c/l}$.

Figure 2. X-Ray pattern of the $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrode obtained by cathodic treatment of a MnO_2 electrode in 0.5 M lanthanum salicylate solution in DMF at $E_c = -2.9$ V, polarization time 0.5 h, 25°C .

As follows from the spectral analysis data, fluorine ions are embedded in the interstices of the oxide crystal lattice, which facilitates the diffusion of fluoride ions throughout the crystal and creates conditions for trapping fluoride ions by cubic centers of a metal (lanthanum) in the structure of the transition metal (manganese) oxide.

The content of lanthanum, oxygen, and manganese (at.%) in the structure of the initial MnO_2 electrode and the modified $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ and $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrodes changes appreciably. This is due to the tetragonal lanthanum centers generated in the structure of MnO_2 and agrees with the assumption that vacancies exist in the immediate environment of La^{3+} , which are able to trap fluoride ions in the interstices. According to the diffusional model of migration, the excitation energy for donors, transfer of excitation energy between La^{3+} ions, and localization of a hole on La^{3+} lead to the transition of a La^{3+} ion from a tetragonal center to a tetragonal position of La^{4+} .

Table 2. Elemental composition (at.%) of the structure of the original MnO_2 electrode and the $\text{La}_y\text{Mn}_{1-y}\text{O}_2$ and $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrodes after cathodic treatment in 0.5 M lanthanum salicylate solution in DMF at a potential of -2.9 V, polarization time 0.5 h, 25°C .

Electrode material	C %	Mn %	O %	La %	F %
MnO_2	3.44	79.28	17.28	–	–
$\text{La}_y\text{Mn}_{1-y}\text{O}_2$	3.54	75.58	20.38	0.5	–
$\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$	5.13	62.09	16.23	5.1	11.45

Table 3 summarizes the potentials of formation of the $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ phase and its conversion to the $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ phase, which in the chosen mode can be observed by a sharp rise of currentless potential, $E_{c/l}$, from -0.4 V (at $C_{\text{LiF}} < 3.5$ g/L) to -0.85 V (at $C_{\text{LiF}} = 14$ g/L, *i.e.*, in the saturated solution) (see Table 3).

It was found from the experimental data on the effect of the LiF concentration on the kinetics of intercalation of lanthanum and fluorine ions into the structure of a MnO_2 electrode that the magnitude of the currentless potential attained a maximum when the LiF concentration was 14 g/L.

The diffusion-kinetic parameters of cathodic intercalation of lanthanum cations in the presence of lithium fluoride ions in the solution (Table 1) indicated that LiF concentration had a strong effect. The currentless chronopotentiograms recorded during the electrochemical modification of a $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrode with lanthanum in a solution of a lanthanum salt showed a noticeable shift of electrode potentials towards more electronegative values once the cathodic polarization of the electrode was finished (Table 3). It proves the fact that the structural changes in the electrode resulted from cathodic intercalation.

Table 3. Effect of the LiF additive in the solution on the values of currentless potentials of a $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrode upon its cathodic polarization in 0.5 M lanthanum salicylate solution in DMF at $E_c = -2.9$ V, polarization time 0.5 h, 25°C .

Concentration of LiF additive, g/L	Currentless potential of $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ electrode at $E_c = -2.9$ V, $t_c = 60$ min	
14	0.85 ± 0.02	0.40 ± 0.02
7	0.80 ± 0.02	0.39 ± 0.02
3.5	0.59 ± 0.02	0.38 ± 0.02
1.75	0.40 ± 0.02	0.32 ± 0.02

Figure 3. Secondary ion mass spectra of $\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$.

The results of mass-spectrometric analysis (Figure 3) showed that the significant amount of LiF that is present in the modified MnO_2 electrode along with lanthanum decreases deeper into the electrode (down to 20 μm).

Therefore, the studies revealed that the rate of lanthanum intercalation into a MnO_2 electrode from an aprotic solution of a lanthanum salicylate salt with addition of fluoride ions, which was determined from the calculated values of diffusion-kinetic process parameters, increased with an increase in the LiF concentration from 1.75 to 3.4 g/L and attained a maximum at a salt concentration of 14 g/L (saturated solution). It was found that the currentless potential of $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$ in a solution of lanthanum salicylate salt with addition of lithium fluoride reached a maximum at a LiF salt concentration of 14 g/L. In view of this, we recommend to use this concentration of the fluoride ion additive in the cathodic synthesis of the matrix multi-component electrochemical system $\text{Li}_x\text{La}_y\text{Mn}_{1-y}\text{O}_{2-\delta}\text{F}_\delta$.

Conclusions

Notably, the possible mutual transitions in the studied structures are associated with deformation and not related to fundamental structural rearrangements [3, 4]. As the content of fluorine is decreased, the conductivity also decreases. Phases with low crystalline packing density possess the highest conductivity; the structural distortion of the anionic sublattice with almost complete population of the cationic sublattice results in defects in the anionic sublattice, while the mobility of F^- ions increases. The F^- ions enter into the oxide lattice and partially substitute O^{2-} . The ensuing charge redistribution leads to the

acceleration of both anodic and cathodic reactions: ($r_F^- = 1.36 \text{ \AA}$; $r_O^{2-} = 1.4 \text{ \AA}$); with an increase in the amount of F^- ions, the potential (stationary, mixed) becomes more negative and the current grows. This growth is more significant in the cathodic region than in the anodic region [5–7]. It was confirmed that along with the cathodic intercalation of lanthanum into the electrode structure, the reaction $MnO_2 + \delta Li^+ + \delta F^- + \delta e^- \rightarrow Li_\delta MnO_{2-\delta} F_\delta$ occurs by the solid-phase mechanism.

The formation and accumulation of the products of interaction of fluoride ions with the surface occur by the layer-by-layer growth mechanism accompanied by the formation of oxofluorides with the compositions $La_y Mn_{1-y} O_{2-\delta} F_\delta$ and $Li_\delta MnO_{2-\delta} F_\delta$.

The results of X-ray powder diffraction analysis disclosed the phases with compositions $La_y Mn_{1-y} O_{2-\delta} F_\delta$, MnO_2 , Mn_3O_4 , and LiF forming in the matrix of the modified $La_y Mn_{1-y} O_{2-\delta} F_\delta$ electrode. Scanning electron microscopy made it possible to identify the composition of MnO_2 , $La_y MnO_2$, and $La_y Mn_{1-y} O_{2-\delta} F_\delta$ electrodes and confirm the vacancy mechanism of intercalation.

The cationic framework dominates in the crystalline structures with heavy and multivalent cations. The cations are distributed in the space by the law of “twelve neighbors”. The anions occupy the tetrahedral voids in the cation packing. The dominant influence of the cation framework, which is the strongest in fluorides, decreases with decreasing ionicity of bonds in the compounds. The fluorite-like structures are typical not only of fluorides but also of oxides and oxofluorides that form Me_7O_{12} type structures. In this case, a tetravalent metal together with a trivalent metal that differ in size and chemical properties are contained in the structure of a cationic sublattice in the ratio that provides the overall stoichiometry. The cationic framework is slightly distorted and stretched along the “fluorite” space diagonal. The element ratio is distorted significantly and depends on the arrangement of anions and type of coordination environment. In the LaF_3 structure which has two cationic tetrahedrons per site-cation occupied by anions, anions occupy eight cationic tetrahedrons and three cationic triangles converging to this cation.

References

1. S.M. Zakirova, Kinetics of reactions and technological aspects of modification of the LiAl electrode properties, *Cand. Sci. (Chemistry) Dissertation*, Saratov, 1997, 210 (in Russian).
2. B.N. Kabanov, L.I. Leikis, I.G. Kiseleva, I.I. Astakhov and D.P. Aleksandrova, Cathodic incorporation of alkali metals into electrodes in aqueous solutions, *Dokl. Acad. Nauk SSSR*, 1962, **144**, 1085–1089 (in Russian).
3. S.V. Borisov and N.V. Podberezoskaya, Stable cationic frameworks in the structure of fluorides and oxides, *Novosibirsk: Nauka*, 1984, 65 (in Russian).
4. N.M. Kompanichenko, A.A. Omel'chuk, A.P. Ivanenko, R.N. Pshenichnyi and E.V. Timukhin, Conductivity of non-stoichiometric fluorides LnF_{2+x} (Ln-Sm, Eu, Yb), *Russ. J. Appl. Chem.*, 2013, **86**, no.12, 1835–1841. doi: [10.1134/S1070427213120069](https://doi.org/10.1134/S1070427213120069)

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5. T. Valand and G. Nilsson, The influence of F^- ions on the electrochemical reactions on oxide-covered Al, *Corros. Sci.*, 1977, **17**, 449–459.
 6. A.A. Potanin, Solid-state chemical current source on the basis of ionic conductor of lanthanum trifluoride type, *Rossiiskii khimicheskii zhurnal (Zh. Ros. khim. obshch-va im. D.I. Mendeleeva)*, 2001, **45**, no. 5–6, 59–63 (in Russian).
 7. D.P. Opra, S.V. Gnedenkov, S.L. Sinebryukhov *et.al.*, Primary lithium current source on the basis of organic fluorinated carbon polymer material, *Vestnik of the Far East Branch of the Russian Academy of Sciences*, 2013, no. 5, 23–32 (in Russian).