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STRUCTURE AND CHARACTERISTICS OF COMPOSITE CARBON-CERAMIC COATINGS FOR CATHODES OF CONTEMPORARY CHEMICAL CURRENT SOURCES

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Abstract. The paper established the relationship between structure and properties of single-layered and multiple-layered composite carbon-ceramic coatings on the basis of lithium-manganese spinel on an aluminum substrate, allowing to optimize the structure of new cathode materials, which is promising for application in chemical current sources. Electrochemical properties were investigated using voltammetry and galvanostatic cycling. Investigation defined the amount of matter that takes part in the electrochemical processes, ability to discharge large currents; and performance during prolonged cycling.

Keywords: cathode material, chemical current source, voltammetry, galvanostatic cycling.

1. Introduction

The development of new effective materials for electrode-cathodes and anodes is the main research area to improve chemical current sources (CCS) and increase its electrical and operating parameters (capacity, charge-discharge rate, number of charge-discharge cycles, *etc.*), and decrease its size up to microns.

Papers [1-3] describe the production conditions and structure formation regularities of high performance cathodes, represented as single-layered and multiple-layered coatings on aluminum substrate.

To reach the required level of cathodes operating characteristics it is important to state bonding formation regularities between synthesis conditions of single-layered and multiple-layered composite coatings on aluminum substrate and its parameters.

It is impossible to use completely and adequately the possibilities of controlled formation of structure, phase composition and other parameters of such cathodes for CCS without reference to technological parameters of coating synthesis process.

Electrochemical characteristics are the most important in terms of using these coatings for synthesis of contemporary CCS cathodes. The paper provides the results of characteristic experimental investigation.

2. Experimental

Cathodes experimental models were synthesized. The working surface was 2 cm², active mass of lithium-manganese spinel (LiMn₂O₄) changed depending on deposition mode from 0.1 to 2.0 mg/cm² in single-layered coatings, and from 4.0 to 8.0 mg/cm² in multiple-layered composite carbon-ceramic coatings.

Cathode models were stored in dry argon atmosphere glove box at the temperature of 293–298 K. Box water and oxygen concentration did not exceed 1 and 2 ppm, respectively. Under these conditions the assembly and testing of electrochemical cells was performed to identify charge-discharge characteristics, number of charge-discharge cycles and cathodes specific capacity. Cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy was used to accomplish our goals.

Cathode electrochemical testing was performed in sealed three-electrode electrochemical cell, composed of investigating operation cathode, auxiliary electrode and reference electrode. Reference electrode represented lithium metal rolled on nickel grid. It was placed directly at operating working electrode. Surface area of reference electrode exceeded surface area of operating electrode compensating electrolyte voltage loss.

Salt LiPF₆ and solvents, consisting of cyclic and lineal carbonate – propylene carbonate (PC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) with low water content were used as electrolyte.

Electrochemical tester Maccor, used to determine charge-discharge cycles at different discharge current density and eight-channel potentiostat VMP 2, used to determine impedance, were involved in electrochemical investigation.

Cyclic voltammetry and galvanostatic cycling. At the first step, after electrochemical cell was assembled, cathodes were characterized by cyclic voltammetry with potential sweep rate from 1 to 10 mV/s. The initial processing included cathodes cycling in a voltage range from 3.0 to 4.5 V. The shape of volt-ampere curve (VAC) at first cycle differs from curve shapes at subsequent cycles. The total number of cycles is from three to five and depends upon setting stationary invariant VAC shape.

The series of charge-discharge cycles was performed to determine discharge rate (C-rate) and to obtain cathode cycling characteristics. Charging was done at galvanostatic mode with direct current 0.1 mA (1 C-rate), after the voltage reached 4.4–4.5 V – the cycling was done at constant voltage. Charging at potentiostatic mode continued until the current reached 20–10 μ A. Total charging duration did not exceed three hours.

Discharge was performed at constant current until 3.0 V voltage was reached. Depending upon the assigned task the current was constant form cycle to cycle to identify cycling, or the current changed within the range from 50 to 120 μ A to identify cathode performance capacity at different discharge rate.

Electrochemical impedance spectroscopy. To analyze in details the operating kinetics of cathode materials and components limiting its work electrochemical impedance spectroscopy was used as one of the most powerful technique of electrochemical processes investigation [4, 5].

Small sinusoidal perturbation (voltage 5–10 mV) was applied on investigating cathode at equilibrium potential and system response. Amplitude response and phase shift in relation to predetermined voltage allowed to calculate active and reactive resistance of the system at given frequency. Value collection of active and reactive resistance at different frequencies was obtained with impedance hodograph as one of the widely used ways of impedance data presentation.

The investigation tried to reach lineal system response to given perturbation as main requirement of impedance spectroscopy.

Impedance measurements methods. Eight-channel potentiostat VMP 2 was used to perform impedance measurements. Variable sinusoidal signal 10 mV with the frequency from 100 kHz to 100 MHz was applied on investigation cathode at different potential and, consequently, at different charge or discharge conditions. Two or three measurements in accordance with

automatically assigned program were performed to reach adequate accuracy of the obtained results at each frequency.

To reach next equilibrium condition electrode potential was shifted and the system was potentiostatic until current declined to a few mA level. Impedance registration and equilibrium attaining was performed and regulated automatically.

Equivalent patterns common for cathode materials in three-electrode cells [5] were used to analyze impedance hodograph. Impedance spectrum analysis included dependence between reactive and active resistance and dependence between full resistance, phase shift and frequency. The analysis of main process parameters changes at different potential allowed to define its influence and to determine limiting process.

3. Results and Discussion

3.1. The Investigation of Current Voltage Characteristics and Galvanostatic Characteristics of New Cathode Materials on Lithium-Manganese Spinel

Fig. 1 shows current voltage characteristic (CVC) of cathode at different potential scanning rate in electrolyte, presented as 1.2 M LiPF₆ solution in mixture of ethylene carbonate/propylene carbonate/diethyl carbonate (EC/PC/DEC) in volume ratio 1:1:3.

As it is seen from Fig. 1, during first charge the structure is formed which has the ability to multiple cycling and first charge curve differs from the subsequent ones. CVCs completely coincide after tow-three cycles.

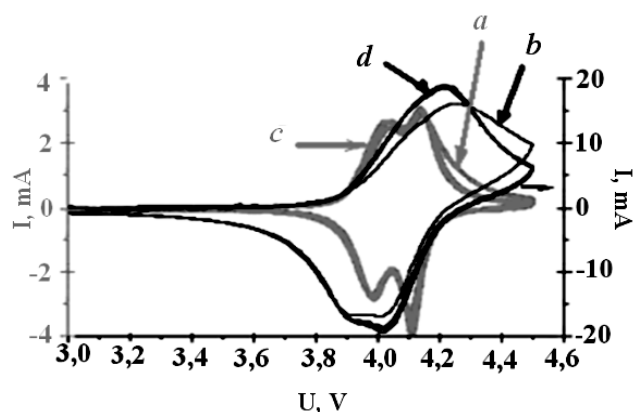


Fig. 1. Volt-ampere curves of cathode on LiMn₂O₄ spinel: at potential scanning rate, mV/s: 1 (a, c) and 10 (b, d)

Cathode capacity Q_{disch} , obtained at different discharge currents, and dependence between discharge capacity and discharge rate C-rate (Table 1, Fig. 2) was defined based on the potentiostatic cycling.

The results of galvanostatic cycling showed that investigated cathodes are characterized by good discharge rate. Thus, at low discharge currents (0.01 and 0.05 mA) cathodes specific capacity changed from 100 to 110 mAh/g, C-rate and amounted to 0.03 and 0.16, respectively. At high discharge currents (100 and 140 mA) cathodes have ability to rapid discharge and sufficiently high cycling (more than 800 cycles).

At discharge rate of 100 mA the discharge capacity was 0.150 mAh, discharge time – 12 s, at the same time cathode output was 48 % of initial capacity. At discharge rate of 140 mA the discharge capacity was 0.140 mAh, discharge time – 8 s, at the same time cathode output was 45 % of initial capacity. C-rate at high discharge currents (100 and 140 mA) increased and made up 313 and 438, respectively.

While long-lasting cycling cathode capacity decreased moderately and amounted to 80 % from the initial one, cathode capacity did not change after 800–900 cycles.

Dependence between output specific discharge capacity and discharge (Fig. 2) rate characterizes cathode capability to operate at high discharge rates. Thus, C-rate equal to 1.0 corresponds to discharge for one hour, and C-rate equal to 100 corresponds to discharge for 0.6 min.

Cathode gave almost 80 % of initial capacity at discharge during 0.6 min.

3.2. The Impedance Characteristic Investigation of New Cathode Materials

Fig. 3 shows cathode impedance hodograph at different discharge levels. Resistance between charge transfer and capacity of double layer forms semi-circle in the range of average frequency on hodograph. System resistance is defined by the value of ohmic resistance at high frequency, more than 10 kHz.

Low impedance value and tendency to impedance value decreasing is observed in cathode cycling process.

The analysis of main process parameters changes at different potential allowed to define each parameter influence and to determine limiting process. The usage of equivalent pattern for three-electrode cell and the usage of special software for impedance hodograph analysis showed high agreement between initial data and spectrum calculated by the software. Standard deviation and squared deviation sum varied within the limit from $(2-5) \cdot 10^{-5}$ and 0.003–0.01 of cathode and all its impedance spectrum in all interval voltage.

Table 2 shows data from microstructure analysis of single-layered coating and cathode electrochemical investigation.

Table 1

Electrochemical cathode properties

Current rate, mA	Q_{disch} , mAh/g	C-rate	Discharge time, s
0.01	103.23	0.031	116129
0.05	100.00	0.156	23076
0.10	98.71	0.313	11501
1.00	93.55	3.125	1152
10.00	83.87	31.250	115
20.00	77.42	62.500	57
40.00	67.74	125.000	28
60.00	59.68	188.000	19
100.00	48.39	313.00	12
140.00	45.16	438.00	8

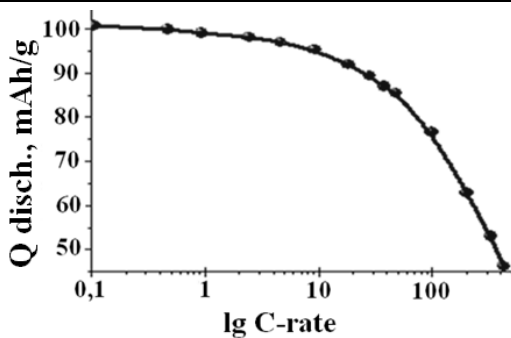


Fig. 2. Dependence between output specific discharge capacity and discharge rate

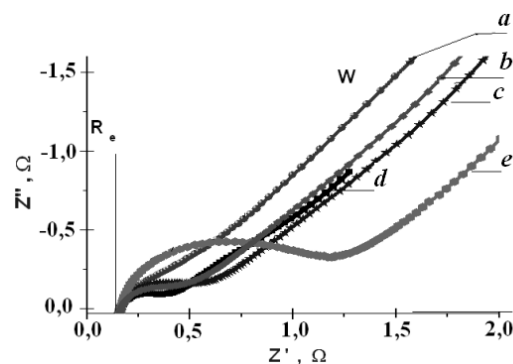


Fig. 3. Cathode impedance hodographs, obtained at different potentials, V: 4.225 (a), 4.075 (b), 4.025 (c), 4.125 (d), and 3.9125 (e)

Table 2

Structural components of single-layered coating LiMn₂O₄ on aluminum substrate and cathode electrochemical parameters

Coating parameters					Cathode electrochemical parameter		
Specific weight, mg/cm ²	Thickness, μm	Composition LiMn ₂ O ₄ %	Average diameter of spinel particles, μm	Volume ratio, %	Thickness, μm	Specific discharge capacity, mAh/g	Number of charge-discharge cycles*
2.0	16.0	97	1.00	25	41	105	495
1.5	12.0	97	0.85	28	37	105	550
1.0	8.0	98	0.67	35	33	108	625
0.5	4.0	99	0.48	47	16	110	775
0.1	0.8	100	0.35	55	13	115	828

Note: * before 80 % of capacity compared to the initial one was lost

Table 3

Structural components of multiple-layered composite carbon-ceramic coatings and cathode electrochemical parameters

Coating parameters									Cathode electrochemical parameters		
Specific weight, mg/cm ²	Thickness, μm	Composition LiMn ₂ O ₄ %	Average size, μm			Volume ratio, %			Thickness, μm	Specific discharge capacity, mAh/g	Number of charge-discharge cycles
			spinel particles	carbon fiber		spinel	carbone	pore			
				length	diameter						
4	40	96	1.50	9.2	2.0	50	27	23	75	103	475
6	60	93	1.75	8.8	2.7	58	24	18	95	99	438
7	70	91	1.87	7.0	3.2	65	20	15	105	94	406
8	80	89	2.00	5.9	7.0	72	16	12	115	85	357

The best electrochemical characteristics had cathodes with specific weight of single-layered coating 0.1 and 0.5 mg/cm² and the thickness of 0.8 and 4.0 μm, respectively. Thereby average diameter of spinel particles was 0.35 and 0.48 μm and pore volume ratio was 55 and 47 %, respectively. Such cathodes are characterized by high specific discharge capacity – 115 and 110 mAh/g. Number of charge-discharge cycles reached 800. While long-lasting cycling cathode capacity decreased lightly and made up 80 % from the initial one, cathode capacity did not change after 800–900 cycles.

Cathode capacity made up from 100 to 105 mAh/g at low discharge currents (0.01 and 0.05 mA). At high discharge currents (100 and 140 mA) cathodes are able to quick discharge and pass great number of charge-discharge cycles (> 800 cycles) due to high coating adhesion to substrate.

Table 3 shows data from microstructure analysis of composite carbon-ceramic coating on aluminum substrate and cathode electrochemical investigation.

The best results of investigated characteristics of composite carbon-ceramic coatings were established for cathodes with specific weight of 4.0 and 6.0 mg/cm² and

the thickness of 40 and 60 μm, respectively. Their structural characteristics are: average diameter of spinel particles 1.5 and 1.7 μm, average value of carbon fibre length – 9.2 and 8.8 μm, its diameter – 2.0 and 2.7 μm, porosity – 23 and 18 %, respectively. Specific discharge capacity made up 103 and 98.7 mAh/g, and number of charge-discharge cycles was 475 and 438 before 80 % of capacity was lost.

Dependence between output specific discharge capacity and discharge rate in the process of prolonged cycling is presented in Fig. 4. Curves represent operating parameters of cathodes on lithium-manganese spinel in three-electrode cell at different discharge current. *Curve a* (Fig. 4) represents arithmetic average of parameters values of 15 cathodes with active deposited material mass from 1.0 to 1.5 mg/sm².

Curves *b* and *c* in Fig. 4 represent changes of discharge capacity and cathode discharge rate after 300 and 800 cycles of charge-discharge in three-electrode cell. At low discharge current (< 0.1 C-rate), cathode capacity loss made up 6 % from initial after 300 cycle of charge-discharge and 20 % after 800 cycles of charge-discharge.

Deviation from the average value is shown by dashed line and depends on mass of deposited active layer

on cathode substrate in large state that forms cell electrolyte composition. Increase of active layer mass leads to curve slope to low C-rate values.

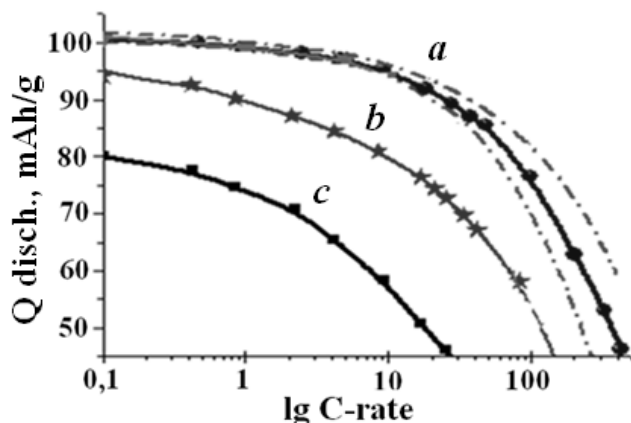


Fig. 4. Dependence between output cathode capacity and discharge rate: in initial stage (a), after 300 (b) and 800 (c) cycles

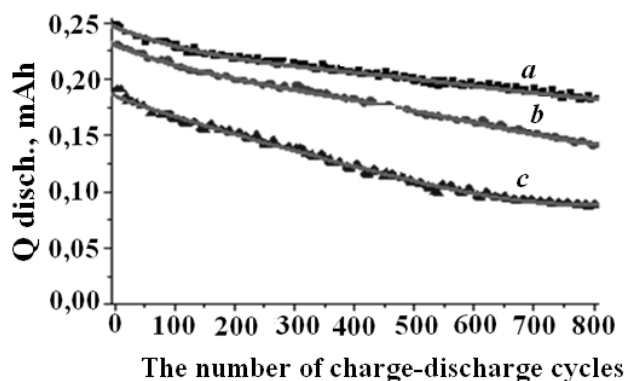


Fig. 5. Results of prolonged cathode cycling at different discharge currents, mA: 0.2 (a), 2 (b) and 20 (c)



Fig. 6. Prototype model of thin battery with new cathode on lithium-manganese spinel

As is shown from data provided in Fig. 4, capacity loss after 300 cycles at 100 discharge rate was 30 % of specific discharge capacity from the capacity at initial cycles at the same discharge current value. Thus, while cycling, decrease of specific capacity occurs.

Fig. 5 shows changes of cathode discharge capacity at prolonged cycling (800 cycles) by discharge currents 0.2; 2.0 and 20.0 mA, which corresponds to 0.8; 8.0 and 80 C-rate, respectively.

At prolonged (800 cycles) by current 0.2 mA, discharge capacity lowers less (around 6 %) than at cycling by discharge current 20 mA.

To check the operating efficiency of new cathodes and its applications in CSC for microsystem equipment an experimental prototype model of thin battery was manufactured (Fig. 6).

Battery consisted of electrodes 2 cm² in area, cathode based on single-layered LiMn₂O₄ coatings 9 μm in thickness, anode – thin silicon oxide coatings deposited on copper foil 15 μm thick and common electrolytes for lithium-iodine current sources (LiPF₆ salt in ethylene carbonate/dimethyl carbonate). Cathode weight was 1.5–2.0 and 0.8–1.0 mg/cm², anode weight – 0.8 mg/cm². Back side or substrates act simultaneously as current conductor and protective covering. Battery was sealed with polymer layer. Battery thickness was 50 μm.

Electrochemical investigation of thin batteries shows that they have high discharge capacity 0.07–0.09 mAh/g and specific energy 150–190 Wh/l. Discharge capacity can increase by means of using cathodes with higher weight of deposited active material and by means of increasing thickness of separator and current collector (of cathodes and anodes metallic substrate). Battery self-discharge amounted to 3 % for the first month.

4. Conclusions

1. Results of investigation of structure and electrochemical parameters of new cathodes on lithium-manganese spinel show that, in the process of its synthesis during deposition, spinel structure preserves on substrate and is capable of reversible electrochemical lithium intercalation/deintercalation:

- specific discharge capacity of deposited material was 115–105 mAh/g;
- galvanostatic cycling results show good cathode cycling, which keeps 800 and more charge-discharge cycles with decreasing discharge capacity up to 60 % from the initial;
- cathode impedance measurement shows its good ability to fast discharge: galvanostatic discharge up to 3.0 V during 12 s with current rate 100 mA allows to preserve 55–60 % of cathode capacity from the initial.

2. Regularities correlation of structure and electrochemical characteristics which allowed to optimize the structure of new cathode materials, likely to be used in chemical current sources, was determined.

3. Experimental investigations of pilot models parameters of thin batteries with new cathodes, represented as thin single-layered coatings, obtained by lithium-manganese spinel vapor deposition on aluminum substrate, show efficacy of its usage as CCS for microsystem equipment. Thin battery with overall thickness of 50 μm and square of 2 cm^2 demonstrated high value of specific capacity (0.07–0.09 mAh/g) and specific energy (150 and 190 Wh/l). Battery self-discharge was 3 % for the first month of investigation.

References

- [1] Kalinushkin E., Pinchuk S., Levko O. and Gorulia N.: *Metallovedenie i Termicheskaya Obrabotka Metallov*, 2006, **4**, 77.
- [2] Pinchuk S. and Levko O.: *Mezhdunar. Symposium "Ingenieriya Poverhnosti, Novye Poroshkovye Kompozicionnye Materialy, Svarka"*. Belarus, Minsk 2011, 154.
- [3] Pinchuk S. and Levko O.: 11 *Mezhdunar. Conf. "Novye Materialy i Technologii: Poroshkovaya Metallurgija, Kompozicionnye Materialy, Zashitnye Pokrytiia, Svarka"*. Belarus, Minsk 2014, 87.
- [4] MacDonald R.: *Impedance Spectroscopy. Emphasizing Solid Materials and Systems*. Wiley, New York 1987.
- [5] Yankovskyi A., Bessalova T. and Kedrinsky I.: *Electrokhimiya*, 1968, **4**, 1483.

СТРУКТУРА ТА ВЛАСТИВОСТІ КОМПОЗИТНИХ ВУГЛЕЦЬ-КЕРАМІЧНИХ ПОКРИТТІВ ДЛЯ КАТОДІВ СУЧАСНИХ ХІМІЧНИХ ДЖЕРЕЛ СТРУМУ

Анотація. В роботі встановлено взаємозв'язок між структурою та властивостями одношарових та багатошарових композитних вуглець-керамічних покриттів на основі літій-манганової шпінелі на алюмінієвій підкладці, що дало можливість оптимізувати структуру нових катодних матеріалів, перспективних для використання в хімічних джерелах струму. За допомогою вольтамперометрії та гальваностатичного циклування вивчені їх електрохімічні властивості, встановлена кількість речовини, що приймає участь в електрохімічних процесах, здатність до розряду великими струмами та працездатність при тривалому циклуванні.

Ключові слова: катодний матеріал, хімічне джерело струму, вольтамперне та гальваностатичне циклування.