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R. Apostolova^a, *E. Shembel*^a, *B. Markovsky*^b, *D. Aurbach*^b**COMPARATIVE BEHAVIOR OF A THIN-LAYER Co_9S_8 IN REDOX REACTIONS WITH LITHIUM IN POLYMER AND LIQUID ELECTROLYTES**^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine^b Bar-Ilan University, Ramat-Gan, Israel

Thin-layer Co_9S_8 electrodes were synthesized via the electrolysis technique onto aluminum foil and tested in redox reactions with lithium in polymer and liquid electrolytes. It was established the difference between the discharge characteristics of the Co_9S_8 -electrode in the polymer electrolyte with a gel-like consistency and in solid film electrolyte. The starting discharge capacity of Co_9S_8 both in a gel-like electrolyte and in a liquid electrolyte may reach 600 mA·h/g, which exceeds its theoretical value (544 mA·h/g). The reversible capacity of $\text{Co}_9\text{S}_8/\text{Li}$ in the polymer electrolyte is about 280–250 mA·h/g at the average discharge voltage of 1.40–1.45 V. During a long cycling, the discharge capacity of Co_9S_8 decreases both in the polymer electrolyte and in the liquid electrolyte. The discharge capacity of a metal-sulfide material/Li system in the polymer electrolyte is mainly reduced due to an increase in the polarization resistance of the lithium electrode caused by the disruption of its contact with the polymer electrolyte and a drying of the electrolyte in the porous space of the polymer gel matrix. The irreversible capacity of $\text{Co}_9\text{S}_8/\text{Li}$ can be reduced under the influence of an anionic polyelectrolyte (sodium polyacrylate) that was used as an additive to the electrolyte for the synthesis of Co_9S_8 . Norit conductive filler added to the electrolyte for the synthesis of Co_9S_8 was tested to improve the electrochemical characteristics of Co_9S_8 . A positive effect of Norit may be associated with the stabilization of the reversible capacity of Co_9S_8 electrodes that reaches 400 mA·h/g.

Keywords: Co_9S_8 , electrolysis, polymer and liquid electrolytes, Norit, discharge capacity, lithium cell.

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Introduction

Cobalt sulfides in lithium power sources with non-aqueous electrolytes are capable of multiple transformations with significant discharge capacity [1]. When Co_9S_8 is used in the redox reaction with lithium in the potential range of 3.00–0.02 V, its high starting capacity is reduced to 200 mA·h/g in the 20th cycle [2]. Parasitic processes are observed as in the case of CoS_2 cathodes [3], for which the starting discharge capacity (1280 mA·h/g) is higher than the theoretical one (871 mA·h/g).

Thin-layer sulfide Co_9S_8 can be obtained by electrolysis technique for the use in lithium and lithium-ion miniature power sources [4–6]. The solution composition and technological parameters of electrolysis for the preparation of Co_9S_8 in aqueous electrolyte are as follows (g/L): $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 25–30, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ 3–5; pH 3.4–2.8; electrolyte

temperature of 60–80°C, $i_{\text{cathode}}=2.5\text{--}4.0$ mA/cm², $S_{\text{cathode}}:S_{\text{anode}}=1:5$. A single-phase thin-layer Co_9S_8 -electrode with the structure of pentlandite was obtained on a plate made of stainless steel. The crystallite size of the synthesized material was about 49 nm as determined by the Debye-Scherrer method. Co_9S_8 film obtained by electrolysis after its heating to 600°C can be considered as a completely stable structure. The surface morphology of the Co_9S_8 electrodes showed the presence of agglomerates of tightly packed ball-like particles having an average size of 8–12 μm. They, in turn, consist of smaller submicron particles of 300–400 nm. The discharge capacity of the Co_9S_8 electrodes in the electrolyte of EC (Merck), DMC (Merck) (1:3 wt.), 1 mol/L LiClO_4 depends on the loading, increasing significantly at 7.3, 3.8 and 0.3 mg/cm² from 200–250 to 850–900 mA·h/g on the 20th cycle at 23°C

[4–6].

It should be mentioned that the electrochemical characteristics of Co_9S_8 prepared by the electrolysis from ionic liquid [7] coincide with the marked characteristics of the Co_9S_8 samples synthesized from an aqueous solution [4–6].

In this study, the thin-layer Co_9S_8 electrodes obtained by the electrolysis in aqueous solution were tested in redox reactions with lithium in polymer electrolytes (PE) that are considered as the most environmentally safe for lithium power sources. The performance of thin-layer Co_9S_8 electrodes was compared with their electrochemical behavior in a liquid electrolyte.

Experimental

Co_9S_8 electrodes were synthesized on aluminum foil by the cathodic reduction of aqueous solutions containing (g/L): cobalt sulfate 7.0–9.0, sodium thiosulfate 3.0–3.5 and sodium sulfide 1.0–1.5. The pH of the solutions was maintained at 3.0–3.2. The cathodic current density was equal to 2.5–4.0 mA/cm². The weight content of Co_9S_8 deposits varied from 1 mg/cm² (the thickness being 2 μm) to 36 mg/cm².

Charge-discharge cycling of Co_9S_8 electrodes was carried out using coin-type cells 2325 with a lithium counter-electrode in PE with a polymer matrix PVDF (polyvinylidene fluoride). PE was prepared by irrigation technology described briefly below. For the preparation of PE, we used a polymer PVdF Solef 21508, LiClO_4 (Iodobrom, Saki, Ukraine) and the following solvents: PC (propylene carbonate, Angarsk Chemical Reagents Plant, Russia) and THF (tetrahydrofuran, Labskan, Ireland). The constituents of PE (solvents, lithium salt, and polymer) were mixed, if necessary with heating, in a predetermined ratio and sequence. The resulting solution was poured on a thin-layer test electrode, forming a polymer solid film with a thickness of 30–60 μm or a viscous gel-like mass. All operations were performed in a glove box under a dry argon atmosphere. PEs were prepared as follows. A portion of the polymer was dissolved in a predetermined amount of solvent (THF), then a lithium salt was introduced. After its dissolution, a plasticizer polypropylene carbonate (PC) was added. The mass ratio of PVDF to 0.5 mol/L salt solution was 1.0:5.5, respectively. Subsequently, THF was removed by heating.

The components of the liquid electrolyte were as follows: ethylene carbonate (EC, Merck):dimethyl carbonate (DMC, Merck)=1:1 (wt.), and 1 mol/L LiClO_4 (Iodobrom). In the study of Co_9S_8 electrodes with carbon conductive filler, Norit A SUPRA USP

30 with a surface area of 1900 m²/g was added (2 g/L) to the base electrolyte for the synthesis of Co_9S_8 at pH 3.26. The electrolysis was conducted under the following conditions: electrolyte temperature of 60°C, cathode current density of 2.0–2.5 mA/cm², duration of electrolysis of 15 min, and the ratio $S_{\text{cathod}}:S_{\text{anod}}=1:5$.

The structure of the synthesized compounds was determined by X-ray diffraction phase analysis (DRON-2). Fourier transform infrared spectra of Co_9S_8 were recorded using a Magma FTIR spectrometer (Nicolet Inc.) in a CO_2 - and H_2O -free atmosphere of glove box using an atmospheric purification capacitor (Balston, Inc.).

The test objects were cycled in a galvanostatic discharge-charge process by means of the software test bench. The VoltaLab PGZ 301 analytical radiometer was used in kinetic studies of Co_9S_8 by cyclic voltammetry.

Results and discussion

According to the X-ray analysis of the deposits, Co_9S_8 with the structure of pentlandite (JCPDS 01-086-2273) was identified in the resulting synthesis products (Fig. 1). The maximum size of its crystallites in accordance with the Debye-Scherrer equation was 71 nm.

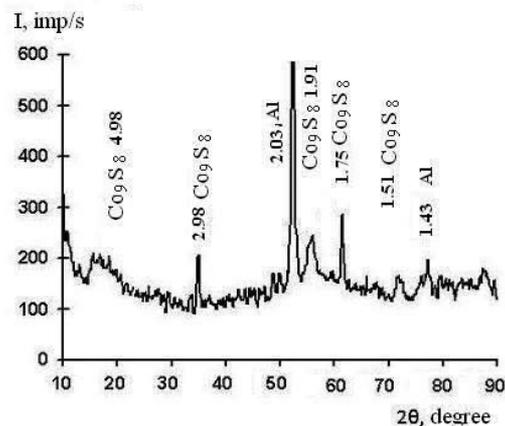


Fig. 1. X-ray diffraction pattern of the Co_9S_8 synthesized by the electrolysis on aluminum foil

Peaks of the FTIR spectra of deposits at the wave numbers of 433.77, 442.78 and 452.91 cm⁻¹ indicate the presence of Co_9S_8 in the as-synthesized products (Fig. 2). FTIR peaks at 575.61, 616.70, 685.37 and 711.26 cm⁻¹ most probably can be ascribed to the ions adsorbed on the surface of the deposits from the electrolyte for the synthesis of Co_9S_8 . They reflect the Co–O bonds of the cobalt oxide compounds and SO_4^{2-} ions [8].

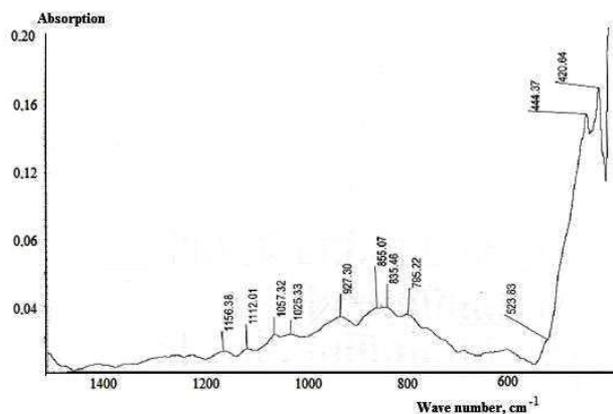


Fig. 2. FTIR spectrum of the as-prepared Co_9S_8 deposits

The discharge and charge profiles of Co_9S_8 electrode in PE and liquid electrolyte show that the mechanism of electrochemical transformations may be similar in both cases (Figs. 3 and 4).

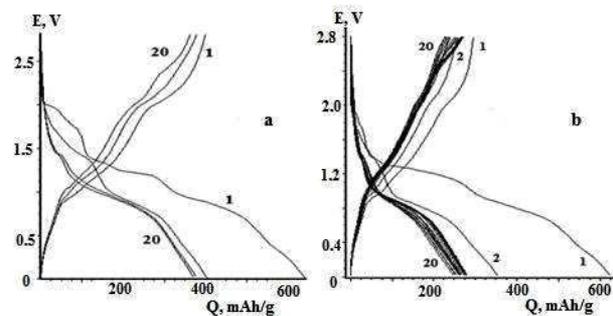


Fig. 3. Discharge-charge curves of Co_9S_8 -electrodes in the electrolytes: a – EC, DMC, 1 mol/L LiClO_4 ($m=3.0 \text{ mg/cm}^2$), b – PVdF-CTFE, EC, DMC, 1 mol/L $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ($m=1.4 \text{ mg/cm}^2$), $i_{\text{discharge}}=0.05 \text{ mA/cm}^2$, $i_{\text{charge}}=0.03 \text{ mA/cm}^2$. «m» stands for «sulfide mass»

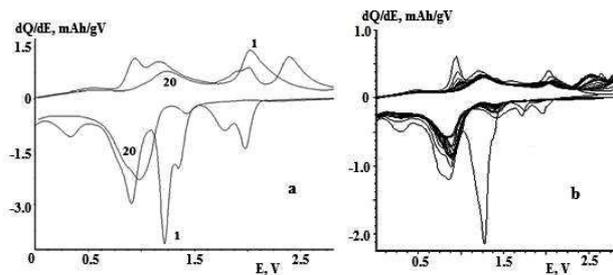


Fig. 4. The dependences of differential capacity of Co_9S_8 -electrodes on the electrode potential, obtained from Fig. 3 in liquid electrolyte (a) and PE (b), accordingly

The discharge capacity of $\text{Co}_9\text{S}_8/\text{Li}$ system with PE differs significantly in values in the first and subsequent cycles, just as it is observed with the

electrochemical conversion of Co_9S_8 in a liquid electrolyte. The starting capacity of Co_9S_8 may reach $600 \text{ mA}\cdot\text{h/g}$, which exceeds its theoretical capacity similar to that of CoS_2 sulfide [3]. The theoretical capacity of Co_9S_8 is equal to $544 \text{ mA}\cdot\text{h/g}$ according to the following reaction:



This excess is explained by the heterogeneity of the process associated with the significant specific contact surface of the nanometer active material and large Norit surface with the electrolyte.

The reversible capacity of $\text{Co}_9\text{S}_8/\text{Li}$ in PE is about $280\text{--}250 \text{ mA}\cdot\text{h/g}$. The discharge voltage in the first cycle is higher than that in the subsequent ones (Fig. 3). This can be explained by the increased resistance of the surface film formed on the sulfide in the first cycle, which transforms and stabilizes it in the subsequent cycles.

The irreversible capacity of Co_9S_8 electrodes can be reduced by the addition of an anionic polyelectrolyte, polyacrylate ($-\text{CH}_2-\text{CH}-\text{I}_n\text{COO}^-\text{Na}^+$) with a molecular mass of $M=1500000$ to the electrolysis solution. This surfactant was synthesized by polymerization of sodium acrylate in the presence of $\text{K}_2\text{S}_2\text{O}_8$. When the Co_9S_8 -electrode prepared in the presence of anionic surfactant, Na-polyacrylate, is cycled, the difference between the specific discharge capacity in the first and the second cycles decreases, as shown in Fig. 5.

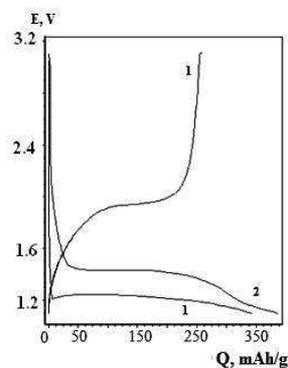


Fig. 5. Discharge-charge profile of the $\text{Co}_9\text{S}_8/\text{Li}$ system with the deposit on aluminum substrate obtained in the presence of anionic surfactant (0.04%). $T_{\text{treatment}}=180^\circ\text{C}$

It is important to compare the discharge characteristics of the Co_9S_8 -electrode in PE with a gel-like consistency and in a solid film electrolyte. The electrochemical characteristics of Co_9S_8 in a solid electrolyte are similar to those in PE (Figs. 6 and 7).

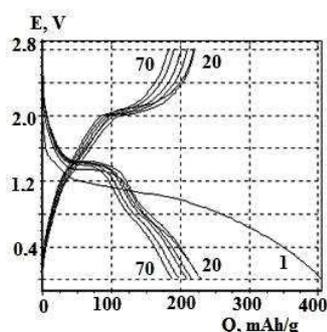


Fig. 6. Discharge-charge curves of Co_9S_8 /solid-like PE/Li system. $m=1.4 \text{ mg/cm}^2$; $i_{\text{disch}}=0.05 \text{ mA/cm}^2$; $i_{\text{charge}}=0.03 \text{ mA/cm}^2$. The numbers show the cycles numbers (1–70)

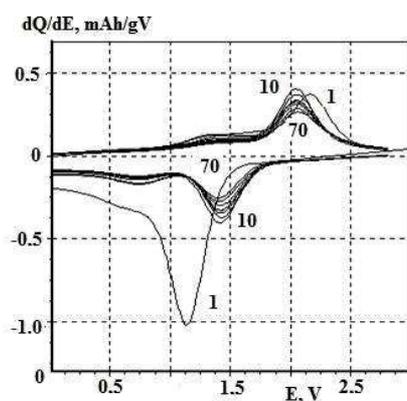


Fig. 7. Dependence of differential capacity of Co_9S_8 -electrode on electrode potential in a solid-like electrolyte in 1–70 cycles

The discharge-charge characteristics of Co_9S_8 with the same weight content of 1.4 mg/cm^2 in solid and gel-like electrolytes differ from each other. The difference is observed both in the starting curves and after cycling for 60–70 cycles. The discharge capacity of Co_9S_8 in the 10th cycle in a gel-like electrolyte exceeds that in a solid electrolyte (Fig. 3,b and Fig. 6). However, the irreversible capacity in a gel-like electrolyte significantly exceeds that in a solid electrolyte. The discharge voltage stably keeps at 1.4 V before moving to a lower voltage in a solid electrolyte. In a gel-like electrolyte, the voltage begins to decline from 1.4 V in the first cycle. In a gel-like electrolyte, the voltage platform of 1.4 V is almost leveled in the second cycle (Fig. 3,b).

When comparing differential capacity curves of specimens with the same weight content of Co_9S_8 (1.4 mg/cm^2), the difference between the processes that take place at around 1.4 V and 0.8 V in the used electrolytes is observed (Fig. 7 and Fig. 8). In Co_9S_8 -

electrodes, sulfide conversion occurred at around 1.4 V, whereas a maximum electrolyte conversion activity in redox reaction with Co_9S_8 can be seen at around 0.8 V. In a solid electrolyte (Fig. 7), a maximum sulfide conversion is observed at around 1.4 V, whereas a maximum electrolyte conversion activity at around 0.8 V in a gel-like electrolyte can be seen (Fig. 8).

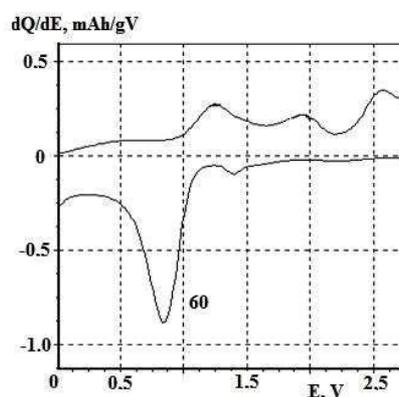


Fig. 8. Dependence of differential capacity of Co_9S_8 -electrode on electrode potential in a gel-like electrolyte in the 60th cycle

In a solid electrolyte at the 60th cycle, the main electrode process is a conversion of a sulfide compound, whereas it is an electrolyte reduction in a gel-like electrolyte. This can be explained by a lower electrochemical activity of the reduction of the solid phase electrolyte than that of the liquid electrolyte. In the solid electrolyte, the solubility of the electrochemically inactive lithium polysulfides, which can be formed when the sulfide compounds are distorted during cycling, is much lower than that in the liquid electrolyte.

Synthesis and study of electrolytic Co-sulfide reinforced with carbon filler Norit

Norit carbon material showed a positive effect on the electrochemical properties of LiMn_2O_4 spinel in a model lithium accumulator [9]. Therefore, Norit filler was tested in this study to improve the electrochemical characteristics of Co_9S_8 prepared by electrolysis.

Norit filler was used with micrometer-sized particles (Fig. 9) and a developed surface of $1900 \text{ m}^2/\text{g}$.

The dependence of the differential discharge capacity of a Co_9S_8 , Norit-electrode on the electrode potential is due to the inclusion of Norit in the electrolytic cobalt sulfide (Fig. 10). The curve reveals three phase transitions at the potentials of 0.19, 0.14 and 0.09 V. It is a reversible process.

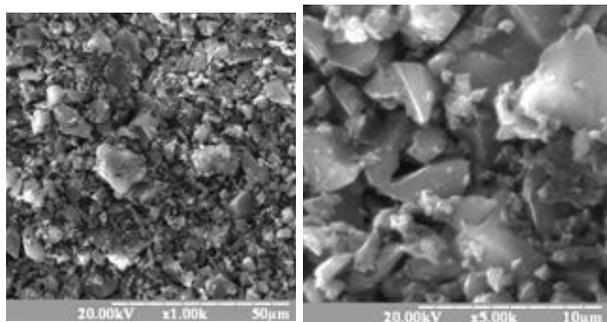


Fig. 9. SEM micrographs of the Norit surface

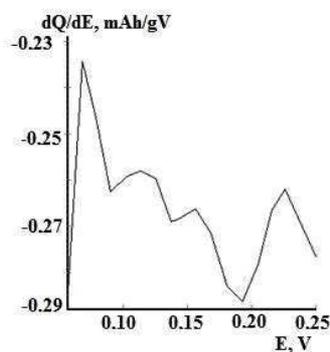


Fig. 10. Dependence of differential intercalation capacity of Co_9S_8 , Norit-electrode on the electrode potential in redox reaction with lithium in PE. $i_{\text{disch}}=0.05 \text{ mA/cm}^2$; $i_{\text{charge}}=0.03 \text{ mA/cm}^2$. The weight content of the deposit was equal to 36 mg/cm^2

Confirmation of the electrochemical participation of Norit in the indicated range of potentials in Fig. 10 is the absence of transients on the discharge curves of Co_9S_8 electrode without Norit filler [4]. In the starting curve of the redox reaction Co_9S_8 with lithium in the region of 0.5–0.0 V, a transition process is only detected at 0.3 V, which is related to the formation of a surface film on a sulfide material. It does not appear in all subsequent cycles. The transient processes in the region of 0.25–0.00 V are absent. The detected transients are presumably related to the electrochemical activity of surface functional groups on the Norit carbon material, which is subjected to an acid treatment [10]. Oxygen-containing functional groups determine the ion-exchange properties of the carbon material. During metal adsorption, ion exchange processes between a metal ion and surface functional groups (for example, carboxylic) are possible.

The implementation of redox adsorption is also possible, as a result of which a part of the metal ions is reduced to a metal [10]. Ion-exchange processes

with the participation of lithium ions and hydrogenions of functional groups can be associated with the transients that we discovered.

The discharge characteristics of the Co_9S_8 films were improved by the incorporation of the Norit filler into Co_9S_8 . From the discharge-charge curves reinforced with the Norit filler (Fig. 11 and Fig. 12), we can see that the capacity of the first discharge cycle is $760 \text{ mA}\cdot\text{h/g}$ and the reversible capacity is stabilized reaching a level of $400 \text{ mA}\cdot\text{h/g}$.

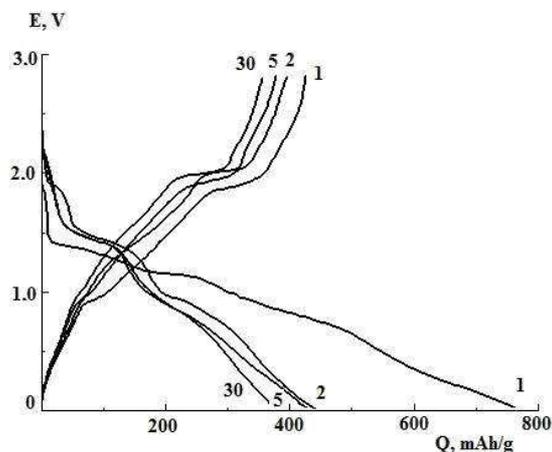


Fig. 11. Discharge-charge characteristics of Co_9S_8 , Norit-electrode in redox reaction with lithium in PE. $i_{\text{disch}}=0.05 \text{ mA/cm}^2$; $i_{\text{charge}}=0.03 \text{ mA/cm}^2$

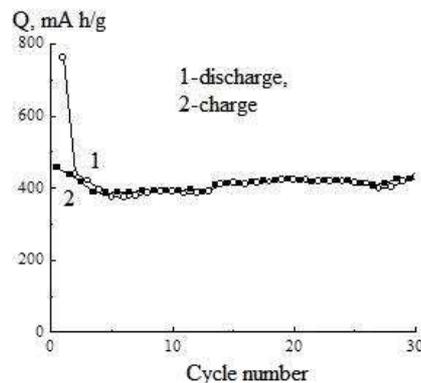


Fig. 12. Dependence of Co_9S_8 , Norit-electrode discharge capacity on the cycle number

Diffusion coefficient of Li^+ in Co_9S_8

Cyclic voltammetry method was used to determine the diffusion coefficient of lithium ions in Co_9S_8 (Fig. 13). The discharge capacity of the Co_9S_8 sample depends on the potential scan rate. As the potential scan rate increases, the capacity

decreases (Table). From the results obtained, we suggest that the cathodic and anodic processes are partially reversible in the specified scanning rate interval.

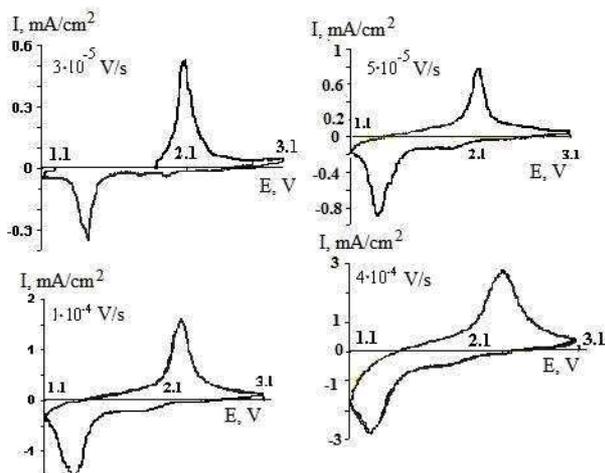


Fig. 13. Cyclic voltammograms of Co_9S_8 (5.6 mg/cm^2) at different potential scan rates

Charge-discharge capacities obtained depending on potential scan rate

ν , V/s	Q_{cathod} , mA·h/g	Q_{anod} , mA·h/g	$Q_{\text{cathod}}/Q_{\text{anod}}$
$3 \cdot 10^{-5}$	222	227	0.965
$5 \cdot 10^{-5}$	200	215	0.930
$1 \cdot 10^{-4}$	188	205	0.915
$3 \cdot 10^{-4}$	185	201	0.920

Cyclic voltammogram measured at the lowest potential scan rate ($3 \cdot 10^{-5} \text{ V/s}$) demonstrated peaks at the potentials of 1.42 and 2.02 V in the discharge and charge regions, respectively. A large difference between peak potentials (0.6 V) at such a low scan rate indicates a thermodynamic irreversibility rather than kinetic irreversibility of intercalation/deintercalation process. High values of the half-width potentials 0.91 V at the discharge and 0.98 V at the charge indicate the existence of a deviation of the equilibrium potential from the Nernst dependence [11].

In a certain interval of potential scan rate ($\nu^{0.5} \cdot 10^2 = 0.5 - 1.0$), the cathodic peak I_{peak} is linearly dependent on the scan rate (Fig. 14), indicating a diffusion controlled electrode process.

In the case of diffusion controlled electrode reactions, the peak current obeys the Randles-Shevchik equation:

$$I_p = 0.446n^{0.5}FS(F/RT)^{0.5}D^{0.5}\nu^{0.5}c_0, \quad (2)$$

where I_p is the peak current of the current-voltage curve (A); n is the number of electrons per Li^+ ion ($n=1$); S is the electrode surface (cm^2); D is the diffusion coefficient of Li^+ in the active material (cm^2/s); ν is the potential scan rate (V/s); C_0 is the concentration of the diffusing solid particles (mol/cm^3).

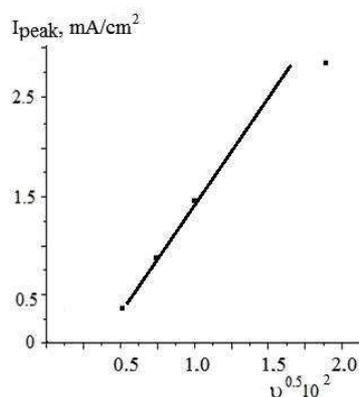


Fig. 14. Dependence of the cathodic current peak on the potential scan rate of Co_9S_8 electrode

Based on the slope of the given lines and equation (2), the average value of the diffusion coefficient of lithium was determined. The concentration of the diffusing solid particles was calculated based on both the density of the cathode material, which was equal to 5.52 g/cm^3 , and the maximum degree of the included Li^+ ions. The value of C_0 was 0.055 mol/cm^3 . The diffusion coefficient corresponding to 1.4 V at intercalation was found to be $2.65 \cdot 10^{-10} \text{ cm}^2/\text{s}$. This coefficient is the so-called «effective» one, since it is a characteristic of a porous macro-system in which a hindered diffusion of lithium ions is also accompanied by some kinetic restrictions of charge transfer through the phase boundaries and other processes.

During prolonged cycling, the discharge capacity of Co_9S_8 in PE also decreases in the redox reaction of electrolytically produced iron oxysulfide with lithium. As was established for iron oxysulfide with the help of dynamic impedance method [12], critical factors in reducing the discharge capacity of oxysulfide material are an increase in the polarization resistance of the lithium electrode, resulted from the disruption of its contact in the PE, and drying of the electrolyte in the porous space of the polymer gel matrix.

Conclusions

Co₉S₈ thin-films were synthesized by the electrolysis onto aluminum foil and tested in redox reactions with lithium in PEs and liquid electrolyte. The as-prepared cobalt sulfide has a pentlandite structure with a crystallite size of ~71 nm.

The starting capacity of Co₉S₈ in a gel-like PE and in a liquid electrolyte may reach 600 mA·h/g, exceeding its theoretical value (544 mA·h/g). The reversible capacity of Co₉S₈/Li in a solid PE is about 280–250 mA·h/g at the average discharge voltage of 1.40–1.45 V. During a long cycling, the discharge capacity of Co₉S₈ decreases in a gel-like PE and in a liquid electrolyte. In a solid electrolyte, the drop of capacitance is 0.3% per cycle after 70 cycles. Critical factors of the reduction in the discharge capacity of metal-sulfide material/PE/Li are an increase in the polarization resistance of the lithium electrode, resulted from the disruption of its contact with PE, and drying of the electrolyte in the porous space of the polymer gel matrix.

The irreversible capacity of Co₉S₈/Li can be reduced by the incorporation of an anionic polyelectrolyte, sodium polyacrylate, which was used as an additive to the electrolyte for the synthesis of Co₉S₈. Norit conductive filler added to the electrolyte for the synthesis of Co₉S₈ was tested to improve the electrochemical characteristics of Co₉S₈ electrodes. It was established that the reversible capacity of Co₉S₈ was stabilized at 400 mA·h/g for electrodes obtained with Norit conductive filler added in the electrolyte for synthesis. Improved electrochemical characteristics were explained by positive effects of Norit: an increase in the electrical conductivity of the active Co₉S₈+Norit mass and an increase in the adhesion of the deposit to the substrate.

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ПОРІВНЯННЯ ПОВЕДІНКИ ТОНКОШАРОВОГО Co₉S₈ В ОКИСЛЮВАЛЬНО-ВІДНОВНИХ РЕАКЦІЯХ З ЛІТІЄМ У ПОЛІМЕРНИХ І РІДКИХ ЕЛЕКТРОЛІТАХ

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Тонкошаровий Co₉S₈ було електролітично осаджено на алюмінію і досліджено в редокс-реакції з літієм у полімерному та рідкому електролітах. Було виявлено різницю між розрядними характеристиками Co₉S₈-електрода у полімерному електроліті з гелеподібною консистенцією та полімерному твердому електроліті. Стартова розрядна ємність Co₉S₈ в гелеподібному електроліті, а також у рідкому електроліті може досягати 600 mA·год/г, що перевищує його теоретичне значення 544 mA·год/г. Оборотна ємність Co₉S₈/Li в полімерному електроліті становить приблизно 280–250 mA·год/г при середній напрузі розряду 1,40–1,45 В. Під

час тривалого циклування розрядна ємність Co_9S_8 зменшується як у полімерному електроліті, так і в рідкому електроліті. Критичними факторами зниження розрядної ємності системи металево-сульфідний матеріал/Li в полімерному електроліті є збільшення опору поляризації літійового електрода внаслідок порушення його контакту з полімерним електролітом, а також висихання електроліту в поруватому просторі полімерної гелевої матриці. Незворотна ємність $\text{Co}_9\text{S}_8/\text{Li}$ може бути знижена під впливом аніонного поліелектроліту (натрій поліакрилат), який використовувався як добавка в електроліт при осадженні Co_9S_8 . Здійснено випробування електропровідного наповнювача Norit, який додавали в електроліт для синтезу Co_9S_8 для поліпшення електрохімічних характеристик осаджуваного сульфиду. Позитивний ефект Norit пов'язаний зі стабілізацією зворотної ємності електродів Co_9S_8 , що досягає 400 мА·год/г.

Ключові слова: Co_9S_8 , електроліз, полімерний і рідкий електроліти, Norit, розрядна ємність, Li-джерело струму.

COMPARATIVE BEHAVIOR OF A THIN-LAYER Co_9S_8 IN REDOX REACTIONS WITH LITHIUM IN POLYMER AND LIQUID ELECTROLYTES

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Thin-layer Co_9S_8 electrodes were synthesized via the electrolysis technique onto aluminum foil and tested in redox reactions with lithium in polymer and liquid electrolytes. It was established the difference between the discharge characteristics of the Co_9S_8 -electrode in the polymer electrolyte with a gel-like consistency and in solid film electrolyte. The starting discharge capacity of Co_9S_8 both in a gel-like electrolyte and in a liquid electrolyte may reach 600 mA·h/g, which exceeds its theoretical value (544 mA·h/g). The reversible capacity of $\text{Co}_9\text{S}_8/\text{Li}$ in the polymer electrolyte is about 280–250 mA·h/g at the average discharge voltage of 1.40–1.45 V. During a long cycling, the discharge capacity of Co_9S_8 decreases both in the polymer electrolyte and in the liquid electrolyte. The discharge capacity of a metal-sulfide material/Li system in the polymer electrolyte is mainly reduced due to an increase in the polarization resistance of the lithium electrode caused by the disruption of its contact with the polymer electrolyte and a drying of the electrolyte in the porous space of the polymer gel matrix. The irreversible capacity of $\text{Co}_9\text{S}_8/\text{Li}$ can be reduced under the influence of an anionic polyelectrolyte (sodium polyacrylate) that was used as an additive to the electrolyte for the synthesis of Co_9S_8 . Norit conductive filler added to the electrolyte for the synthesis of Co_9S_8 was tested to improve the electrochemical characteristics of Co_9S_8 . A positive effect of Norit may be associated with the stabilization of the reversible capacity of Co_9S_8 electrodes that reaches 400 mA·h/g.

Keywords: Co_9S_8 ; electrolysis; polymer and liquid electrolytes; Norit; discharge capacity; lithium cell.

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