

Electrochemical behaviour of LiMn_2O_4 and LiCoO_2 in water electrolyte

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Li-Ion Batteries can afford quite large energy densities based on organic electrolytes with highly toxic and flammable solvents and its preparation is complicated and expensive, partly because the electrolyte is moisture and air sensitive. Utilization of aqueous electrolytes in rechargeable lithium batteries will increase their safety, economical, and environmental issues. The electrochemical properties of LiMn_2O_4 and LiCoO_2 as positive electrode materials for Li-ion battery with water electrolytes against LiV_3O_8 as negative electrode were investigated. The used salts are 6M LiNO_3 and 2M Li_2SO_4 dissolved in distilled water. LiMn_2O_4 was prepared by conventional solid state reaction heating stoichiometric mixtures of LiNO_3 and MnO_2 at temperature under 650°C for 24 h. LiCoO_2 was obtained via sol-gel method with final thermal treatment at 800°C for 24 h. Lithium vanadate was prepared via solid state reaction. All materials are stable in the aqueous solution and intercalation/deintercalation of lithium ions occurs within the window of electrochemical stability of the water, which was determined using slow cycling voltammetry. Manganese spinel exhibit specific capacity of 99mAh.g^{-1} in 6M LiNO_3 and 94mAh.g^{-1} in 2M Li_2SO_4 water electrolyte, while its capacity in organic electrolyte is 135mAh.g^{-1} . The obtained capacities from lithium cobaltate in water electrolytes were 99mAh.g^{-1} and 79mAh.g^{-1} respectively while that in organic electrolyte is 145mAh.g^{-1} . The cycling behavior and specific capacity of these active compounds in electrochemical cell with vanadate as a negative active mass is not as stable as in organic electrolytes.

Key words: Manganese spinel, Lithium cobaltate, Water electrolyte, Li-ion Battery

INTRODUCTION

The present commercially available lithium ion batteries contain flammable organic liquid electrolyte, which are major safety problem [1]. In recent years, spinel LiMn_2O_4 has been intensively investigated as a promising candidate for positive materials for lithium-ion batteries (LIBs) due to its low cost, non-toxicity, environmental friendliness, easy preparation, excellent voltage profile, and operating safety characteristics [2,3]. The LiCoO_2 has provided a good balance between high energy density and good cyclability. The specific capacity of LiCoO_2 remains 160mAh.g^{-1} or less when it is charged up to 4.2 V, which is 60% of the theoretical capacity of 274mAh.g^{-1} for one electron reaction. Elevating the charging voltage beyond 4.2 V can be one promising approach to utilize more lithium ions in the LiCoO_2 and to increase the capacity and energy density of the lithium-ion batteries [4]. Aqueous Rechargeable Lithium Batteries (ARLB) can solve the safety problems in some extents, which can assemble the battery without gas protection and humidity control. The inorganic electrolyte is cheaper; the ion conductivity is two orders of magnitude higher than in the organic electrolyte. The capacity of LiCoO_2 and LiMn_2O_4 are well known and shown in our

pervious papers [5-7]. Especially, the ARLB is the green environmental protection battery indeed [8-13]. The manganese spinel LiMn_2O_4 is cited in the literature as suitable for application as active material in li-ion battery with LiNO_3 aqueous solution electrolyte [14-17]. The lithium cobaltate LiCoO_2 show also reversible Li intercalation in LiNO_3 water electrolyte [17]. In the literature LiNO_3 and Li_2SO_4 are cited as promising conducting salts for li-ion battery with water electrolyte [18, 19].

That preliminary information gives rise to the following questions:

-What is the better conducting salt for water electrolyte?

-What is the difference of capacity in water electrolyte and organic one?

-Is it possible to use LiMn_2O_4 as a negative active material?

The aim of the present work is to study the impact of synthesis methods, physicochemical characteristics, and electrochemical behaviour of LiMn_2O_4 and LiCoO_2 in LiNO_3 and Li_2SO_4 water electrolyte.

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EXPERIMENTAL

Preparation of active compounds, electrodes and electrolyte

Samples studied of LiMn_2O_4 were prepared by heating of stoichiometric mixture of MnO_2 and LiNO_3 in a nickel crucible for 12 to 48 h in the temperature range of 450-850 °C. The Li salt used is LiNO_3 , commercial product of Fluka, the manganese dioxide is CMD Faradizer M supplied by Sedema. The precursors were mixed, dried at 80°C for 12 h and milled. After that, the obtained mixture was preheated at 450°C for 12h and then heated finally on 650°C for 24h. The LiCoO_2 was prepared by sol-gel method by stoichiometric mixture of $\text{Co}(\text{NO}_3)_2$ and LiNO_3 . Appropriated amount of lithium and cobalt nitrate (Fluka) salts with the cationic ratio of Li:Co 1:1 were dissolved in distilled water and mixed well with an aqueous solution of citric acid (Fluka). Citric acid was used as a chelating agent in making a gel. The resultant solution was evaporated at 80°C with magnetic stirring until a transparent pink sol was formed. As water evaporated further, the sol turned into a viscous transparent pink gel. The gel obtained was heated at 800°C for 8 h. The inorganic electrolyte, which was used, was neutral saturated solution of LiNO_3 or Li_2SO_4 (Fluka) in distilled water.

Electrochemical measurements were performed in a three-electrode glass test cell containing 6 M LiNO_3 or 2M Li_2SO_4 water electrolyte. The active mass of the test electrodes was a mixture of tested active electrode materials studied and teflonized acetylene black at 1:1 ratio by weight. After that test, electrodes were formed by pressing 25 $\text{mg}\cdot\text{cm}^{-2}$ of thus prepared mixture onto an expanded nickel grid at a pressure of 3t. cm^{-2} .

Characterization techniques

Cyclic voltammetry (CV) was performed with an Arbin 320 potentiostat/galvanostat (Arbin Instruments Co.) in a three-electrode glass cell at 200 and 50 $\mu\text{V s}^{-1}$ scan rate in various voltage ranges, using LiMn_2O_4 or LiCoO_2 as working electrode, counter electrode were LiV_3O_8 , LiCoO_2 and LiMn_2O_4 , and reference electrodes Ag/AgCl , respectively. X-ray analysis was carried out on a Philips APD 15 diffractometer with $\text{Cu K}\alpha$ radiation.

RESULTS AND DISCUSSIONS

Fig. 1(a) shows the XRD patterns of LiMn_2O_4 samples having the spinel structure without any impurity phases, which belongs to Fd3m face cubic crystal system (ICSD, no. 087775). In this crystal structure, lithium atom occupies the tetragonal 8a

position, manganese atom occupies 16d position, and oxygen atom is in the position of 32e.

In Fig. 1(b) X-ray diffraction patterns for LiCoO_2 obtained by nitrate gel treated at 800°C for 24h as described above. The peaks marked as (#) correspond to Co_3O_4 impurity.

The diffraction pattern shows clear (006)/(102) peaks and (018)/(110) split peaks indicating a perfect layered-structure for LiCoO_2 [19]. The pattern of LiCoO_2 prepared at 800°C comprises a major LiCoO_2 phase crystallizing in rhombohedral structure with a small amount of Co_3O_4 as impurity.

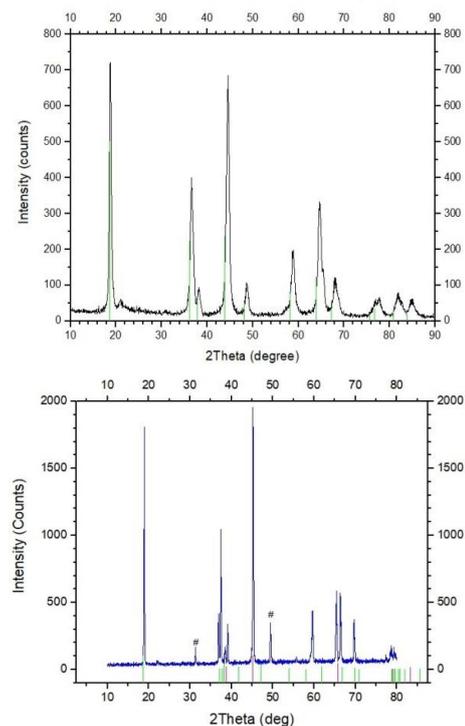


Fig. 1. The X-ray diffraction pattern of the materials. (a) LiMn_2O_4 and (b) LiCoO_2

Fig.2 shows the SEM micrographs of the LiMn_2O_4 sample synthesized by solid-state reaction from MnO_2 Faradizer M (CMD) and LiNO_3 heated at 850°C a) and b) and heated at 650°C c) and d) for 24h. From Fig. 2a and 2b it is seen that the resultant LiMn_2O_4 sample mainly consists of large quantities of particles with a size about 1 μm . Fig.2b gives a high-magnification image of several selected LiMn_2O_4 particles. It is found that the prepared LiMn_2O_4 sample is composed of particles with well-developed octahedral shapes [20, 21]. In addition, very few quasi-spherical particles can also be observed in Fig. 2c. However, a high-magnification micrograph in Fig. 2d indicates the outer part of this quasi-spherical LiMn_2O_4 particle has been evolved to many small polyhedral particles, suggesting better electrochemical performance.

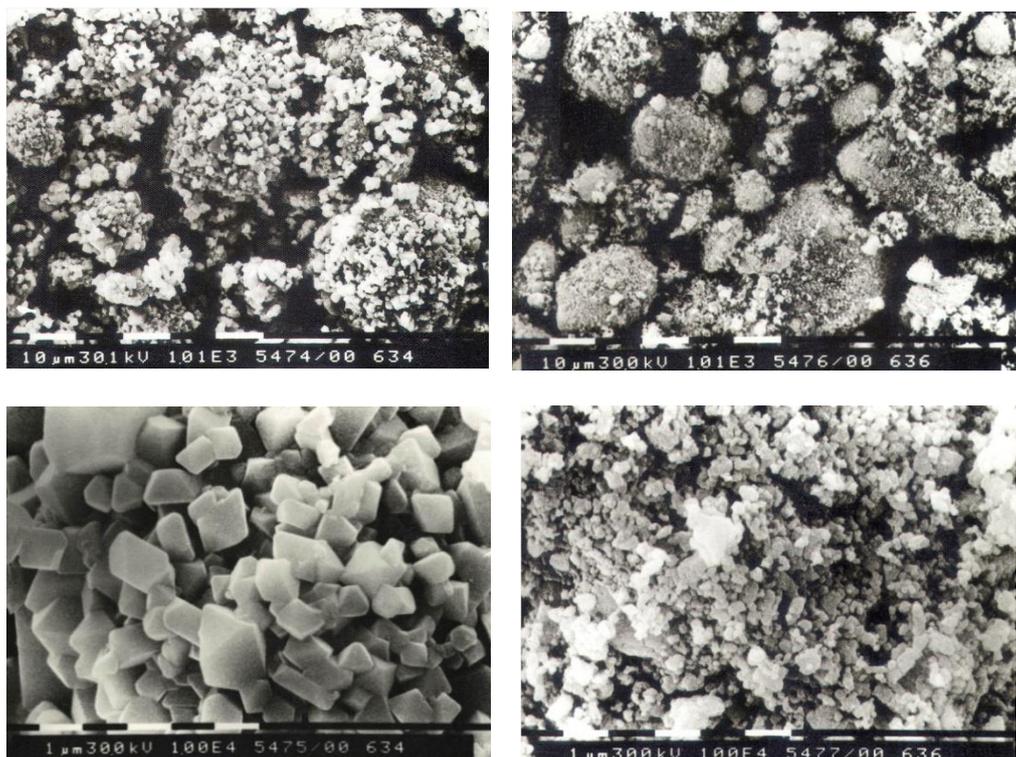


Fig.2 EM images of the LiMn_2O_4 synthesized by the solid-state reaction at 850°C a), b) and at 650°C c), d) for 24h from -0.6 to 0.02V vs. Ag/AgCl using two different aqueous electrolytes, 6M

LiNO_3 and 2M Li_2SO_4 . This involved the use of a LiV_3O_8 as a counter electrode. The results are shown on Fig.4, Fig.5 and Fig.6. The scan rates were rather low, $50\mu\text{V}\cdot\text{s}^{-1}$. In all cases, an electrochemical process was clearly observed. The electrochemical behavior of LiMn_2O_4 in 6M LiNO_3 and in 2M Li_2SO_4 is very close. The specific capacities in two water electrolytes are almost the same as the nitrate is slightly higher, respectively, $99\text{mAh}\cdot\text{g}^{-1}$ and $94\text{mAh}\cdot\text{g}^{-1}$, which correspond to 80% of the theoretical capacity of the material. The material works in the range of electrochemical stability of water, the evolution of O_2 starting after 1.15V (Fig.4).

Fig.3 shows SEM images of the LiCoO_2 synthesized by sol-gel method a) and by solid state reaction - SSR b). It is clear that both materials are characterized by good crystallinity and have similar morphology. As can be seen from Fig.3, the resulting materials are not monodispersed and consist of both particles of less than $1\mu\text{m}$ and agglomerates of about $1\text{-}2\mu\text{m}$. Better

dispersion of the precursor particles in the sample sol-gel method results in particle size reduction (Figure 3b).

To understand the electrochemical behavior of LiCoO_2 and LiMn_2O_4 in aqueous solutions, we performed voltammograms from -0.2 to 1.6V and

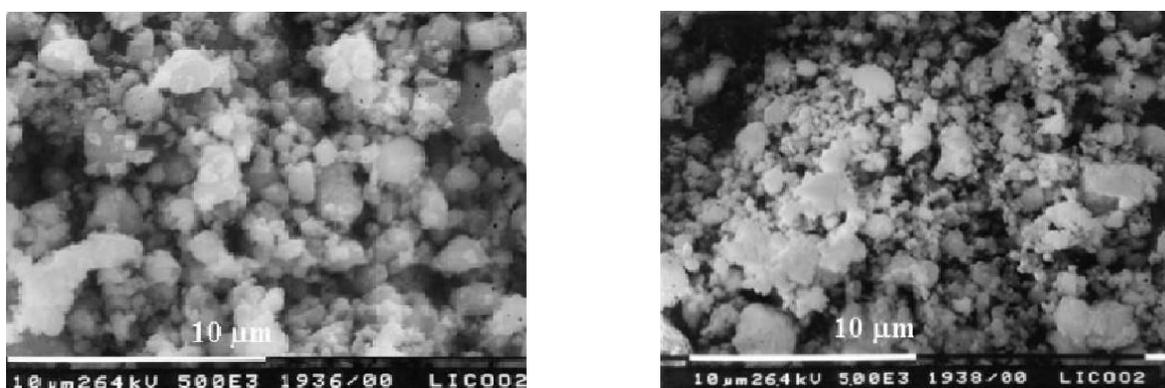


Fig. 3. SEM images of the LiCoO_2 synthesized by sol-gel method treated at 800°C a) and SSR at 650°C b) for 24h

Using 6M LiNO_3 as electrolyte, Ag/AgCl as reference electrode and scan rate of $50 \mu\text{V}\cdot\text{s}^{-1}$ the first peak of Li^+ ions extraction appears at 0.92V and the corresponding insertion peak is located at 0.9V. The second peak of extraction, was at 1.05V and peak of insertion was at 1.01V and the specific capacity of 99 mAh g^{-1} . Observed difference between both couple of peaks is only 20-30mV that means the processes are in quasi equilibrium (Fig.4a). The CV carried out in the same conditions but with $200 \mu\text{V}\cdot\text{s}^{-1}$ showed difference of 50mV and almost the same specific capacity ($95 \text{ mAh}\cdot\text{g}^{-1}$) which indicate a fast electrochemical process for this material. On the Fig. 4b are shown the curves

of works of LiMn_2O_4 in Li_2SO_4 with scan rate $50 \mu\text{V}\cdot\text{s}^{-1}$. The specific capacity is 94 mAh g^{-1} and all peaks are shifted with 100 mV to the potential of reference electrode in comparison with this in LiNO_3 , this is most probably due to the nature of electrolyte. This shifting to the lower potentials reduces probability of O_2 evolution. The last electrochemical system realized in real cell will work more stable and safety. The capacity of delithiation (lithium extraction) is little higher using LiNO_3 (in both rates) than those of delithiation in Li_2SO_4 cause of proximity of peaks to the evolution of O_2 in LiNO_3 electrolyte.

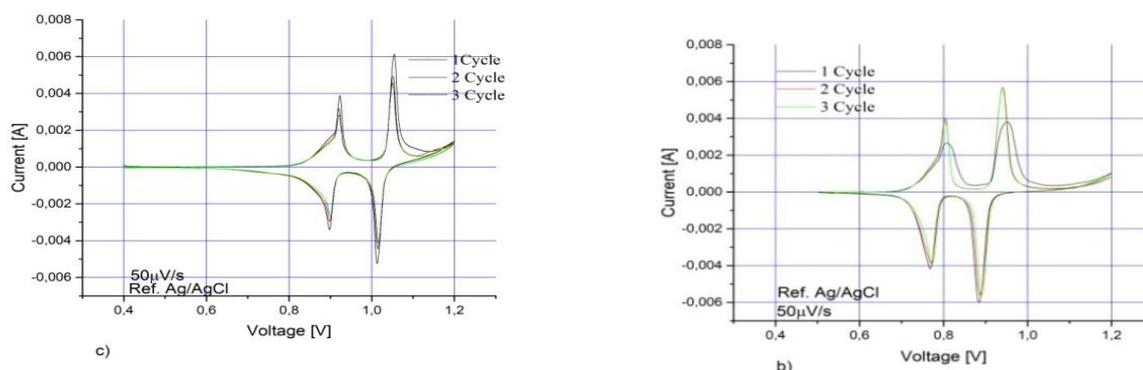


Fig.4. Cyclic voltammograms of LiMn_2O_4 synthesized by SSR method at 650°C in 6M saturated aqueous LiNO_3 , a), in 2M Li_2SO_4 b) scan rate $50 \mu\text{V}\cdot\text{s}^{-1}$.

Fig.5 shows cyclic voltammograms of LiCoO_2 . In the first cycle of the sol-gel-synthesized LiCoO_2 , a deintercalation peak at 0.92V and intercalation peak at 0.67V were observed (Fig.5a). These potency values are typical of the LiCoO_2 presented. In the second cycle, the peak potential values of deintercalation/intercalation are respectively 0.7 and 0.9V. The value of the second peak of the potential is higher than that of the first. This polarization difference is most likely due to rearrangement of the structure after the first cycle. The voltammogram in Li_2SO_4 shows that deintercalation peaks were at 0.76V and the intercalation were at 0.66V. The difference is about 50 mV. The process of extraction of Li^+ in Li_2SO_4 is easier compared to process in LiNO_3 (Fig.5b). The specific capacities in the two water electrolytes are $99\text{mAh}\cdot\text{g}^{-1}$ and $79\text{mAh}\cdot\text{g}^{-1}$ respectively for LiNO_3 and Li_2SO_4 , which is 68% of the theoretical capacity of the material.

The manganese spinel LiMn_2O_4 has two voltage plateaus at 3 and 4 V vs. Li, both of them located in the electrochemical window of aqueous electrolyte.

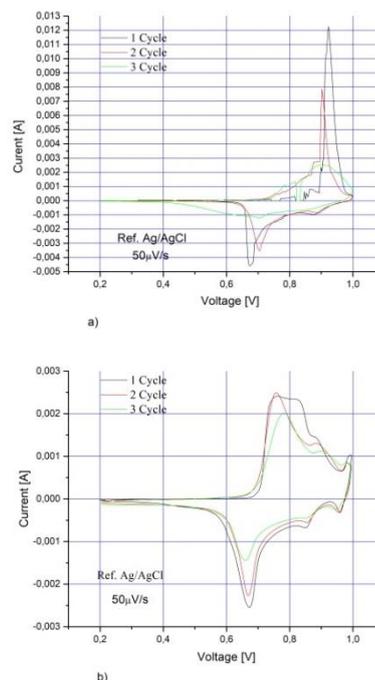


Fig.5 Cyclic voltammograms of LiCoO_2 as synthesized by sol-gel method and treated at temperature 800°C in 6M saturated aqueous LiNO_3 a) and 2M Li_2SO_4 ; scan rate was $50 \mu\text{V}\cdot\text{s}^{-1}$.

Therefore, LiMn_2O_4 could be utilized as both the cathode and anode in such an aqueous cell. We focused on the performance of the aqueous negative active material. The results are shown in Fig. 6. We present voltammograms within 0.2 to -0.6V vs. Ag/AgCl in the lithium nitrate aqueous solutions. This include, the use of a LiCoO_2 (Fig.6 a)) and LiMn_2O_4 (Fig.6 b) as counter electrode.

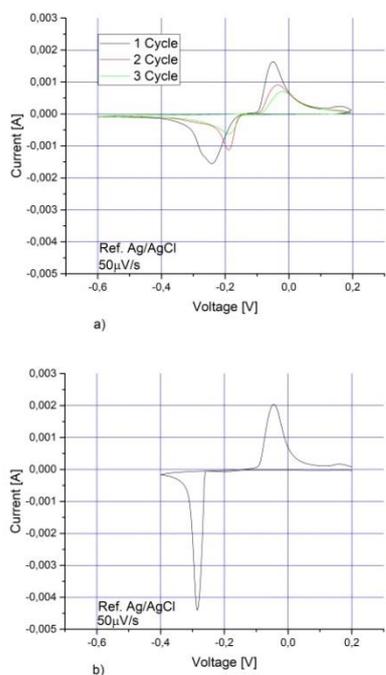


Fig. 6 Cyclic voltammograms of LiMn_2O_4 for negative electrode in 6M saturated aqueous LiNO_3 vs. LiCoO_2 as counter electrode a) and vs. LiMn_2O_4 as counter electrode b); scan rate was $50 \mu\text{Vs}^{-1}$

Fig.6 a) shows use of spinel LiMn_2O_4 as anode material. In the first cycle an intercalation peak at -0.25V and deintercalation peak at -0.048V were observed. In second cycle, the peaks are shifted to -0.19 and -0.035V and in the third cycle the peaks position were 0.19 and -0.14V. In the beginning is observed polarization of electrode, but in the next cycles the process of charge/discharge becomes stable. Charge capacity in the first cycle was 40mAh.g^{-1} and the discharge capacity - 32mAh.g^{-1} . In second cycle the values were 26mAh.g^{-1} and 21mAh.g^{-1} and in the third cycle - 21mAh.g^{-1} and 16mAh.g^{-1} . The efficiency is about 80% from the theoretical one that means the material is stable and work good.

Fig.6 b) shows the rechargeable lithium-ion cell with LiMn_2O_4 as a use of spinel LiMn_2O_4 as anode material, working and counter electrodes. In this way, we have fully symmetric cell with same active electrode materials as cathode and anode. The intercalation peak appears at -0.28 V and the deintercalation is at -0.043V. The charge capacity is

49mAh.g^{-1} and the discharge is 41mAh.g^{-1} , values very close each other. In reality, the discharge capacity is exactly 84% from the charge capacity.

CONCLUSION

The electrochemical characteristics of LiMn_2O_4 and LiCoO_2 used as cathode were studied in aqueous electrolyte containing lithium nitrate or sulfate with respect to its use as a new kind of rechargeable battery system. Cyclic voltammetry showed that spinel LiMn_2O_4 and LiCoO_2 reversibly intercalated/deintercalated Li^+ ions at potentials lower than the potentials of hydrogen or oxygen evolution in present aqueous solution with neutral pH.

The use of spinel and cobaltate as a positive active material for rechargeable battery delivers $95\mu\text{mAh.g}^{-1}$ and $99\mu\text{mAh.g}^{-1}$ discharge capacity. The capacity of cobaltate is lower in sulfate solution - 79mAh.g^{-1} . The use of manganese spinel LiMn_2O_4 as anode were investigate against LiCoO_2 as counter electrode in nitrate solution. This electrochemical system is stable but the discharge capacity was very low - 32mAh.g^{-1} .

The experiments show that the capacity in lithium nitrate is higher but the process of extraction of Li^+ is easier in sulfate. A symmetric electrochemical system based on manganese spinel in LiNO_3 electrolyte was tested for the first time and shows very promising results for large-scale energy storage and energy conversion.

The cost of the aqueous cell will be lower than that of conventional Li-ion battery cell, because electrode and electrolyte materials are not expensive and toxic compared with those used in conventional lithium ion batteries. The assembling process is simple, environmental friendly and trouble-free.

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ЕЛЕКТРОХИМИЧНИ СВОЙСТВА НА LiMn_2O_4 И LiCoO_2 ВЪВ ВОДНИ ЕЛЕКТРОЛИТИ

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(Резюме)

Литиево-йонните батерии базирани на органичен електролит дават възможност за постигане на големи енергийни плътности. Тези електролити представляват силно токсични и запалими разтворители, а подготовка им е сложна и скъпа, отчасти защото са чувствителни към влагата от въздуха. Използването на водни електролити в акумулаторни литиево-йонни батерии ще увеличи безопасността, екологичността им и ще намали стойността им. Разгледани са електрохимичните свойства на LiMn_2O_4 и LiCoO_2 като положителни електроди за литиево-йонна батерия с воден електролит срещу LiV_3O_8 като отрицателен електрод. Използваните електролити са 6M LiNO_3 и 2M Li_2SO_4 , разтворени в дестилирана вода. LiMn_2O_4 е получен чрез приготвяне на стехиометрична смес от LiNO_3 и MnO_2 в твърдо състояние и нагряване при температура 650°C в продължение на 24 часа. LiCoO_2 се получава чрез зол-гел метод с крайно термично третиране при 800°C в продължение на 24 часа. Литиевият ванадат се получава чрез твърдофазен синтез. Всички материали са стабилни във водния разтвор и интеркалацията/деинтеркалацията на литиевите йони се извършва в прозореца на електрохимична стабилност на водата, който се определя при използване на бавна циклична волтаметрия. Манганоксидният шпинел има специфичен капацитет от 99 mAh.g^{-1} в 6M LiNO_3 и 94 mAh.g^{-1} в 2M Li_2SO_4 воден електролит, докато неговият капацитет в органичния електролит е 135 mAh.g^{-1} . Полученият капацитет от литиев кобалтат във водните електролити е съответно 99 mAh.g^{-1} и 92 mAh.g^{-1} , докато този в органичния електролит е 145 mAh.g^{-1} . Цикличното поведение и специфичният капацитет на тези активни материали са изследвани в електрохимичните клетки и като отрицателна активна маса.

Ключови думи: манганов шпинел, литиев кобалтат, воден електролит, литиево-йонна батерия