Electrochemical behaviour of LiMn$_2$O$_4$ and LiCoO$_2$ in water electrolyte

T. Petkov$^{1,*}$, T. Stankulov$^2$, K. Banov$^{1,2}$, and A. Momchilov$^2$

$^1$University of Chemical Technology and Metallurgy – UCTM, bul. “Kl. Ohridski” N:8, 1756 Sofia
$^2$IEES, ”Acad. E. Budevski” – BAS, “Acad. G. Bonchev” str. BL10, IEES-BAS, 1113 Sofia

Received September 11, 2017; Accepted October 09, 2017

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$_2$O$_4$ and LiCoO$_2$ as positive electrode materials for Li-ion battery with water electrolytes against LiV$_2$O$_4$ as negative electrode were investigated. The used salts are 6M LiNO$_3$ and 2M Li$_2$SO$_4$ dissolved in distilled water. LiMn$_2$O$_4$ 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$_2$SO$_4$ 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 behaviour 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, Lithiumcobaltate, 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$_2$O$_4$ 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% at 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$SO$_4$ 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$_2$O$_4$ 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$_2$O$_4$ and LiCoO$_2$ in LiNO$_3$ and Li$_2$SO$_4$ water electrolyte.

* To whom all correspondence should be sent.
E-mail: todorvp@abv.bg

© 2018 Bulgarian Academy of Sciences, Union of Chemists in Bulgaria
EXPERIMENTAL

Preparation of active compounds, electrodes and electrolyte

Samples studied of LiMn$_2$O$_4$ 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 12 h and then heated finally on 650°C for 24 h. The LiCoO$_2$ was prepared by sol-gel method by stoichiometric mixture of Co(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 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$_2$SO$_4$ (Fluka) in distilled water.

Electrochemical measurements were performed in a three-electrode glass test cell containing 6 M LiNO$_3$ or 2 M Li$_2$SO$_4$ water electrolyte. The active mass of the test electrodes was a mixture of tested active electrode materials and teflonized acetylene black at 1:1 ratio by weight. After that test, electrodes were formed by pressing 25 mg cm$^{-2}$ of thus prepared mixture onto an expanded nickel grid at a pressure of 3 t 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 μV s$^{-1}$ scan rate in various voltage ranges, using LiMn$_2$O$_4$ or LiCoO$_2$ as working electrode, counter electrode were LiV$_3$O$_8$, LiCoO$_2$, and LiMn$_2$O$_4$, and reference electrodes Ag/AgCl, respectively. X-ray analysis was carried out on a Philips APD 15 diffractometer with Cu Kα radiation.

RESULTS AND DISCUSSIONS

Fig. 1(a) shows the XRD patterns of LiMn$_2$O$_4$ samples having the spinel structure without any impurity phases, which belongs toFd3m 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 32c.

In Fig. 1(b) X-ray diffraction patterns for LiCoO$_2$ obtained by nitrate gel treated at 800°C for 24 h as described above. The peaks marked as (#) correspond to Co$_3$O$_4$ impurity.

The diffraction pattern show 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$_3$O$_4$ as impurity.
Fig. 2 EM images of the LiMn$_2$O$_4$ synthesized by the solid-state reaction at 850°C a), b) and at 650°C c), d) for 24h

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 1μm and agglomerates of about 1-2μm. 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$_2$O$_4$ in aqueous solutions, we performed voltammograms from -0.2 to 1.6V and from -0.6 to 0.02V vs.Ag/AgCl using two different aqueous electrolytes, 6M LiNO$_3$ and 2M Li$_2$SO$_4$. This involved the use of a LiV$_3$O$_8$ as a counter electrode. The results are shown on Fig. 4, Fig. 5 and Fig. 6. The scan rates were rather low, 50μV.s$^{-1}$. In all cases, an electrochemical process was clearly observed. The electrochemical behavior of LiMn$_2$O$_4$ in 6M LiNO$_3$ and in 2M Li$_2$SO$_4$ is very close. The specific capacities in two water electrolytes are almost the same as the nitrate is slightly higher, respectively, 99mAh.g$^{-1}$ and 94mAh.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. 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 $\mu$Vs$^{-1}$ 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 $\mu$V.s$^{-1}$ showed difference of 50mV and almost the same specific capacity (95 mAh.g$^{-1}$) which indicate a fast electrochemical process for this material. On the Fig. 4b are shown the curves of works of LiMn$_2$O$_4$ in Li$_2$SO$_4$ with scan rate 50 $\mu$V.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$_2$SO$_4$ cause of proximity of peaks to the evolution of O$_2$ in LiNO$_3$ electrolyte.

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$_2$SO$_4$ 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$_2$SO$_4$ is easier compared to process in LiNO$_3$ (Fig.5b). The specific capacities in the two water electrolytes are 99mAh.g$^{-1}$ and 79mAh.g$^{-1}$ respectively for LiNO$_3$ and Li$_2$SO$_4$, which is 68% of the theoretical capacity of the material.

The manganese spinel LiMn$_2$O$_4$ has two voltage plateaus at 3 and 4 V vs. Li, both of them located in the electrochemical window of aqueous electrolyte.
Therefore, LiMnO₄ 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 LiCoO₂ (Fig.6 a)) and LiMn₂O₄ (Fig.6 b) as counter electrode.

Fig. 6 Cyclic voltammograms of LiMn₂O₄ for negative electrode in 6M saturated aqueous LiNO₃ vs. LiCoO₂ as counter electrode a) and vs. LiMn₂O₄ as counter electrode b); scan rate was 50 µVs⁻¹

Fig.6 a) shows use of spinel LiMn₂O₄ 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 positions 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 26 mAh.g⁻¹ and 21 mAh.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 LiMn₂O₄ as a use of spinel LiMn₂O₄ 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 49 mAh.g⁻¹ and the discharge is 41 mAh.g⁻¹, values very close each other. In reality, the discharge capacity is exactly 84% from the charge capacity.

CONCLUSION

The electrochemical characteristics of LiMn₂O₄ and LiCoO₂ 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 LiMn₂O₄ and LiCoO₂ 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±mAh.g⁻¹ and 99±mAh.g⁻¹ discharge capacity. The capacity of cobaltate is lower in sulfate solution – 79 mAh.g⁻¹. The use of manganese spinel LiMn₂O₄ as anode were investigate against LiCoO₂ as counter electrode in nitrate solution. This electrochemical system is stable but the discharge capacity was very low – 32 mAh.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 LiNO₃ 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.

REFERENCES

T. Petkov et al.: Electrochemical behaviour of LiMn$_2$O$_4$ and LiCoO$_2$ in water electrolyte


ЕЛЕКТРОХИМИЧНИ СВОЙСТВА НА LiMn$_2$O$_4$ И LiCoO$_2$ ВЪВ ВОДНИ ЕЛЕКТРОЛИТИ

Т. Петков$^1$, Т. Стаикулов$^2$, К. Банов$^{1,2}$, А. Момчилов$^2$

$^1$Химикотехнологичен и металургичен университет, бул. "Климент Охридски" 8, 1756 София, България
$^2$Институт по обща и неорганична химия, Българска академия на науките, ул. "Акад. Георги Бончев" бул. 11, 1113 София, България

Постъпила на 11 септември, 2017 г.; приета на 09 октомври, 2017 г.

(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$_2$O$_4$ и LiCoO$_2$ като положителни електроди за литиево-йонна батерия с воден електролит срещу LiV$_3$O$_8$ като отрицателен електрод. Използваните електролити са 6M LiNO$_3$ и 2M Li$_2$SO$_4$, разтворени в дестилирана вода. LiMn$_2$O$_4$ е получена 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 интеркалация/деинтеркалация на литиевите йони се извършва в прозореца на електрохимична стабилност на водата, който се определя при използване на бавна циклична волтаметрия. Мангансоединеният шпинел има специфичен капацитет от 99 mAh.g$^{-1}$ в 6M LiNO$_3$ и 94 mAh.g$^{-1}$ в 2M Li$_2$SO$_4$ воден електролит, докато неговият капацитет в органичния електролит е 135 mAh.g$^{-1}$. Полученият капацитет от литиев кобалтат във водни електролити е съответно 99 mAh.g$^{-1}$ и 92mAh.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: мангансов шпинел, литиев кобалтат, воден електролит, литиево-йонна батерия