

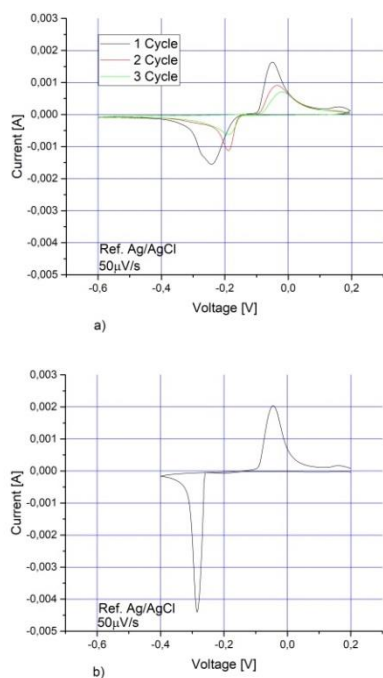








Therefore,  $\text{LiMn}_2\text{O}_4$  could be utilized as both the cathode and anode in such an aqueous cell. We focused on the performance of the aqueous negative active material. The results are shown in Fig. 6. We present voltammograms within 0.2 to -0.6V vs. Ag/AgCl in the lithium nitrate aqueous solutions. This include, the use of a  $\text{LiCoO}_2$  (Fig.6 a)) and  $\text{LiMn}_2\text{O}_4$  (Fig.6 b) as counter electrode.



**Fig. 6** Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  for negative electrode in 6M saturated aqueous  $\text{LiNO}_3$  vs.  $\text{LiCoO}_2$  as counter electrode a) and vs.  $\text{LiMn}_2\text{O}_4$  as counter electrode b); scan rate was  $50 \mu\text{Vs}^{-1}$

Fig.6 a) shows use of spinel  $\text{LiMn}_2\text{O}_4$  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  $40\text{mAh.g}^{-1}$  and the discharge capacity -  $32\text{mAh.g}^{-1}$ . In second cycle the values were  $26 \text{mAh.g}^{-1}$  and  $21 \text{mAh.g}^{-1}$  and in the third cycle -  $21\text{mAh.g}^{-1}$  and  $16\text{mAh.g}^{-1}$ . 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  $\text{LiMn}_2\text{O}_4$  as a use of spinel  $\text{LiMn}_2\text{O}_4$  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

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

## CONCLUSION

The electrochemical characteristics of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$  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  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$  reversibly intercalated/deintercalated  $\text{Li}^+$  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 -  $79 \text{mAh.g}^{-1}$ . The use of manganese spinel  $\text{LiMn}_2\text{O}_4$  as anode were investigate against  $\text{LiCoO}_2$  as counter electrode in nitrate solution. This electrochemical system is stable but the discharge capacity was very low -  $32 \text{mAh.g}^{-1}$ .

The experiments show that the capacity in lithium nitrate is higher but the process of extraction of  $\text{Li}^+$  is easier in sulfate. A symmetric electrochemical system based on manganese spinel in  $\text{LiNO}_3$  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 $\text{LiMn}_2\text{O}_4$ И $\text{LiCoO}_2$ 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  $\text{LiMn}_2\text{O}_4$  и  $\text{LiCoO}_2$  като положителни електроди за литиево-йонна батерия с воден електролит срещу  $\text{LiV}_3\text{O}_8$  като отрицателен електрод. Използваните електролити са 6M  $\text{LiNO}_3$  и 2M  $\text{Li}_2\text{SO}_4$ , разтворени в дестилирана вода.  $\text{LiMn}_2\text{O}_4$  е получен чрез приготвяне на стехиометрична смес от  $\text{LiNO}_3$  и  $\text{MnO}_2$  в твърдо състояние и нагряване при температура 650°C в продължение на 24 часа.  $\text{LiCoO}_2$  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  $\text{mAh.g}^{-1}$  в 6M  $\text{LiNO}_3$  и 94  $\text{mAh.g}^{-1}$  в 2M  $\text{Li}_2\text{SO}_4$  воден електролит, докато неговият капацитет в органичния електролит е 135  $\text{mAh.g}^{-1}$ . Полученият капацитет от литиев кобалтат във водните електролити е съответно 99  $\text{mAh.g}^{-1}$  и 92  $\text{mAh.g}^{-1}$ , докато този в органичния електролит е 145  $\text{mAh.g}^{-1}$ . 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