

Ag/AgCl. The oxidation curves of SG50 and MP65DR also appear to be similar in shape with two peaks for each sample at -0.35 and -0.19 V vs Ag/AgCl (SG50), and -0.39 and -0.25 V vs Ag/AgCl (MP65DR). SG55 shows three anodic peaks (-0.31, -0.27 and -0.23V vs Ag/AgCl) which are merged into one broad feature during the de-intercalation process. After integration of the areas, the initial delivered intercalation and following de-intercalation capacities are 64.35 and 55.43 mAh g⁻¹ (SG50), 92.68 and 67.48 mAh g⁻¹ (SG55), and 123.87 and 73.12 mAh g⁻¹ (MP65DR), respectively. These capacity values delivered in aqueous electrolyte are much lower in comparison to their organic counterparts (20-50% lower) [12].

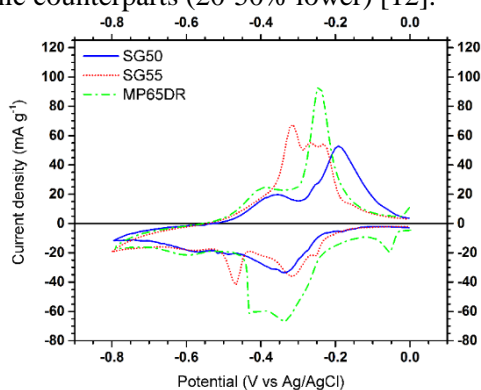


Fig. 6 Cyclic voltammetry of SG50, SG55 and MP65DR at a scan rate of 50 $\mu\text{V s}^{-1}$ in the voltage range of 0 and -0.8 V vs. Ag/AgCl.

Galvanostatic tests were conducted in order to investigate the electrochemical performance of the studied materials. Fig. 7a shows initial charge-discharge profiles of the samples at C/10 (0.1C) in the voltage range 0.7-1.9 V vs LiMn_2O_4 (LMO). Both SG50 and SG55 present solid-solution-type (shape) of the de/intercalation curves. These samples deliver 35.45 (SG50) and 75.23 (SG55) mAh g⁻¹ during the first lithiation, and 30.57 (SG50) and 51.50 (SG55) mAh g⁻¹ in the consecutive delithiation process. Although MP65DR delivers the highest capacities in potentiodynamic mode (fig. 6), it performs very poorly in galvanostatic mode, marking 4.2 and 0.3 mAh g⁻¹ during first intercalation (Int) and de-intercalation (Dei). Even when the current load is lowered as much as C/100 (fig. 7b), the delivered capacities are unsatisfactory: 47.77 (Int) and 9.8 (Dei) mAh g⁻¹, implying kinetic difficulties thus hindered diffusion.

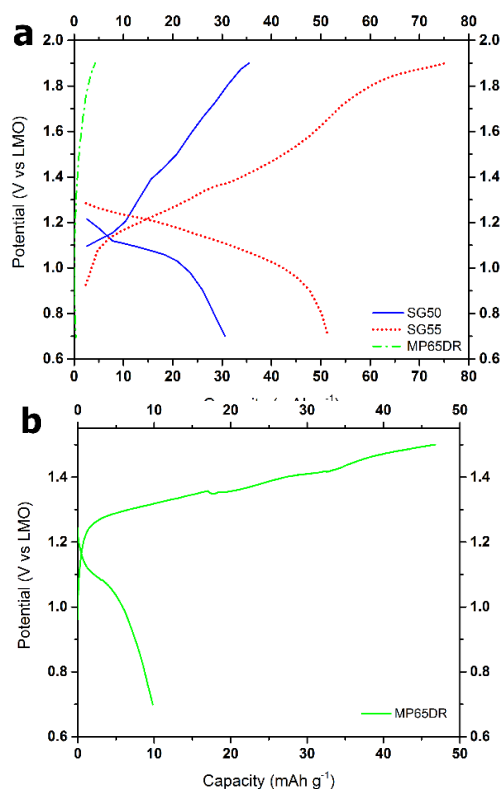


Fig. 7 Galvanostatic tests: (a) charge-discharge profiles of all materials at C/10 in the voltage range 0.7-1.9 V vs LMO; (b) charge-discharge profiles of MP65DR at C/100 in the voltage range 0.7-1.5 V vs LMO.

The de-intercalation specific capacity of the studied materials (discharge mode for the whole LVO-LMO system) as functions of the cycles at C/10 in the voltage range 0.7-1.9 V vs LMO are presented in fig. 8a. SG55 marks highest delithiation capacity of ~55 mAh g⁻¹ in the 4th cycle. After 10th cycle the materials becomes unstable expressed by fluctuations and rapid capacity loss of ~40% in the 30th cycle (fig. 8b). Although the capacity of SG50 is lower, this material display steady behavior with varying capacity of 30-33 mAh g⁻¹. The capacity retention (fig. 8b) in every cycle is calculated as follows:

$$\text{CapRet} = \frac{C_n}{C_1} * 100 [\%],$$

where C_n and C_1 are the capacities of the respective and first cycles, respectively. Therefore the capacity retention of sample SG50 (2-30 cycles) exceeds 100% due to the lowest capacity (30.57 mAh g⁻¹) is delivered in the first cycle. The coulombic efficiency (95-97% after 4th cycle) of this sample is also much better compared to SG55 (70-90%) (Fig. 8c).

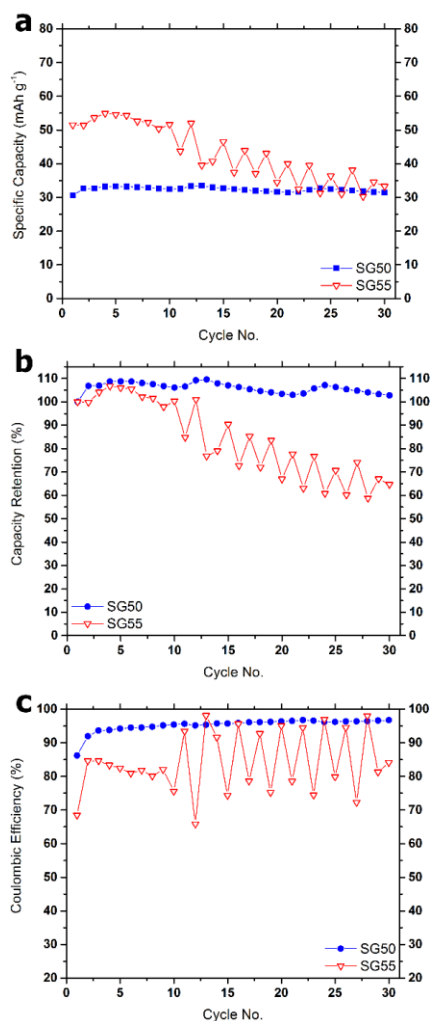


Fig. 8. Specific capacity (a), capacity retention (b) and coulombic efficiency (c) as functions of the cycles at C/10 in the voltage range 0.7-1.9 V vs LMO.

CONCLUSIONS

LiV_3O_8 active materials were synthesized via sol-gel followed by solid state reaction at 500 and 550 °C, and melting process at 650 °C with subsequent hydrothermal treatment and drying. X-ray diffraction patterns show that samples were successfully indexed as LiV_3O_8 . However, there are additional small peaks at 9.3° and 12.3° 2θ in the patterns of SG50 and SG55 which can be attributed to small amounts of absorbed water from the atmosphere. Among all samples SG55 delivers the highest capacities of 75.23 and 51.50 mAh g^{-1} during

the first lithiation and de-lithiation, respectively, in galvanostatic mode. However, SG50 appears to be more stable throughout the cycles. Although MP65DR shows highest intercalation and de-intercalation capacities (123.87 and 73.12 mAh g^{-1}) in potentiodynamic mode, this material performs very poorly in galvanostatic mode.

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ЕЛЕКТРОХИМИЧНИ СВОЙСТВА НА LiV₃O₈, ПОЛУЧЕН ЧРЕЗ РАЗЛИЧНИ МЕТОДИ НА СИНТЕЗ, КАТО ОТРИЦАТЕЛЕН АКТИВЕН МАТЕРИАЛ В ЛИТИЕВО-ЙОННА БАТЕРИЯ С ВОДЕН ЕЛЕКТРОЛИТ

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(Резюме)

Изследвани са електрохимичните свойства на литиевия триванадат (LiV₃O₈, LVO) като отрицателен електроден материал за литиево-йонна батерия с воден електролит. Два метода на синтез бяха приложени за подготовка на LiV₃O₈: метод зол-гел, последван от реакция в твърдофазен синтез (SSR) при 500 и 550°C и процес на топене с последващо хидротермично третиране и сушене. Като за противоелектрод беше използван LiMn₂O₄ (LMO), получен чрез конвенционален твърдофазен синтез. Интеркалирането / деинтеркалирането на литиевия йон се извършва в прозореца на електрохимичната стабилност на водата. LiV₃O₈, получен по метода на топене, третиран хидротермично и изсушен (MP65DR), показва по-лошо представяне в галваностатичен режим в сравнение с тези, получени чрез сол-гел. Пробата, получена чрез зол-гел, нагрята при 550°C (SG55), показва първоначален специфичен капацитет от ~ 75 (интеркалация) и ~ 52 (де-интеркалация) mAh.g⁻¹, който е около 4-5 пъти по-нисък в сравнение с капацитета, в неводни електролити. Въпреки че е с по-малък капацитет (30-33 mAh.g⁻¹), другата проба от сол-гел, нагрята при 500 ° C (SG50), показва по-добро запазване на капацитета и ефективност при циклите.

Ключови думи: водна литиево-йонна батерия, аноден активен материал, литиев триванадат