Potassium vanadates — promising materials for secondary lithium batteries

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Abstract

The electrochemical performance of the phases $K_3V_5O_{14}$, KV_3O_8, $K_2V_8O_{21}$ and KV_5O_{13}, in view of their use as positive electrodes for secondary lithium cells, has been investigated. While the two potassium richer compounds showed very low recharge efficiency, a good reversibility and high capacity performance have been observed for the $K_2V_8O_{21}$ and KV_5O_{13} compounds. The remarkable specific capacity of KV_5O_{13}, which is about 210 mA h g^{-1} at 2 h discharge rate, and its excellent cycleability proves it as a promising alternative for a positive electrode of secondary lithium batteries.

Introduction

The idea of employing potassium vanadates as insertion compounds in positive electrodes for lithium batteries was introduced nearly a decade ago by Raistrick and Huggins [1, 2]. However, mainly cointercalation compounds of Li^+ and K^+ in V_2O_5 designated by the general formula $Li_xK_yV_2O_5$ have been investigated so far [1–3]. The excellent results obtained recently with LiV_3O_8 bronze in secondary lithium cells [4, 5] is a serious challenge initiating electrochemical studies of $K_xLi_yV_3O_8$ compounds, since the partial substitution of Li ions with K ones may significantly enhance the reversibility of the insertion process of Li ions. This possibility was investigated by West *et al.* [6], who performed parallel studies on $K_3V_5O_{14}$ as well. They found that insertion of a considerable amount of lithium ions may occur in the layered structure of the KV_3O_8 and $K_3V_5O_{14}$ compounds. However, it has not been established so far whether these processes are sufficiently reversible or if they proceed at an acceptably high rate to be used as positive electrodes for secondary lithium cells.

In contrast to LiV_3O_8, which is the only existing phase in the equilibrium phase diagram between V_2O_5 and $LiVO_3$ [7], four different phases $K_3V_5O_{14}$, KV_3O_8, $K_2V_8O_{21}$ and KV_5O_{13} are distinguished in the phase diagram between V_2O_5 and KVO_3 [8]. The existence of those four phases was confirmed in a number of works by other authors [9–14].

The investigation of the electrochemical behaviour of $K_3V_5O_{14}$, KV_3O_8, $K_2V_8O_{21}$ and KV_5O_{13} phases, tested in view of their use as positive electrodes for secondary lithium cells, was the goal of the present work.

Experimental

Two different approaches were applied to produce the three-phase $K_3V_5O_{14}$. First, the phase was obtained at low temperature following the method suggested by Bystrom and Evans [9] and subsequently used by West *et al.* [6], comprising rapid evaporation of dilute solution of a stoichiometric mixture of V_2O_5 and KOH. The other approach was to synthesize the compound by solid-phase reaction of an appropriate mixture of V_2O_5 and K_2CO_3 in a platinum crucible at 410 °C as proposed by Pouchard [8].

To synthesize the KV_3O_8 phase we again employed both the high and low temperature methods. The compound was produced by solid-phase reaction at 420 °C [8] and acidification of a KVO_3 solution up to pH 5, as described by Block and Kelmers [10–12].

The $K_2V_8O_{21}$ and KV_5O_{13} phases were produced by solid-state reactions of stoichiometric mixtures of V_2O_5 and K_2CO_3 or of V_2O_5 and KNO_3, using continuous heating at 500 °C for 200 h in accordance with the conditions disclosed by Pouchard [8]. Our efforts to obtain these phases in solutions, following procedures analogous to those described by Block and Kelmers [10–12], have been unsuccessful so far.

The electrochemical measurements were performed on test electrodes in a three-electrode cell with $LiClO_4/PC$–DME electrolyte. The active mass of the test electrodes was a mixture of the compounds studied and teflonized acetylene black (TAB-2) [15] at 2:1 ratio by weight, homogenized by continuous stirring in ethyl ether. After drying, test electrodes were formed by pressing 25 mg cm^{-1} of the active mass onto an expanded nickel grid at 5 t cm^{-2}. The methods for preparation of electrolytes and cells have been described in details in ref. 4.

Results and discussion

The phase compositions of the synthesized compounds $K_3V_5O_{14}$, KV_3O_8, $K_2V_8O_{21}$ and KV_5O_{13} were verified by X-ray analysis and their typical diffraction patterns are presented in Fig. 1. The comparison of the diffractograms with those presented by Pouchard [8] and Kelmers [10, 12] shows a good agreement, excepting some negligible differences in the peaks intensity.

The differential capacity–potential dependences of the compounds $K_3V_5O_{14}$ and KV_3O_8 obtained at very low scan rate of 0.01 mV sec^{-1} are shown in Fig. 2. The Fig. includes curves obtained for compounds produced by solid-state reactions (SSR) as well as for those synthesized from solutions. Some slight differences in shape are observed, depending on the method used. It can also be seen that the $K_3V_5O_{14}$ curve is similar to the KV_3O_8 one, though shifted by about 300 to 400 mV to the lower potentials.

The differential capacity–potential dependences for the compounds $K_2V_8O_{21}$ and KV_5O_{13} obtained at the same scan rate as in Fig. 2, are presented in Fig. 3. A negligible difference in the values of the integral capacity and the capacity distribution as a function of the potential of KV_5O_{13} and $K_2V_8O_{21}$ is observed, while these dependences are completely different in comparison with $K_3V_5O_{14}$ and KV_3O_8 ones. Moreover, from Figs. 2 and 3 it can be concluded that the integral capacities of the two compounds with low potassium content are nearly twofold higher than those of the two potassium-rich compounds.

The discharge curves of the four compounds tested at 2 h discharge rate, presented in Fig. 4, confirm the substantial difference in the electrochemical behaviour of KV_5O_{13}
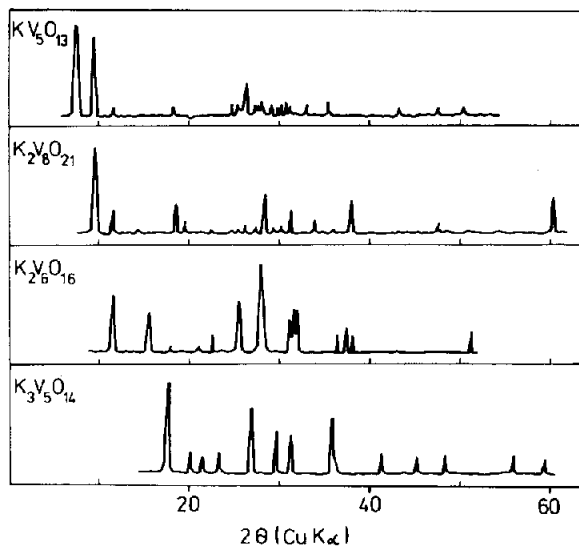
Fig. 1. Powder X-ray diffraction pattern of synthesized $K_3V_5O_{14}$, $K_2V_2O_{16}$, $K_2V_8O_{21}$ and KV_5O_{13} compounds.
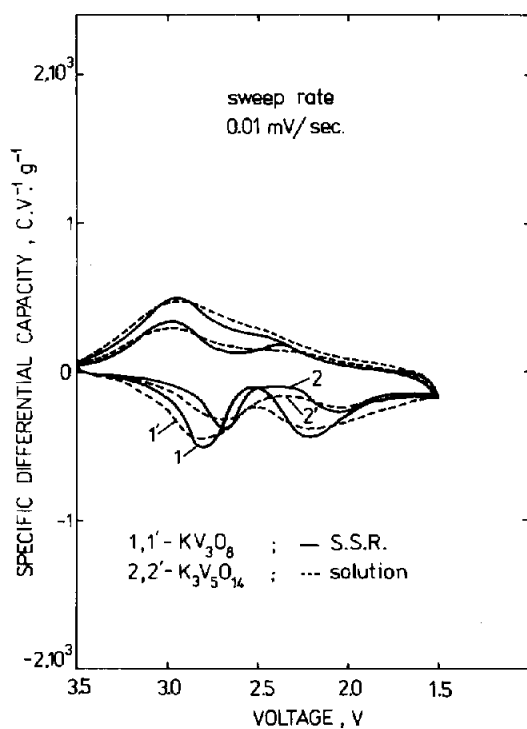

Fig. 2. Differential capacity–potential plots of the compounds $K_3V_5O_{14}$ and KV_3O_8 obtained at scan rate of 0.01 mV sec^{-1}, over the potential range 1.5–3.5 V.

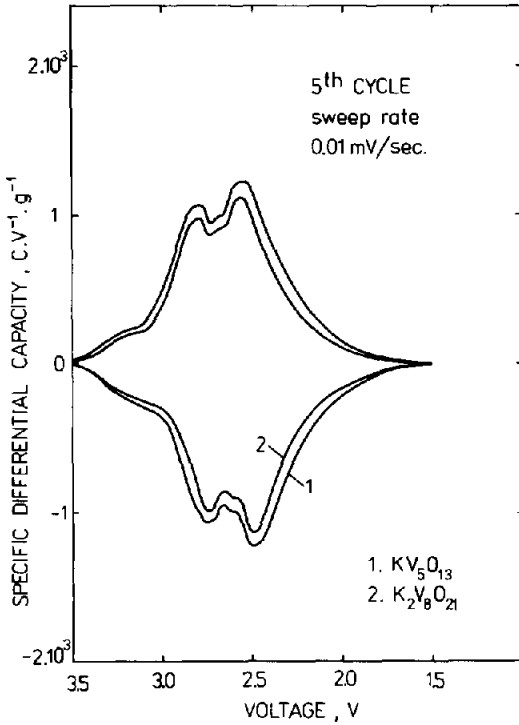Fig. 3. Differential capacity–potential plots of the compounds $K_2V_8O_{21}$ and KV_5O_{13} obtained at scan rate of 0.01 mV sec^{-1}, over the potential range 1.5–3.5 V.
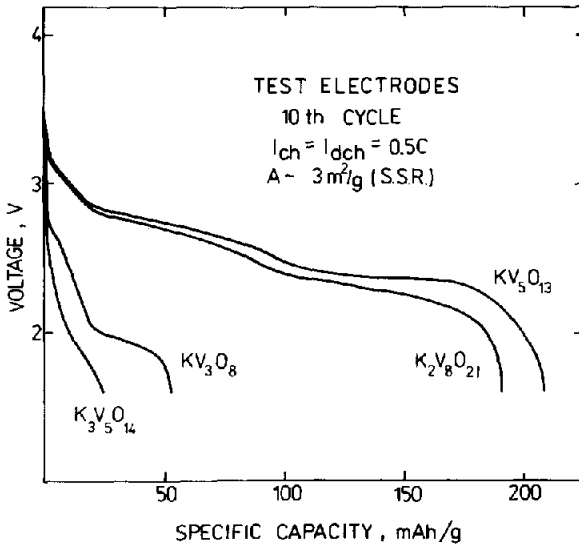

Fig. 4. Discharge curves of the KV_5O_{13}, $K_2V_8O_{21}$, KV_3O_8 and $K_3V_5O_{14}$ compounds with specific surface areas of about 3 m^2 g^{-1} at 2 h discharge rate.

and $K_2V_8O_{21}$ as compared with KV_3O_8 and $K_3V_5O_{14}$, which has already been observed (Figs. 2 and 3). For precise comparison of their performance, all four materials were continuously ground until nearly equal specific surface areas of about 3 m^2 g^{-1} were obtained. From Fig. 4 can be concluded that at 2 h discharge rate ($I = 0.5$ C) KV_5O_{13} and $K_2V_8O_{21}$ retain high specific capacities close to their theoretical ones 267 and 261 mA h g^{-1}, respectively, while the KV_3O_8 and $K_3V_5O_{14}$ capacities remain far too low to be useful for positive electrodes in real lithium cells.

The remarkable effect of the specific surface area on the electrochemical behaviour of potassium vanadates at 2 h rate is demonstrated in Fig. 5 presenting the discharge curves of KV_5O_{13} electrodes with specific surface areas of 0.7, 2.9 and 9.6 m^2 g^{-1}. However, it appears that a specific surface area of 9.6 m^2 g^{-1} is sufficient only up to 1 h discharge rates. As can be seen from Fig. 6, the increase of the discharge current above $I = C$ leads to a substantial reduction of the capacity obtained.

The long-term cycling tests of the materials studied are presented in Fig. 7. These tests show a satisfactory stability of the $K_2V_8O_{21}$ compound, while for KV_5O_{13}, after a slight initial capacity rise, a unique independence of the specific capacity versus the cycle number is observed. However, the test results obtained for the two potassium-rich compounds again demonstrate their infeasibility to real systems.

The emission spectroscopy analysis of the electrolyte in the used electrochemical cells showed that there was no potassium ions exchange between the $K_2V_8O_{21}$ and KV_5O_{13} host structures and the electrolyte. Nevertheless, the existence of even potassium ion traces in a real lithium battery can reduce significantly the lithium electrode reversibility. For this reason, comparative studies of KV_5O_{13} and LiV_3O_8 were performed in a real button cell whose design was described in details [5]. The tests were performed on electrodes with nearly equal initial capacities in cells containing 1 M $LiAsF_6$ in

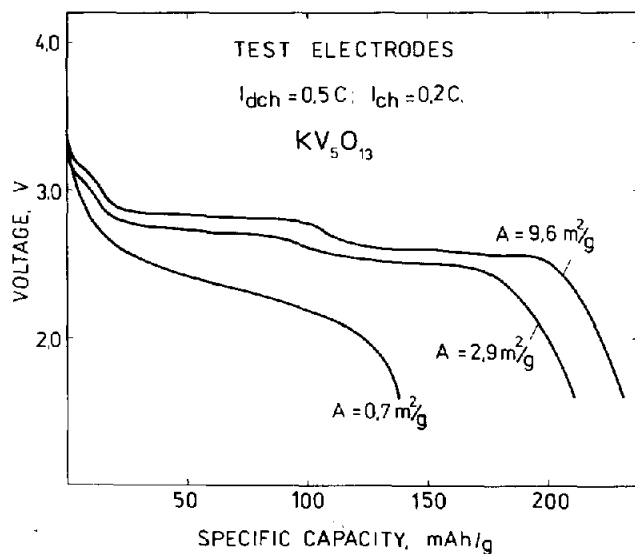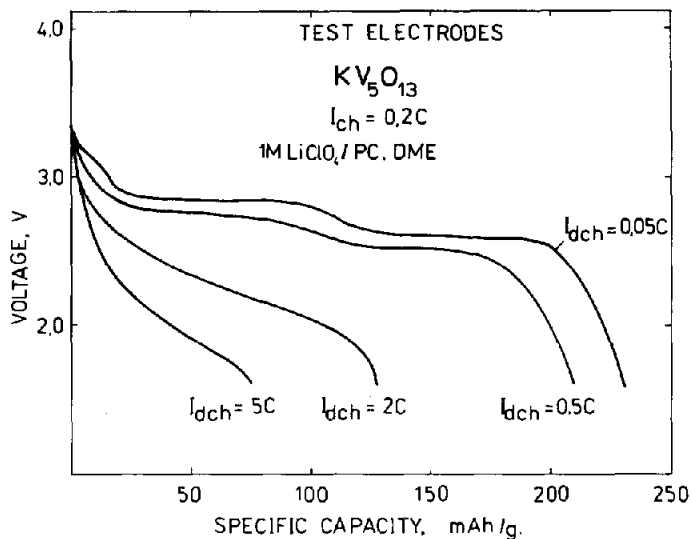Fig. 5. Discharge curves of KV_5O_{13} electrodes with specific surface areas of 0.7, 2.9 and 9.6 m^2 g^{-1}.

Fig. 6. Discharge curves of KV_5O_{13} electrodes with specific surface areas of 9.6 m^2 g^{-1} at different discharge rates.
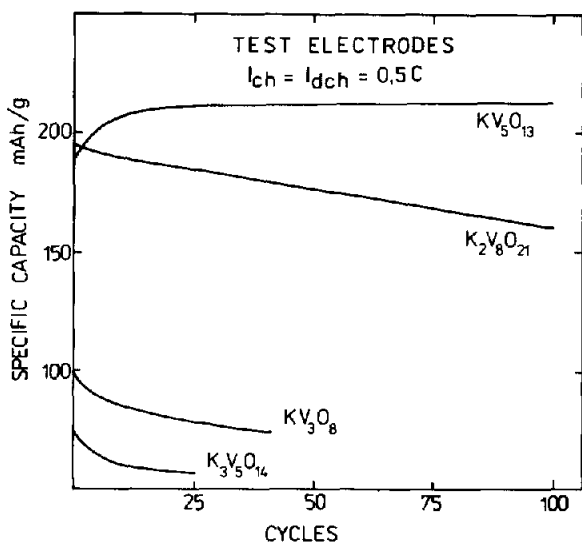

Fig. 7. The specific capacity obtained vs. cycle number for the KV_5O_{13}, $K_2V_8O_{21}$, KV_3O_8 and $K_3V_5O_{14}$ compounds with specific surface areas of about 3 m^2 g^{-1} in the voltage range of 1.5–3.5 V.

propylene carbonate (Fig. 8). Conversely to our expectations, the cells with KV_5O_{13} positive electrodes displayed even better cycleability than those employing LiV_3O_8 electrodes. This result can be attributed to the fact that LiV_3O_8 is slightly soluble in the solvents used in lithium cells, and thus the resulting dissolved products may
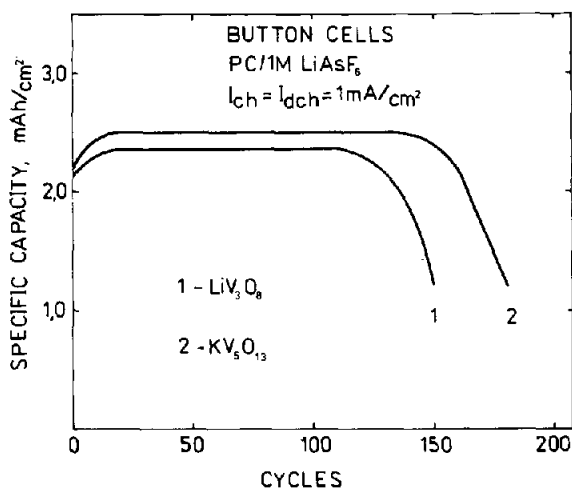
Fig. 8. Cell capacity vs. cycle number for button cells with KV_5O_{13} and LiV_3O_8 positive electrodes having nearly equal initial capacities, in cells containing 1 M $LiAsF_6$ in PC electrolyte.

influence the reversibility of the lithium electrode, while for KV_5O_{13} no similar effect was observed.

Conclusions

It can be concluded from the data obtained in this work that the increase of the vanadium:potassium molar ratio in the compounds studied, where vanadium is of $5+$ valency, increases both their specific capacity and reversibility with respect to the Li^+ ion insertion in their structure. The remarkable specific capacity of KV_5O_{13}, which is about 210 mA h g^{-1} at 2 h discharge rate, and its excellent reversibility make it a promising alternative for the development of a positive electrode for secondary lithium batteries.

Acknowledgement

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