

## Secondary lithium cell based on $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$ obtained in potassium polysulphide melts\*

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### Abstract

The composition and structure of layered compounds described by the general formula  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  ( $0 < y < 0.5$ ), synthesized in potassium polysulphide melts, have been investigated. The electrochemical performance of these compounds with regard to their application in high-energy-density, secondary lithium batteries is discussed. It is found that when  $\text{Cr}^{3+}$  is replaced with  $\text{V}^{3+}$  in the range  $0.1 < y < 0.5$ , the specific capacity of the samples varies from 185 to 205 A h  $\text{g}^{-1}$ . All electrodes tested exhibit remarkably high reversibility, which is not affected by their vanadium content, and display about 20% loss of their initial capacity after 300 cycles. Significant differences are observed in the initial capacity distribution versus electrode potential, depending on the  $\text{V}^{3+}$  content. After long term cycling, however, the capacity distribution of all samples tends to display similar form, independent of the chromium/vanadium ratio. These redistributions determine a mean discharge voltage of about 2.4 V for the  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  ( $0.1 < y < 0.5$ ) electrodes subjected to long term cycling tests.

### Introduction

The physicochemical and electrochemical properties of layered compounds described by the general formula  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$ , synthesized by a solid state reaction in an  $\text{H}_2\text{S}$  atmosphere, have been investigated previously [1–4]. A detailed study of an analogous compound has been undertaken, where  $\text{NaCr}_{1-y}\text{V}_y\text{S}_2$  was first synthesized in a sodium polysulphide melt and the sodium was then replaced with lithium by chemical oxidation, electrochemical oxidation, or ion exchange [6–9].

The satisfactory electrochemical performance of the sodium thiocromite ( $\text{Li}_x\text{Na}_{0.1}\text{CrS}_2$ ) and vanadium-doped sodium thiocromite ( $\text{Li}_x\text{Na}_{0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$ ) electrodes was confirmed during long-term tests in electrochemical cells with excess electrolyte [6–9]. Further investigations into the behaviour of these intercalation compounds in real lithium cells showed that the vanadium-doped sodium thiocromite electrodes exchange their sodium ions for lithium

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ions. This process is enhanced by the electrode cycling. As a result,  $\text{Li}_x\text{Na}_{0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$  is transformed into  $\text{Li}_{x+0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$  without any alteration in its structure or properties. However, the generation of sodium ions in the real cell electrolyte substantially reduces the reversibility of the lithium electrode and the cell cyclability.

There are alternative solutions to this problem: preliminary substitution of the sodium ions with lithium ions by ion exchange, or direct synthesis of compounds having the general formula  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$ . A study of the first possibility led to the conclusion that it is too expensive to be used in practice. Therefore methods for the direct synthesis of vanadium-doped lithium thiocromite were investigated.

The aim of the present work was to investigate the structure and electrochemical behaviour of vanadium-doped lithium thiocromite obtained in a potassium polysulphide melt.

## Experimental

The synthesis of vanadium-doped lithium thiocromite was successfully performed in a potassium polysulphide melt containing  $\text{K}_2\text{CrO}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Li}_2\text{S}$  and S in the correct ratio. The potassium polysulphides present a medium in which the transient metal oxides are sufficiently soluble, while  $\text{Li}_2\text{S}$  provides the lithium required for the synthesis. The potassium polysulphides and  $\text{Li}_2\text{S}$  were produced during the synthesis from  $\text{K}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and a large excess of sulphur in the melt. The reactant mixture was heated at 500, 550 and 600 °C for 2 h in a covered glass or quartz crucible. Analogous products can also be obtained by synthesis above 600 °C, but these temperatures require a platinum crucible and a protective atmosphere of sulphur vapours. After cooling, the reaction mixture was washed consecutively with 5 wt.% KOH, 1 wt.% LiOH, ethyl alcohol, and ether.

The composition and structure of the vanadium-doped lithium thiocromite samples were monitored by chemical analysis, X-ray analysis, and emission spectroscopy. The  $\text{V}^{3+}$  content of the investigated compounds was varied within the range  $0 < y < 0.5$ .

The X-ray analysis was carried out on a Philips APD 15 diffractometer with  $\text{Cu K}\alpha$  radiation. The dependences of the differential capacity as a function of the electrode potential were obtained by slow cyclic voltammetry [10] at a scan rate of  $0.01 \text{ mV s}^{-1}$ . The measurements of the specific capacity as a function of the cycle number were performed under galvanostatic conditions using cycling devices which reverse the process automatically at preset values (1.8 and 3.2 V) of the electrode potential.

The preparation of the test electrodes, electrolytes, and electrochemical cells has been described in detail elsewhere [6–9]. The real electrodes consisted of a mixture of 70% active material and 30% Teflonized acetylene black homogenized with THF in a mixer for 1 h. After drying, the mixture was pressed at  $12 \text{ t cm}^{-2}$  onto an expanded nickel mesh and then sintered at 350 °C for 10 min.

## Results and discussion

### Phase and composition studies

The diffraction patterns of pure lithium thiochromite obtained at 500, 550 and 600 °C are presented in Fig. 1. These results are compared with the diffraction pattern of  $\text{LiCrS}_2$  (Fig. 1(d)) produced by solid-state reaction in  $\text{H}_2\text{S}$  atmosphere [1]. The patterns shown display a slight difference in the intensity of the peaks, while their positions fully correspond to the standard material [1]. The absence of some peaks in the diffraction patterns of the samples synthesized at 500 °C is due to the considerable reduction of their crystallinity with decrease in temperature. Along with the reduction of crystallinity, a significant increase in the specific surface area can be observed, from  $5.6 \text{ m}^2 \text{ g}^{-1}$  for samples synthesized at 600 °C to  $18.2 \text{ m}^2 \text{ g}^{-1}$  for those obtained at 500 °C. Diffraction lines of other phases are not visible in the spectra of the samples studied.

Chemical analysis indicated that the Cr/S ratio in the samples shown in Fig. 1 corresponds to the stoichiometry of  $\text{LiCrS}_2$ . Emission spectroscopy confirmed that the potassium content of the samples was below  $10^{-3}\%$ . The absence of potassium is easy to explain, considering that the lithium ion radius is  $0.65 \text{ \AA}$ , while that of the potassium ion is  $1.35 \text{ \AA}$ . It is evident that the larger potassium ion cannot replace the small lithium ion in these compounds. An analogous result was obtained when  $\text{NaCrS}_2$  was synthesized in mixed sodium–potassium polysulphides [11]. The presence of potassium

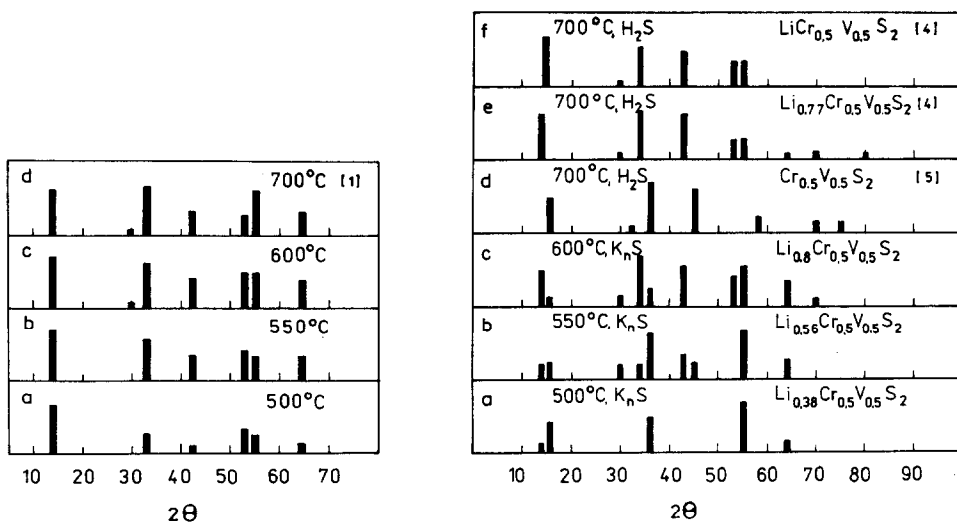


Fig. 1. X-ray diffraction patterns of lithium thiochromite synthesized in potassium polysulphide melts at (a) 500 °C, (b) 550 °C, (c) 600 °C, compared with the pattern (d) of the same material produced by solid-state reaction [1].

Fig. 2. X-ray patterns of  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  synthesized in potassium polysulphide melts at (a) 500 °C, (b) 550 °C, and (c) 600 °C, compared with the patterns of (d)  $\text{LiCr}_{0.5}\text{V}_{0.5}\text{S}_2$  [4], (e)  $\text{Li}_{0.77}\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  [4], and (f)  $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  [5] produced by other methods.

was not observed in the prepared  $\text{NaCrS}_2$ , indicating that the potassium ion cannot replace the sodium ion (1.05 Å) in a similar compound though the latter is considerably larger than the lithium ion. The chemical analysis and emission spectroscopy results are therefore in agreement with the diffraction patterns of Fig. 1.

Figure 2 gives the diffraction patterns of  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  obtained in the potassium polysulphide melt. The diffraction patterns of samples synthesized at 500, 550, and 600 °C are compared with those of compounds such as  $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  [5],  $\text{Li}_{0.77}\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  [4], and  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  [4], produced by solid-state reaction in an  $\text{H}_2\text{S}$  atmosphere. As can be seen, the diffraction patterns of all synthesized samples comprise lines of partially, fully, and unoxidized forms of  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ . The oxidation state obtained by the electrochemical titration and chemical analysis specified in the Figure, indicates that the  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  samples are partially oxidized. These data are in agreement with the existence of spectra of oxidized  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  forms in the diffraction patterns.

When the reactant mixture was washed with LiOH and KOH solutions presaturated with inert gas after the synthesis, only the diffraction pattern of the unoxidized form (Fig. 2(f)) was observed. This shows that the partial oxidation of the  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  samples is due to the oxygen dissolved in the aqueous alkaline solutions used for treatment of the samples after synthesis.

An essential difference exists between these results and the data obtained from the studies of pre-oxidized, vanadium-doped sodium thiocromite [8, 9]. While the values of  $y$  in the  $\text{Li}_x\text{Na}_{0.15}\text{Cr}_{1-y}\text{V}_y\text{S}_2$  samples cannot exceed 0.16 (at  $y > 0.16$  pure  $\text{NaVS}_2$  is formed), for  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  the  $y$  value may reach up to 0.5. This shows that the method discussed can be used successfully for the synthesis of  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  compounds with  $y$  varying from 0 to 0.5.

### *Discharge and cycling performance*

The differential capacity–potential dependences of  $\text{Li}_x\text{CrS}_2$ ,  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  and  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  test electrodes [7] are shown in Fig. 3. A significant difference in the values of the integral capacity and the capacity distribution as a function of the potential is observed. By substituting 0.25 M  $\text{Cr}^{3+}$  ions with  $\text{V}^{3+}$  ions the integral capacity increases more than twice. A further increase in the vanadium ion content up to 0.5 M results in an insignificant increase in the integral capacity and considerable changes in the capacity distribution. As a result the mean discharge voltage decreases from 2.5 V for  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  to 2.2 V for  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ .

The discharge curves for the first cycle of  $\text{Li}_x\text{CrS}_2$ ,  $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$ ,  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ , and  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  real electrodes at 3 h discharge rate are presented in Fig. 4. The specific capacity was calculated with regard to the active material in the electrodes. At this comparatively high discharge rate the values of the specific capacity are 195 mA h  $\text{g}^{-1}$  for  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  and 205 mA h  $\text{g}^{-1}$  for  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ , while that obtained for  $\text{Li}_x\text{CrS}_2$  is below 100 mA h  $\text{g}^{-1}$ . The respective values of the equivalent amount of lithium

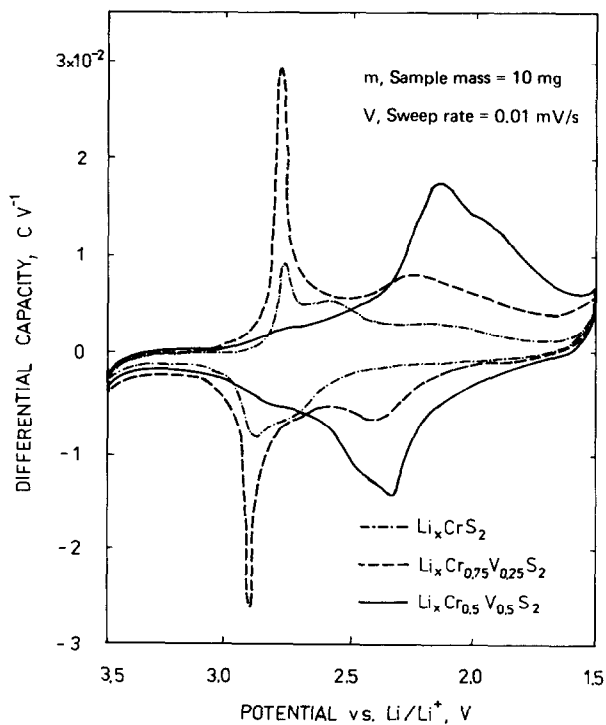


Fig. 3. Differential capacity/potential dependences of  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  test electrodes with  $y$  equal to 0, 0.25, and 0.5.

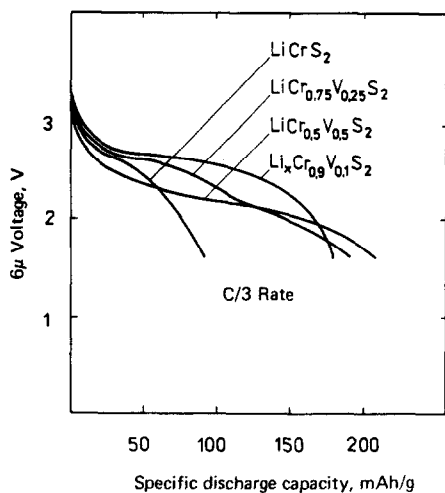


Fig. 4. Discharge curves of  $\text{Li}_x\text{CrS}_2$ ,  $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$ ,  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ , and  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  electrodes at 3 h discharge rate.

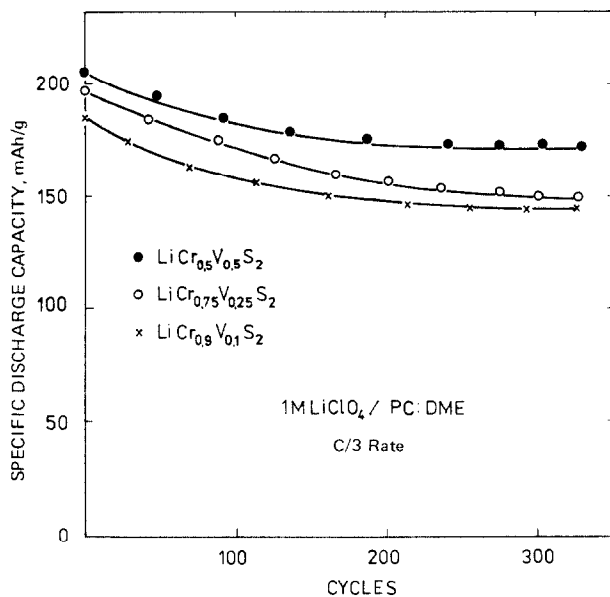


Fig. 5. Dependence of the specific capacity of  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ ,  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ , and  $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$  electrodes on the cycle number.

intercalated into  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  and  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  are  $x=0.94$  and  $x=0.98$ , respectively.

A slight capacity loss was observed in all the cycling tests of vanadium-doped lithium thiocromite electrodes (Fig. 5). The electrode cycling was carried out at the  $C/3$  rate which corresponds to a current density of about  $1 \text{ mA cm}^{-2}$ . It can be seen (Fig. 5) that the vanadium-doped lithium thiocromite electrodes have a remarkably high reversibility that is unaffected by their vanadium content. When subjected to long-term cycling, they display a loss of about 20% of their initial capacity after 300 cycles.

#### *Differential capacity redistribution*

The results presented in Figs. 4 and 5 may lead to the conclusion that the specific energy of the electrodes described by the general formula  $\text{Li}_x\text{Cr}_{1-y}\text{V}_y\text{S}_2$  does not differ when  $y$  is varied from 0.1 to 0.5. For electrodes with lower  $\text{V}^{3+}$  content ( $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$  and  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ ) subjected to long-term cycling, however, a substantial decrease in the mean discharge voltage is observed, while the electrode with  $y=0.5$  displays a reverse tendency. There are two possible explanations of this phenomenon. On the one hand, the decrease in the mean discharge voltage may be due to the degradation of the electrode macrostructure, which increases the contact resistances between the particles. The reverse tendency observed for  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  electrodes may be attributed to their remarkably higher (nearly two orders of magnitude) electronic conductivity. On the other hand, the change in the mean discharge voltage can be explained by some redistribution of the

capacity as a function of the electrode potential, resulting from essential changes in the microstructure of the active material during cycling.

To elucidate this phenomenon, electrodes subjected to long-term cycling were tested over definite time intervals using slow cyclic voltammetry. To eliminate the influence of the macrostructure changes, prior to each test the electrodes were washed, additionally pressed at  $12 \text{ t cm}^{-2}$ , and sintered to restore the initial adhesion of their particles.

Figure 6 presents the differential capacity/potential dependences of an  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  test electrode obtained at the 1st, 10th and 100th cycle. It can be seen that with the increase in the cycle number the sharp peak at 2.8 V decreases remarkably, whereas the wide peak at 2.3 V rises. During these changes the specific capacity is redistributed with regard to the electrode potential, but its integral value remains constant. The rise of the peak at 2.3 V with regard to the peak at 2.8 V naturally leads to a decrease in the mean discharge voltage and the specific energy during long-term cycling. The analogous behaviour of  $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$  was established.

The redistribution of the differential capacity versus voltage for an electrode of  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  synthesized at  $550^\circ\text{C}$  is illustrated in Fig. 7. The opposite effect, by comparison with  $\text{Li}_x\text{Cr}_{0.9}\text{V}_{0.1}\text{S}_2$  and  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$ , is observed with increase in cycle number. The peak at 2.8 V rises, while the height of the main peak at 2.3 V decreases. In this case the areas enclosed

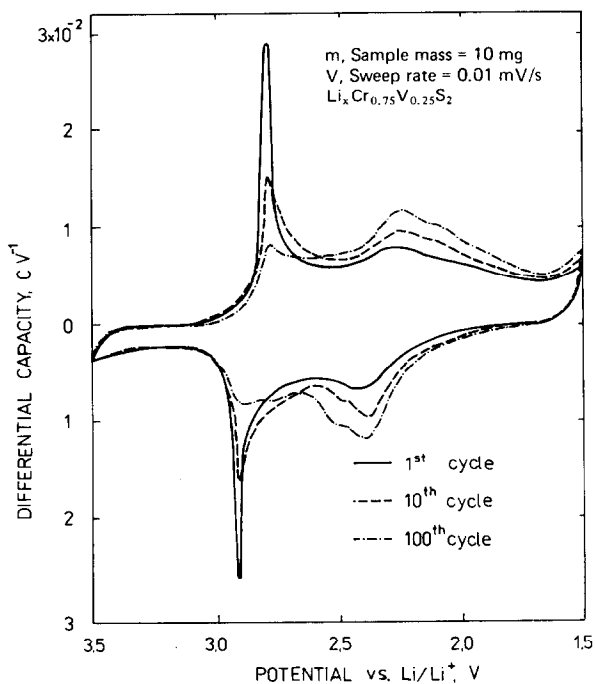


Fig. 6. Differential capacity/potential dependences of an  $\text{Li}_x\text{Cr}_{0.75}\text{V}_{0.25}\text{S}_2$  test electrode obtained at the 1st, 10th, and 100th cycle.

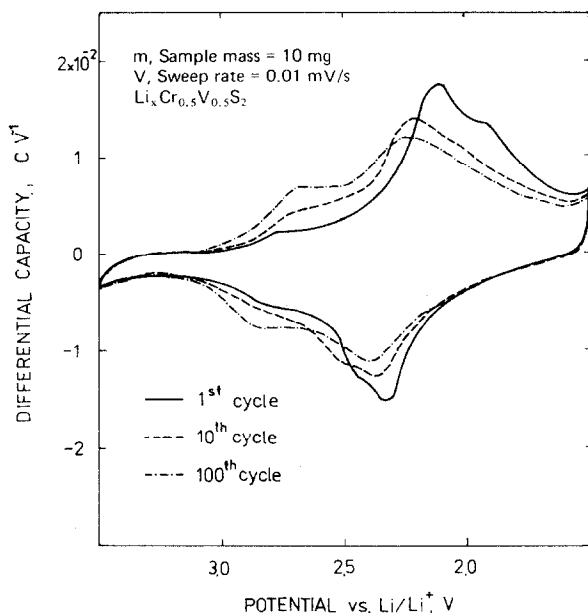


Fig. 7. Differential capacity/potential dependences of an  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  test electrode obtained at the 1st, 10th, and 100th cycle.

by the curves have the same values, which indicates that during long-term cycling the specific capacity of the  $\text{Li}_x\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  electrodes remains unchanged. The rise of the peak at 2.8 V obviously leads to an improvement in the specific energy of this electrode.

A comparison of the capacity distribution curves as a function of the potential after 100 deep cycles (Figs. 6 and 7) shows that they differ insignificantly with regard to the composition of the active electrode material in the range  $0.1 < y < 0.5$ . However, the compounds with higher vanadium content have a slightly higher integral capacity. In both cases, the changes in capacity distribution lead to a configuration whereby 30–40% of the capacity is available around a flat maximum at 2.8 V and 60–70% is present around a maximum at 2.3 V. Such a capacity distribution has also been obtained for the sodium thiochromite [6]. Presumably this configuration reflects some optimum distribution of the alkaline ions in the thiochromites.

The studies performed on samples synthesized at 500 °C display the same effects, though the capacity redistribution proceeds much faster — 10 cycles were sufficient to reach a redistribution corresponding to the 100th cycle for the samples obtained at 550 °C (Figs. 6 and 7). The samples synthesized at 600 °C display the same behaviour as those produced at 550 °C, though the changes take place more slowly.



## Conclusions

Summarizing the results obtained from these studies, we conclude that the substantial differences in the electrochemical behaviour of vanadium-doped lithium thiocromite electrodes with vanadium contents ranging from 0.1 to 0.5 occur during the initial cycles only. Subjected to long-term cycling, the samples richer in vanadium display some advantages in respect of their specific energy.

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