Vanadium-doped lithium thiochromite: properties, crystal structure and electrochemical performance in rechargeable Li cells*

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Abstract

The physicochemical properties and crystal structure of vanadium-doped lithium thiochromite, produced by thermal synthesis in a sulfur melt and a subsequent delithiation in oxygen-containing aqueous suspension, are described. The compound is characterized by a rigid crystal structure, which can sustain the mechanical tensions developed during lithium intercalation and deintercalation upon cycling. The electrochemical performance of this compound as cathode material in lithium secondary cells, specific capacity of 0.15–0.16 mA h g^{-1}, mid-discharge voltage of 2.5 V, and cycling efficiency above 99%, make it attractive for practical applications.

Introduction

The properties, crystal structure, and electrochemical performance of the de-sodiated, vanadium-doped sodium thiochromite, $Na_{0.1}Cr_{0.9}V_{0.1}S_2$, obtained by electrochemical and chemical de-sodiation from the stoichiometric sodium thiosalt, prepared by thermal synthesis in a sodium polysulfide melt, have been described in previous papers [1–3]. It was shown that when used as a cathode material in a rechargeable lithium cell this compound yields a large specific capacity (0.15–0.17 A h g^{-1}) at a high mid-discharge voltage (2.4–2.5 V), and is capable of delivering some 300–500 deep cycles at a 3 h rate between 1.6 and 3.2 V. As pointed out, however [3], the electrochemical de-sodiation of the compound is not practical, while the chemical procedure, although fast and easily performed, consumes iodine, which adds to the cost of the product.

This investigation was aimed at developing a method for the direct synthesis of lithium thiochromite doped with vanadium, as well as studying its properties and electrochemical performance.

As far as we are aware, there is only one method for the synthesis of lithium thiosalts ($LiCrS_2$ and $LiVS_2$), described first by Van Laar and Ijdo

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[4]. It is based on the reaction of a mixture of the corresponding oxides (Cr_2O_3 or V_2O_5) with Li_2CO_3 in a stream of hydrogen sulphide for 16–20 h at 700 °C. The same method was employed by Murphy *et al.* [5], and also by Abraham *et al.* [6], for the synthesis of the mixed thiosalt $LiCr_{0.5}V_{0.5}S_2$, from which, by chemical oxidation with iodine, the mixed disulphide $Cr_{0.5}V_{0.5}S_2$ is obtained. Chemical oxidation is considered as being indispensable for the preparation of a more fine grained cathode material with high performance characteristics [6].

Experimental

According to Rüdorff and Stegeman [7] the synthesis of sodium and potassium thiochromites proceeds in a polysulphide melt medium rich in S_2^{2-} ions at high temperatures (600–700 °C), where the reaction with Cr^{6+} ions is fast and complete. This method was, however, never used for the synthesis of $LiCrS_2$ since lithium does not form polysulphides. A modification of Rüdorff's method was developed in this laboratory for the synthesis of the vanadium-doped lithium thiochromite, which avoids the use of the toxic hydrogen sulphide and the costly oxidation with iodine. A mixture of Cr_2O_3 and V_2O_5, with an excess of Li_2CO_3 and sulphur, was heated to 400–500 °C for several hours.

The raw product, containing soluble lithium salts was purified by washing in dilute, aqueous LiOH solutions. After filtering and drying under vacuum at 120 °C, the purified material was characterized by X-ray diffraction in a Philips APD-15 apparatus with Cu $K\alpha$ irradiation. The lithium content was assessed by atomic adsorption spectroscopy and vanadium was determined spectrophotometrically in the form of the red peroxide–sulfate complex after separation from chromium. The electrical conductivity was measured at 1 kHz on pellets with an area of 1 cm^2 and ~0.25 cm thick, pressed at 1 ton cm^{-2}.

The electrochemical performance of the vanadium-doped lithium thiochromite was studied with cathodes prepared by pressing a blend of the material with 20% Teflonized acetylene black on a nickel exmet disc. Two types of cell were used in these measurements.

(i) All-glass 4-compartment cells with a lithium reference and two large Li counter electrodes with a large excess of electrolyte (1 M $LiClO_4$ in propylene carbonate dimethoxyethane mixture (PC + DME) 1:1). In these cells the cathode material was tested in respect of its charge–discharge characteristics and cycling stability.

(ii) Electrolyte-starved, coin-type cells with a very limited electrolyte volume (1 M $LiAsF_6$ in tetrahydrofuran + 2-methyltetrahydrofuran (THF + 2-MeTHF, 1:1)) and one sheet of Celgard 2400 as separator. The close-packed, disc-shaped electrode package, comprising a lithium anode, was placed under a constant pressure of ~5 kg cm^{-2} by means of a steel spring. The conditions in these cells are similar to those in a commercial coin cell where, due to

the close packing and the limited amounts of lithium and electrolyte, the interaction between the active materials is more strongly expressed.

Cycling was performed continuously and automatically under galvanostatic conditions between 1.6 and 3.2 V.

Results and discussion

Delithiation, hydration, and ion exchange of the lithium thiosalt

The final product prepared by the modified Rüdorff method, $Li_{(1-x)}Cr_{(1-y)}V_yS_2$ with $(0.1 < x < 0.4)$ and $(0.05 < y < 0.12)$, is a dark brown, almost black powder with a high surface area (BET 12–18 m^2 g^{-1}) and an average grain size ranging from 0.3 to 1.0 μm, as revealed by SEM photographs. As seen in Table 1, the X-ray diffraction pattern is similar to that reported by Van Laar and Ijdo [4] for the $LiCrS_2$ phase, and obtained by the hydrogen sulphide method.

It was established that the lithium content in the purified compound depends on the washing conditions and, more specifically, on the concentration of LiOH and of the raw product in the washing solution. It appeared that the washing process is accompanied by a topotactical delithiation of the thiosalt and donation of electrons from the transition metal (Cr, V) to oxygen dissolved in the washing solution.

The oxidation of alkali thiosalts in oxygen-containing aqueous solutions was first studied by Schöllhorn *et al.* [8]. It was found that in neutral solutions the partial oxidation of $NaCrS_2$ leads to the topotactical formation of a hydrated phase, $Na_{1-x}(H_2O)_y[CrS_2]^{-(1-x)}$, consisting of negatively charged disulfide layers and mobile, hydrated sodium ions between them. The polyelectrolyte character of this compound was exhibited by a number of cation, water, and solvent-exchange reactions.

The present study revealed that the vanadium-doped lithium thiochromite behaves similarly when kept in contact with diluted LiOH aqueous solutions

TABLE 1

X-ray diffraction data of Li thiochromites

$Li_{0.8}Cr_{0.9}V_{0.1}S_2$			$LiCrS_2$ [4]	
d (Å)	I/I_o	$h\,k\,l$	d (Å)	I/I_o
6.03	70	$0\,0\,\bar{1}$	6.03	100
2.98	16	$0\,0\,\bar{2}$	2.99	10
2.67	100	$1\,0\,\bar{1}$	2.69	100
2.11	123	$1\,0\,\bar{2}$	2.13	40
1.73	47	$1\,1\,0$	1.73	35
1.67	83	$1\,0\,\bar{3}$	1.67	100
1.49	34	$1\,1\,\bar{2}$	1.49	12
1.45	6	$2\,0\,0$	1.45	35
1.34	30	$1\,0\,\bar{4}$		

containing oxygen, i.e., the thiosalt is delithiated topotactically according to

$$Li^+[(Cr, V)S_2]^- + x/2H_2O + x/4O_2 = Li^+_{(1-x)}[(Cr, V)S_2]^{-(1-x)} + xLiOH \qquad (1)$$
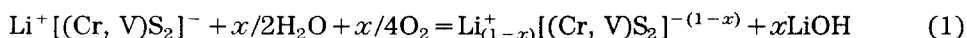
It was found that the degree of delithiation, x, depends on the amount of the powdered raw product suspended in the solution, the available oxygen, and the equilibrium LiOH concentration in the solution above the sedimented phase. Provided that the suspension was stirred and/or stored in the solution for a sufficiently long time, so that the supply of oxygen was not the limiting step of the reaction, the degree of delithiation was determined by the equilibrium LiOH concentration in the solution, established after 7–8 h. Experimentally, the delithiation was raised by increasing the dilution of LiOH in the final washing solution, where the product was allowed to stand overnight.

Another factor affecting oxidation and hydration reaction (1) is the level of vanadium doping of the compound. The substitution of Cr^{3+} with V^{3+} in the disulfide layers considerably enhances the reactivity of the thiosalt with regard to hydration and oxidation. It was found that if a lithium thiochromite sample with a higher vanadium content (0.2–0.3 eq/mol) was suspended in a slightly acid or even in a neutral aqueous solution containing oxygen, the phase was partially decomposed and red, soluble complexes formed. Hence, in order to avoid this decomposition, the vanadium content in the compound was limited to below 0.12 eq/mol.

As reported earlier [1] in the case of $NaCrS_2$, the introduction of vanadium into the thiochromite brings about a substantial increase in the electronic conductivity, this leading to a considerable improvement in the electrochemical performance of the cathodes prepared from the doped compound. The optimum vanadium content in the lithium thiochromite, providing, simultaneously, sufficient chemical stability during the washing process as well as high electrochemical performance, was found to be, as in the case of $NaCrS_2$, from 0.05 to 0.12 eq/mol. The electrical conductivity of the pellet pressed from these samples was in the range 2–10 mS cm^{-1}. Hence, most of our experiments were carried out using samples with this vanadium concentration.

The experiments revealed that if the concentration of LiOH in the solution above the suspension of the raw product, established after 7–8 h, is decreased by dilution from 10^{-2} to 10^{-3} M the delithiation degree, x, is raised from 0.1 to 0.4. The topotactical character of the delithiation reaction (1) is exhibited by the X-ray patterns of samples containing 0.9–0.6 eq/mol of lithium and 0.07 eq/mol of vanadium. These patterns are similar to those shown in Table 1 and Fig. 1(a) except for a small decrease in the peak intensities. When, however, samples with the same vanadium content were so washed that the final equilibrium LiOH concentration in the washing solution was reduced to 10^{-4}–10^{-5} M, the delithiation proceeded more deeply ($0.5 \leqslant x \leqslant 0.8$), whereby part of the phase was hydrated. The X-ray pattern of such samples (Fig. 1(b)) exhibits peaks of this new, 'hydrated' phase (marked with a full dot), along with those of the non-hydrated phase, both with a considerably reduced intensity. It appears that the reflection of the 001 plane of the hydrated phase at $2\theta = 10.4°$ corresponds to an interlayer
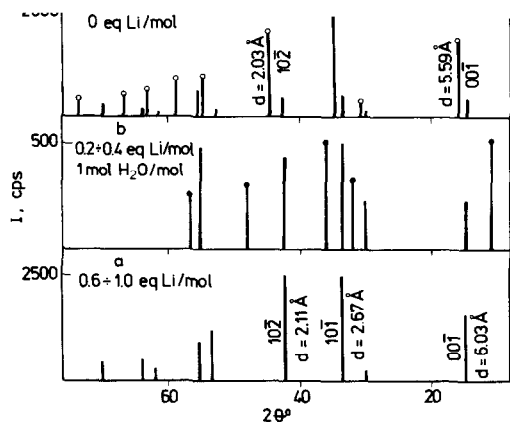
Fig. 1. X-ray diffraction patterns of V-doped Li thiochromite: (a) non-hydrated and partially delithiated sample; (b) hydrated and deeply delithiated sample (the peaks of the hydrated phase are marked with filled circles; (c) deeply charged cathode of a non-hydrated sample (open circles, peaks of binary phase), Cu Kα.

spacing of 8.6 Å, i.e., 2.3 Å larger than that of the non-hydrated phase, 6.3 Å. This expansion along the c axis corresponds tolerably well to the van der Waals diameter of the water molecule, 2.8 Å and, hence, to a monomolecular intercalation layer of H_2O.

This intercalated water could not be removed from the phase by heating at moderate temperatures, e.g., up to 120 °C, under vacuum. It was completely extracted, however, by heating at 300–400 °C under vacuum, as evidenced by the X-ray diffraction patterns showing no peaks of the hydrated phase and all the peaks of the non-hydrated phase. The weight loss of the hydrated samples after heat treatment at 330 °C under vacuum, $ca.$ 10–12%, corresponds to about 1 M H_2O per mole of the solid phase.

The effect of the intercalated water on the electrochemical performance of the thiochromite was studied with samples initially containing 0.21 eq/mol of lithium and $ca.$ 10–12% of water after drying at 110 °C under vacuum. The samples were heat treated under vacuum at various elevated temperatures, again under vacuum, thus eliminating part or all of the water from the phase. Cathodes prepared from these samples were slowly discharged in a glass cell. The amount of lithium intercalated in the first discharge presumably reflects the vacant sites initially available in the sample. As seen in Table 2, this amount increases as the intercalated water is removed. Parallel with this, the specific capacity of the cathode at the 5th cycle increases. Unfortunately, the mid-discharge voltage drops markedly.

A possible explanation of the increase in the capacity upon dehydratation is that the water molecules hinder the intercalation of Li^+ in the phase. This, however, seems unlikely, since, as shown in ref. 8, hydrated thiocromites can readily intercalate, electrochemically, up to 1 eq/mol of an alkali metal. Another explanation is based on the cation exchange properties of the
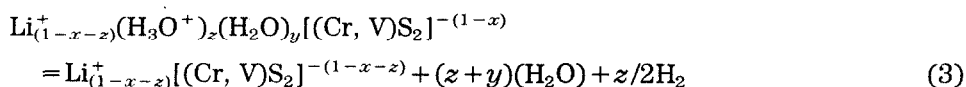
TABLE 2

Effect of thermal treatment on hydrated, V-doped Li thiochromite

Characteristics	Treatment temperature (°C)			
	110	280	300	330
Water content (%)	10–12	5–6	2–3	none
Amount of Li intercalated in the first discharge (eq/mol)	0.54	0.62	0.78	0.79
Specific capacity at the fifth discharge (eq/mol)	0.65	0.70	0.85	0.90
Mid-discharge voltage at the fifth discharge (V)	2.5	2.4	2.3	2.2

hydrated phase, reported in ref. 8 for the case of $NaCrS_2$. In less alkaline solutions one could expect that, parallel with oxidation reaction (1), a cation-exchange reaction (2) between Li^+ and H_3O^+ also proceeds. Because of the extremely low H_3O^+ concentration in the solution this reaction would be feasible only if the equilibrium constant of the cation-exchange reaction is very large.

$$Li^+_{(1-x)}(H_2O)_y[(Cr, V)S_2]^{-(1-x)} + zH_3O^+$$
$$= Li^+_{(1-x-z)}(H_3O^+)_z(H_2O)_y[(Cr, V)S_2]^{-(1-x)} + zLi^+ \qquad (2)$$
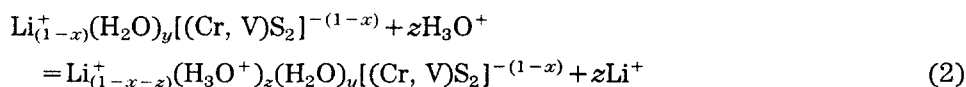
It should be noted that since no electrons are exchanged in reaction (2) the simple removal of water during the subsequent heat treatment could not account for the increased capacity of the dehydrated samples. It can be supposed that the dehydration of the phase at 300–330 °C under vacuum is accompanied by the oxidation of the transition metals in the disulfide layers by the intercalated protons, i.e.,

$$Li^+_{(1-x-z)}(H_3O^+)_z(H_2O)_y[(Cr, V)S_2]^{-(1-x)}$$
$$= Li^+_{(1-x-z)}[(Cr, V)S_2]^{-(1-x-z)} + (z+y)(H_2O) + z/2H_2 \qquad (3)$$

The decrease in the mid-discharge voltage and, correspondingly, in the oxidation potential of the thermally dehydrated compound suggests that some irreversible changes in the electron structure of the compound are caused by this thermal treatment in the presence of water.

The practical significance of these findings is that in order to acquire the optimum electrochemical performance of the cathode material, the raw material washing process should be carried out so as to avoid the hydration of the phase. This is very important since, in order to achieve a higher mechanical stability during cycling, the cathodes, containing Teflon as a binder, are usually sintered at 330–340 °C.

TABLE 3

Effect of the delithiation degree x on the discharge capacity, mid-discharge voltage, and energy density of cathodes prepared from non-hydrated samples

x (eq/mol)	C (A h g^{-1})	U_d (V)	E (W h g^{-1})
0.12	0.120	2.65	0.32
0.25	0.142	2.60	0.37
0.30	0.155	2.55	0.39
0.38	0.165	2.50	0.41

On the other hand, the increase in the degree of lithiation, x, in the range $0.1 \leqslant x \leqslant 0.4$, where no hydration of the phase occurs, has a beneficial effect on the discharge capacity of the cathodes, with only a slight decrease in the mid-discharge voltage, as shown by the data in Table 3, obtained at the 5th cycle. The cycling was performed at 2 mA cm^{-2} (2.4 h rate) in glass cells. It is seen that, despite the slight lowering of the mid-discharge voltage, the energy density of the cathode is increased by $\sim 28\%$ as the degree of delithiation is raised from 0.12 to 0.38.

The increase in discharge capacity with the value of x can be only partially explained by the higher purification of the raw product when washed in a more diluted LiOH solution. It should be supposed that other factors hitherto not studied contribute to this beneficial effect.

Structural evolution of the crystal lattice during charge and discharge and after prolonged cycling

The changes in the X-ray pattern of the phase during cycling were studied with cathodes sintered at 330 °C under very limited air access. The diffraction patterns of the sintered cathodes are indentical with those of the thiosalt from which they were prepared (Table 1). After charging or discharging in a glass cell the cathodes were allowed to stand in the electrolyte for 16–20 h, this allowing the Li ions to be evenly distributed in the crystal lattice. After washing in acetonitrile and drying under vacuum the cathodes were subjected to X-ray diffraction analysis. The pattern after the first slow discharge (20 h) to a 1.5 V cut off, where the lithium content is close to 1 eq/mol does not differ from the uncycled cathode pattern. Pattern (c) of Fig. 1 pertains to the same cathode after the subsequent slow charge to a 3.2 V cut off where the lithium content in the phase is almost exhausted. It is seen that, although with a much lower intensity, eight out of all nine peaks of the lithium-rich ternary phase are still present. Nine, new, strong peaks (marked with circles) appear, presumably pertaining to the lithium-free or binary phase. The peaks of the new phase, or rather the new polymorph, are all shifted to shorter interplanar distances with regard to those of the ternary phase. Thus the shift of the 001 plane reflects the contraction of the lattice constant c from 6.03 to 5.59 Å (7.3%), while that of the 110

plane corresponds to the contraction of the lattice constant $a/2$ from 1.73 to 1.68 Å (2.9%). In the diffraction pattern recorded after the next slow discharge of the same cathode to 1.5 V cut off, all the peaks of the binary phase disappear, while those of the ternary phase recover their intensity almost completely.

The strongest peaks of the binary ($2\theta = 44.6°$, $d = 2.03$ Å) and ternary ($2\theta = 42.8°$, $d = 2.11$ Å) phases, both pertaining to the $10\bar{2}$ plane, were used to study the phase transition during cycling. The evolution in the intensity of these peaks during discharge (intercalation of lithium) is shown in Fig. 2. The peak positions of both phases remain constant with the increase in the content of lithium, $1 - x$, whereas their intensities change proportionally with the lithium content in the phase. The coexistence of two phases is typical for a first-order phase transition, observed previously in the case of the vanadium-doped sodium thiochromite [3].

At the end of the second discharge all peaks of the binary phase vanished, except for that of the 102 plane. Within the first 5–6 cycles the intensity of this peak in the fully discharged cathode gradually increases from zero to 150 cps, whereafter it remains constant, this indicating that a small amount of the binary phase is always present in the fully discharged cathodes. This finding is probably related to the unusual behavior of the cathodes exhibited by the first 4–6 charging curves. They reveal that the mid-charge voltage, which is 3.0 V at the first charge, gradually decreases in the next cycles to reach 2.8 V at the 6th charge, whereafter it remains invariable. It might be supposed that the presence of the binary phase at the beginning of the charge somehow reduces the energy of deintercalation during the entire charge half-cycle. The higher voltage in the first charge is consistent with the finding that, contrasting with the vanadium-doped sodium thiochromite [3], which can be desodiated up to 95% by its treatment with iodine in acetonitrile solutions, the vanadium-doped lithium thiochromite is delithiated only up to 30% by the same treatment.
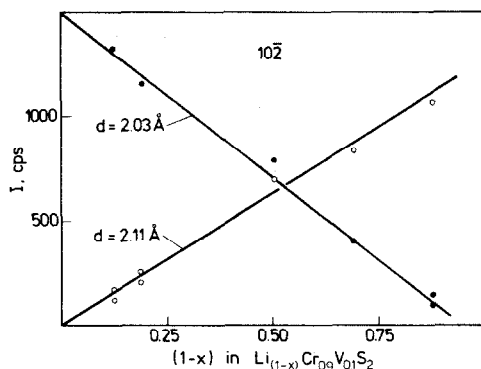

Fig. 2. Evolution in the intensities of the $10\bar{2}$ peaks of the ternary ($d = 2.11$ Å) and the binary ($d = 2.03$ Å) phases with the increase in Li content.
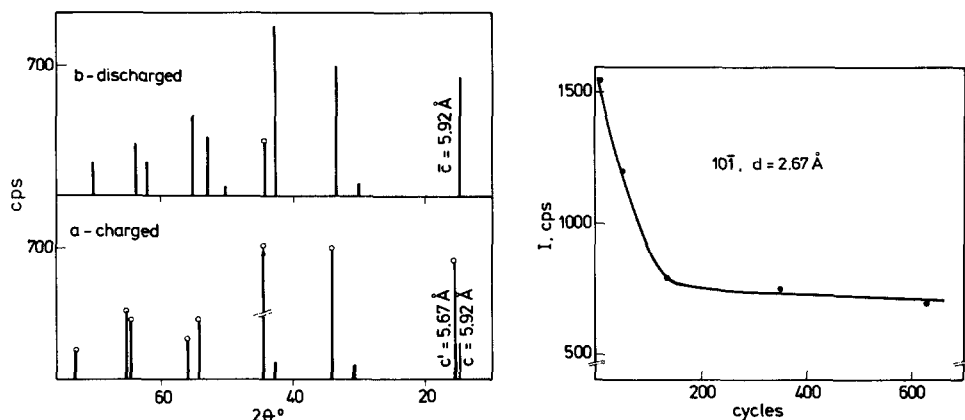
Fig. 3. Diffraction pattern of a cathode after 650 cycles: (a) charged; (b) discharged. Note: the height of the strongest peak in pattern (a) has been artificially truncated.

Fig. 4. Decay in the intensity of the 10$\bar{1}$ peak of the discharged cathode during cycling.

It was found that the first-order phase transition exhibited in the first cycles (Fig. 2) can be observed in the course of a prolonged cycling of the cathode. As shown by Fig. 3, the diffraction pattern of the cathode from a coin-type cell cycled 650 times at a 2.5 h rate reveals the presence of the two phases.

It was further established that the initial contraction, 0.44 Å (7.3%), of the interlayer spacing upon charging drops to 0.27 Å after 130 cycles and reaches 0.25 Å (4.2%) after the 650th cycle. The comparatively minor dilatations during the larger part of the cycle life of the cathode material are most likely the main factor determining its cycling stability.

The decrease in crystallinity of the phase is exhibited by Fig. 4, plotting the intensity of the 001 reflection as a function of the number of cycles. The intensity drops steeply in the first 100 cycles, thereafter it maintains a fairly constant value during the next 550 cycles.

Cycling of coin-type cells

Figure 5 demonstrates the results of the cycling test of a cathode-limited coin-type cell described in the Experimental Section. The cell was cycled at a charge c.d. of 1.0 mA cm^{-2} (3.3 h rate) and a discharge c.d. of 1.67 mA cm^{-2} (2 h rate), which after 450 cycles was lowered to 1.0 mA cm^{-2}. The excess capacity of the lithium anode was 90 mA h. The geometric surface area of each electrode was 1.8 cm^2. The initial cell capacity at the selected voltage range (1.6–3.2 V) was 6.1 mA h, i.e., the depth of discharge of the lithium electrode was 3%. The cell failed at the 651st cycle because of dendrite shorting. After its disassembly it was found that the amount of metallic lithium was negligible. The same cathode was used in the assembly of a new cell with a fresh electrolyte and a new lithium anode. The mean
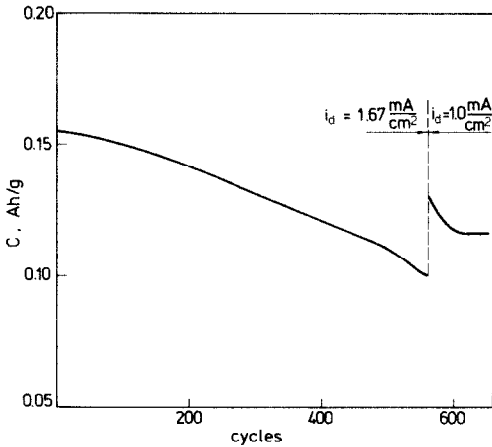
Fig. 5. Decay of the specific capacity of the coin-type cell with cycling.

capacity of this cell during the first 10 cycles, 5.7 mA h, was close to that of the original cell, 6.1 mA h.

Curve 1 in Fig. 5 shows the slow decay of the cell capacity during cycling. Being cathode-limited this decay is actually that of the cathode. Using the logarithmic decay law proposed by Yamaki [9].

$$\log E_c = \log(C_n/C_1)/(n-1)$$

where C_1 and C_n are the capacities of the first and the nth cycle, and n — the number of cycles, the mean cycling efficiency of the cathode material, E_c, was found to be 99.94%. The cycling efficiency of the lithium anode, on the other hand, was estimated by the well known equation

$$E_a = 1 - Q_{ex}/\sum_1^n C_n$$

where Q_{ex} is the excess of lithium. At the 650th cycle the value of E_a reached 97.4%, which is a reasonably good result for the electrolyte solution used. It is equal to one of the best results for this electrolyte, reported by Abraham et al. [10] for a lithium secondary cell with the same electrolyte solution, cycled under similar conditions but with a TiS_2 cathode.

The decrease in the initial mid-discharge voltage, $U_d = 2.50$ V during cycling, amounts to ~ 0.05 V per 100 cycles on average. Most of the decrease may be attributed to the increase in the IR drop in the cell, caused basically by the formation and growth of a porous layer of passivated lithium grains that have lost electrical contact with the lithium electrode. Galvanostatic pulse measurements with coin cells provided with a lithium reference electrode revealed [11] that the increase in the IR drop due to electrolyte degradation or to cathode swelling is of minor importance.

Conclusions

Vanadium-doped lithium thiochromite is prepared by direct thermal synthesis in a sulfur melt, followed by a controlled partial delithiation in aqueous suspension. The product, $Li_{1-x}Cr_{0.9}V_{0.1}S_2$, is characterized by a high specific surface area, considerable electronic conductivity, and very good electrochemical performance in secondary lithium cells.

The good cyclability of the cathodes made from this compound with a trigonal crystal lattice is attributed to its exceptionally stable crystal structure and comparatively small dilatation during cycling. The high specific capacity $(0.15-0.16 \text{ mA g}^{-1})$ and the convenient mid-discharge voltage (twice that of the nickel–cadmium cell) render this compound a promising cathode material in secondary lithium batteries. Added to this is the advantage of the simple and reproducible method for its synthesis.

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