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# Lithiated Vanadium Oxide (LVO), $\gamma$ -Lithium Vanadium Bronze ( $\gamma$ -LiV<sub>2</sub>O<sub>5</sub>) and Vanadium Dioxide (VO<sub>2</sub>) as Thermal Battery Cathode Materials

by

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**LITHIATED VANADIUM OXIDE (LVO),  $\gamma$ -LITHIUM VANADIUM BRONZE  
 ( $\gamma$ -LiV<sub>2</sub>O<sub>5</sub>) AND VANADIUM DIOXIDE (VO<sub>2</sub>) AS THERMAL BATTERY  
 CATHODE MATERIALS**

by

A. G. Ritchie

K. Warner\*

**SUMMARY**

Lithiated vanadium oxide (LVO),  $\gamma$ -lithium vanadium bronze ( $\gamma$ -LiV<sub>2</sub>O<sub>5</sub>) and vanadium dioxide (VO<sub>2</sub>) have been compared as potential cathode materials for high temperature thermal batteries by electrochemical discharges in a laboratory single cell tester. The three materials showed similar performance though LVO may be superior at the highest current density (1A/cm<sup>2</sup>). VO<sub>2</sub> has the advantage of being commercially available.

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## 1 INTRODUCTION

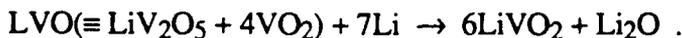
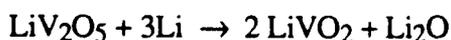
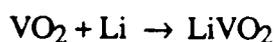
Thermal batteries are high temperature reserve batteries, predominantly used in missiles. Modern designs use a lithium (or lithium-alloy) anode, an immobilised molten salt electrolyte and an iron-disulphide cathode<sup>1-5</sup>. These batteries have many advantages: high reliability, long storage life without maintenance, wide temperature range of operation and, sometimes, high power. However, the energy density is rather low and this could be improved if the individual cell voltage could be raised above the present 2.2 V/cell open-circuit-voltage for the lithium/iron-disulphide couple. A new cathode material, lithiated vanadium oxide (LVO), has been invented at RAE with the advantage of the much higher open-circuit-voltage of 2.6 V/cell versus lithium<sup>6,7</sup>. The properties of LVO have been investigated and it has been shown that LVO consists of vanadium dioxide as the major component with a small proportion of  $\gamma$ -lithium vanadium bronze as the minor electroactive component. Some lithium bromide is also present<sup>8</sup>. Thermal batteries have been made using LVO as the cathode material and these have shown successful discharges<sup>9</sup>.

LVO is made by heating the vanadium oxide  $V_6O_{13}$  with lithium bromide. The reaction proceeds according to the equation<sup>8</sup>



and so LVO is expected to contain  $VO_2$  and  $LiV_2O_5$  in a 4:1 molar ratio. LVO usually also contains some residual lithium bromide from the reaction. This synthesis has the disadvantages (i) that  $V_6O_{13}$  is difficult to make pure as it is normally made by the thermal decomposition of ammonium metavanadate in an inert atmosphere and this reaction needs careful control to avoid production of  $VO_2$  as an impurity and (ii) that the reaction of  $V_6O_{13}$  with  $LiBr$  produces bromine, which is highly toxic.  $LiV_2O_5$  can however be made pure by a simple synthesis.  $VO_2$  is available commercially. None of these materials will be as cheap as iron disulphide, which they are intended to replace, as that can be mined as a mineral, without the need for chemical synthesis.

Electrochemical discharges in a single cell tester have shown that the vanadium compounds in LVO are reduced by lithium to the trivalent state<sup>8</sup>. LVO,  $LiV_2O_5$  and  $VO_2$  therefore react electrochemically with lithium according to the equations:



According to these equations, the theoretical Coulombic capacities for  $\text{VO}_2$ ,  $\text{LiV}_2\text{O}_5$  and LVO are 1160, 1530 and 1300 C/g, respectively. These capacities are for the complete reduction of the various materials to trivalent vanadium; the practical capacities obtainable at useful cut-off voltages will be less. The actual capacities from these materials have been measured experimentally in single cell tests at 500 and 580°C and at current densities of 0.1 to 1.0 A  $\text{cm}^{-2}$ .

## 2 EXPERIMENTAL

### 2.1 Materials

The LVO was made under contract to RAE according to the above method. All the LVO used in these experiments was designated "Bx6". Its bromide content was 13.4%.

The vanadium dioxide was bought from Aldrich (Catalogue number 21582-1, batch number 00818TWAX). X-ray diffraction analysis showed it to be the stable, low-temperature monoclinic form (see Fig 1). Some early experiments using vanadium dioxide<sup>8</sup> are included here; these used either Aldrich gold label  $\text{VO}_2$  or  $\text{VO}_2$  made by J. Knight at RAE by heating together vanadium trioxide ( $\text{V}_2\text{O}_3$ ) and vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) in either 1:1 or 1.1:1 proportions (see Appendix A.3 of Ref 8).

The  $\gamma$ -lithium vanadium bronze ( $\gamma\text{-LiV}_2\text{O}_5$ ) was made by the same procedure as used in earlier work (see Appendices A.1 and A.2 of Ref 8) which was based on the published method of Murphy *et al*<sup>10</sup>. 26.68 g of lithium iodide were added slowly to 64 g acetonitrile, taking care that the solution did not overheat. 15.03 g vanadium pentoxide were then added to the solution of lithium iodide in acetonitrile. The colour of the vanadium pentoxide immediately changed from orange to dark brown. The mixture was then left to react for 72 hours while the solution was stirred with a magnetic stirrer. After completion of the reaction, the product ( $\delta\text{-LiV}_2\text{O}_5$ ), which was now a finely divided black powder, was quantitatively filtered off and was washed with acetonitrile until the washings were colourless. The solid was dried by heating it in a vacuum at 80°C. The product was dried to constant weight (15.724 g) giving quantitative conversion of the vanadium pentoxide into  $\delta$ -lithium vanadium bronze. This was then heated in a tube furnace in an argon atmosphere at 10°C/min to 600°C and then held at 600°C for 3 hours to convert the  $\delta$ -lithium vanadium bronze to the  $\gamma$ -form. After baking, the product was still a relatively free-flowing powder. It was characterised by X-ray diffraction which confirmed that  $\gamma\text{-LiV}_2\text{O}_5$  was the product obtained (see Fig 2) and by thermal analysis (simultaneous thermogravimetric analysis, TGA, and differential thermal analysis, DTA, see Fig 3). This showed a transition (presumably solid-state) at 591°C and a second transition at 751°C. The first peak is in good agreement with a differential scanning calorimetry (DSC) test on material made by J. Knight and used in the work described in Ref 8 (see Fig 4). The additional DSC peaks in Fig 4 at 50-120°C are probably evolution of water absorbed in storage. The second DTA peak in Fig 3 (751°C) is the melting of the  $\text{LiV}_2\text{O}_5$  (literature melting point 772°C<sup>11</sup>).

Ternary eutectic (lithium chloride-lithium fluoride-lithium bromide) was added to the cathode materials to improve the cathode conductivity. For the experiments using LVO or  $\text{LiV}_2\text{O}_5$  the proportions were 70 wt% LVO or  $\text{LiV}_2\text{O}_5$ : 30 wt% ternary eutectic as these proportions had been established as standard in earlier work<sup>8</sup>. For the experiments using  $\text{VO}_2$ , the  $\text{VO}_2$ :ternary proportions were varied somewhat to obtain an optimum mixture.

The electrolyte was ternary electrolyte containing 70 wt% ternary eutectic immobilised on 30 wt% magnesium oxide which acts as a binder to keep the molten ternary eutectic in place during the single cell tests.

The anode material was 24 wt% lithium aluminium alloy.

In all the single cell tests, the current collectors were made of iron.

## 2.2 Experimental procedures

The cathode material was ground with the chosen amount of ternary eutectic to form a homogeneous mixture. For some of the experiments using  $\text{VO}_2$ , the  $\text{VO}_2$ /ternary mixtures were fused together. Details of the various batches of these mixtures are given in Table 1. 0.3 g of cathode mixture was weighed out and loaded into the press. 0.15 to 0.3 g of ternary electrolyte was weighed into the press and a two-layer cathode-electrolyte pellet was pressed at a force of 6 tonnes (3 tonnes/cm<sup>2</sup> for the 16 mm diameter, 2.0 cm<sup>2</sup> pellets used). Anode pellets were 0.3 g 24 wt% lithium-aluminium alloy, pressed at 10 tonnes (5 tonnes/cm<sup>2</sup>). All pellets were pressed inside a dry air glove box (about 10 ppm water vapour) as the ternary eutectic is extremely hygroscopic (see Fig 5 for a photograph of the press in the dry air glove box). Except for LVO run number 211, which was carried out in a dry air box flushed with argon, all the single cell tests were carried out in an argon glove box. Fig 6 shows the single cell tester inside the argon glove box and Fig 7 shows a close-up of the single cell tester. The operation of the single cell tester can best be understood from the simplified diagram in Fig 8. The anode and bi-layer cathode/electrolyte pellets were transferred in sealed containers from the dry air glove box containing the press to the argon glove box and loaded into the single cell tester with the anode pellet on the lower current collector, the electrolyte over the anode with the cathode layer on top underneath the upper current collector. The boron nitride platens were heated to the chosen temperature and then the hydraulic rams were operated to clamp the cell firmly together, normally at a force of 6 kg. Heat rapidly diffused from the platens into the cell components, melting the electrolyte and activating the single electrochemical cell. After a short wait to establish a stable open-circuit potential, a constant current load was applied and the discharge was recorded down to 0 V. All voltages are referred to 24 wt% lithium-aluminium alloy. The discharge curves were recorded using a chart recorder. The recorder traces were measured, recalculated into absolute units (voltage versus electrochemical capacity) and stored in a computer. All the discharges illustrated here are plotted from the computer using an interpolation routine to draw a smooth curve between the measured points.

### 3 RESULTS

The results for single cell tests of LVO and  $\text{LiV}_2\text{O}_5$  are listed in Table 2 and for  $\text{VO}_2$  in Table 3. The results for LVO and  $\text{LiV}_2\text{O}_5$  at  $580^\circ\text{C}$  are plotted in Figs 9 and 10 respectively. It can be seen that better discharges are obtained using the thinner electrolyte pellets (0.15 g *cf* 0.3 g), particularly at the higher current densities where the IR drop due to the internal resistance of the electrolyte is greater. Similarly, better discharges are obtained at the lower currents. Discharges for LVO and  $\text{LiV}_2\text{O}_5$  at  $500^\circ\text{C}$  are plotted in Figs 11 and 12, respectively. As at  $580^\circ\text{C}$ , the achievable capacities are lower at the higher currents, indicating significant internal resistance, and no useful capacity was obtained from the 2 A discharge for  $\text{LiV}_2\text{O}_5$ . The discharge curves for  $\text{VO}_2$  are plotted in Figs 13 to 20. It is clear that the later batches of the  $\text{VO}_2$ /ternary eutectic, which were fused together and had higher proportions of ternary eutectic in them, gave better discharges than the earlier experiments in which the  $\text{VO}_2$  and ternary eutectic were simply ground together and not fused. The best results were obtained for batch 5 in which the  $\text{VO}_2$  was sieved below  $38\ \mu\text{m}$  both before and after fusing with ternary eutectic. Electrolyte weights for each test are given in Table 3.

The present results for LVO can be compared with results obtained during previous laboratory studies using the single-cell tester, whenever comparable results exist. At  $580^\circ\text{C}$  and 200, 1000 and 2000 mA there are comparable results (runs 577, 637 and 638 of the early work and runs 109, 110 and 115 of the present series). The results are plotted in Fig 21 and it can be seen that both sets of results are quite similar except that there is a lower voltage (higher internal resistance) in the present work at the highest current (2 A).

The present results for  $\text{LiV}_2\text{O}_5$  can be compared with results obtained earlier (Ref 8). Fig 22 compares results at  $580^\circ\text{C}$  and 1 and 2 A. The older results (runs number 515 and 516) were for  $\delta\text{-LiV}_2\text{O}_5$  which gave the best discharges in the earlier work. It can be seen that the present work agrees very well with earlier results, which were not carried out over such a wide range of temperatures and current densities.

Similarly, present and earlier work with  $\text{VO}_2$  can be compared. Fig 23 shows similar results between present and earlier work at  $580^\circ\text{C}$  and 0.8/1.0 A and Fig 24 shows a similar comparison at  $580^\circ\text{C}$  and 2 A for one recent run with three older ones. Again, recent results are similar to earlier ones, where experiments at comparable conditions exist.

### 4 DISCUSSION

Discharge curves for LVO,  $\text{LiV}_2\text{O}_5$  and  $\text{VO}_2$  are plotted in Figs 25 to 32 for comparison. The curves for LVO and  $\text{LiV}_2\text{O}_5$  are for 0.15 g electrolyte; the  $\text{VO}_2$  curves are for batch 5 material, except in one case ( $580^\circ\text{C}$ , 2000 mA) where the batch 5 material gave a very poor discharge and a curve for batch 4 is included also. All three materials showed very similar discharges with insufficient grounds for ranking them in a particular order due to statistical variations. On the basis of one test at each condition, the only case where LVO was superior to  $\text{LiV}_2\text{O}_5$  and  $\text{VO}_2$  was at  $500^\circ\text{C}$  and 2 A. It was

however better than  $\text{VO}_2$  at  $580^\circ\text{C}$  and 2 A, though, in this case, it was inferior to  $\text{LiV}_2\text{O}_5$ . These results indicate that  $\text{LiV}_2\text{O}_5$  or  $\text{VO}_2$  are probably preferable to LVO, except at the highest current densities though the differences are small and a larger number of experiments would be needed to obtain statistical quantification of the differences.

A simple means of quantitative comparison of the different materials is to compare the Coulombic capacities obtainable to realistic cut-off voltages, as it is this parameter which is used when designing thermal batteries to decide the amount of cathode material needed. The cathode capacities for LVO,  $\text{LiV}_2\text{O}_5$  and  $\text{VO}_2$  to 2.0 V and 1.75 V are compared in Table 4 and they are plotted in Fig 33 (for results at  $500^\circ\text{C}$ ) and in Fig 34 (for results at  $580^\circ\text{C}$ ). The available capacities are always lower at the higher current densities as the voltages are lower due to the higher IR drop. There are no significant differences in the practical capacities achieved for the different materials, notwithstanding the differences in capacities theoretically available (see Introduction) except that LVO tended to have the greatest capacity at the highest current density ( $1 \text{ A/cm}^2$ ) particularly at  $580^\circ\text{C}$ . As most of the previous work (Ref 8) was done at  $580^\circ\text{C}$  and  $1 \text{ A/cm}^2$ , this accounts for the previous conclusion that LVO had better discharges than  $\text{LiV}_2\text{O}_5$  or  $\text{VO}_2$ . In practice, thermal batteries typically operate at current densities of 0.1 to  $0.5 \text{ A/cm}^2$  with  $1 \text{ A/cm}^2$  only rarely being needed, and also many battery discharges would not experience temperatures as high as  $580^\circ\text{C}$ , at least for any significant time.

Of the three materials tested here, LVO is a new invention and so not available commercially, neither is there a commercial supply of  $\text{LiV}_2\text{O}_5$ .  $\text{VO}_2$  is a simple chemical compound, readily available commercially in the crystalline form used here. As its electrochemical properties are at least as good as LVO (or  $\text{LiV}_2\text{O}_5$ ) except possibly at very high current densities (over  $1 \text{ A/cm}^2$ ), it is recommended that it should be tested in prototype thermal batteries.

## 5 CONCLUSIONS

LVO,  $\text{LiV}_2\text{O}_5$  and  $\text{VO}_2$  have been compared as thermal battery cathode materials in isothermal single cell tests at 500 and  $580^\circ\text{C}$  and at 100, 250, 500 and  $1000 \text{ mA/cm}^2$  current density. Little difference was found between these materials, though LVO may be the best at the highest current density ( $1 \text{ A/cm}^2$ ). Optimisation of cathode material:salt eutectic in the cathode pellet made significant differences to the discharges for  $\text{VO}_2$ . Selection of  $\text{VO}_2$  with a particle size below  $38 \mu\text{m}$  further improved the  $\text{VO}_2$  discharges and optimisation of the particle size distribution is clearly worthwhile.

It is recommended that prototype thermal batteries with  $\text{VO}_2$  cathode material should be built as this is a readily available commercial material with equally good electrochemical discharge properties, and could well be less costly to use than LVO.

Table 1

## VANADIUM DIOXIDE/TERNARY EUTECTIC CATHODE MIXTURES

Batch 1 Vanadium dioxide and ternary eutectic weighed out individually and ground together for each cathode pellet. Actual weights of vanadium dioxide and ternary eutectic used for each experiment listed in Table 3.

Batch 2	Vanadium dioxide	2.009 g	(71.1%)
	Ternary eutectic	<u>0.817 g</u>	(28.9%)
	Total	<u>2.826 g</u>	

The mixture was baked at 460°C under argon, ground and sieved through a 212 µm sieve. Sieve analysis of the product was as follows:-

>212 µm	Nil	0.0%
>150 µm	381 mg	14.2%
106-150 µm	537 mg	19.9%
38-106 µm	1275 mg	47.4%
<38 µm	<u>499 mg</u>	18.5%
Total recovered	<u>2692 mg</u>	(95.3% of starting material)

Batch 3	Vanadium dioxide	1.987 g	(65.9%)
	Ternary eutectic	<u>1.027 g</u>	(34.1%)
	Total	<u>3.014 g</u>	

Mixture baked under argon at 460°C. Weight recovered after baking was 2.929 g (97.2% of material).

Batch 4	Vanadium dioxide	2.00 g	(62.5%)
	Ternary eutectic	<u>1.20 g</u>	(37.5%)
	Total	<u>3.20 g</u>	

Mixture baked under argon at 460°C. Weight recovered after baking was 3.09 g (96.6% of starting material). Product sieved through 212 µm sieve.

Batch 5	Vanadium dioxide	2.075 g	(63.3%)
	Ternary eutectic	<u>1.203 g</u>	(36.7%)
	Total	<u>3.278 g</u>	

The vanadium dioxide was sieved through a 38 µm sieve, mixed with the ternary eutectic and baked at 460°C under argon. The weight after baking was 3.156 g (96.3% of starting material). The product was sieved through a 38 µm sieve before use.

**Table 2**  
**SINGLE CELL TEST RESULTS FOR  $\text{LiV}_2\text{O}_5$  AND LVO**

Run number	Cathode	Electrolyte Weight (g)	Temperature (°C)	Current (mA)	Capacity (C/g) to	
					2.0 V	1.75 V
211	LVO	0.27	580	200	607	672
101	$\text{LiV}_2\text{O}_5$	0.3	580	200	540	691
102	$\text{LiV}_2\text{O}_5$	0.3	580	500	511	667
103	LVO	0.3	580	500	433	567
104	$\text{LiV}_2\text{O}_5$	0.3	580	1000	393	543
105	LVO	0.3	580	1000	348	533
106	$\text{LiV}_2\text{O}_5$	0.3	580	2000	76	238
107	LVO	0.3	580	2000	119	283
108	$\text{LiV}_2\text{O}_5$	0.15	580	1000	469	633
109	LVO	0.15	580	1000	386	593
110	LVO	0.15	580	200	457	706
111	$\text{LiV}_2\text{O}_5$	0.15	580	200	600	640
112	LVO	0.15	580	500	583	640
113	$\text{LiV}_2\text{O}_5$	0.15	580	500	348	488
114	$\text{LiV}_2\text{O}_5$	0.15	580	2000	351	524
115	LVO	0.15	580	2000	233	471
116	$\text{LiV}_2\text{O}_5$	0.15	500	200	486	643
117	LVO	0.15	500	200	337	514
118	$\text{LiV}_2\text{O}_5$	0.15	500	500	457	636
119	LVO	0.15	500	500	386	531
120	$\text{LiV}_2\text{O}_5$	0.15	500	2000	0	0
121	LVO	0.15	500	2000	236	395
122	$\text{LiV}_2\text{O}_5$	0.15	500	2000	0	255
125	LVO	0.15	500	1000	290	457
126	$\text{LiV}_2\text{O}_5$	0.15	500	1000	371	543

Table 3  
SINGLE CELL TESTS USING VANADIUM DIOXIDE CATHODE

Run number	Electrolyte weight (mg)	Cathode			Temperature (°C)	Current (mA)	Capacity to	
		(mg VO <sub>2</sub> )	(mg ternary)	Batch			2.0 V (C/g VO <sub>2</sub> )	1.75 V (C/g VO <sub>2</sub> )
1A	200	194	106	1	580	2000	186	351
2A	198	201	89	1	580	201	312	414
3A	188	194	99	1	580	201	426	507
1	161	209	97	1	580	1000	110	215
2	166	190	80	1	580	1000	158	289
3	201	194	73	1	580	1011	193	307
4	170	196	79	1	580	470	163	235
5	200	200	76	1	580	2007	95	208
6	198	200	77	1	500	200	246	453
7	175	204	73	1	500	500	172	265
8	192	207	73	1	500	1000	34	101
9	187	203	87	1	500	2001	84	217
10	205	190	78	2	580	1988	115	262
11	169	193	79	2	580	1011	257	398
12	203	203	83	2	580	502	356	500
13	221	188	77	2	580	202	357	485
14	190	193	96	3	580	1000	124	311
15	196	183	92	3	580	2019	143	309

Table 3 (continued)

Run number	Electrolyte weight (mg)	Cathode			Temperature (°C)	Current (mA)	Capacity to	
		(mg VO <sub>2</sub> )	(mg ternary)	Batch			2.0 V (C/g VO <sub>2</sub> )	1.75 V (C/g VO <sub>2</sub> )
16 <sup>1</sup>	175	187	94	3	580	508	76	235
17	191	203	102	3	580	204	494	579
18	190	194	96	3	500	1000	211	371
19	192	200	100	3	500	500	325	485
20	193	182	90	3	500	200	349	514
21	174	202	100	3	580	500	396	545
22	211	203	119	4	580	1012	344	494
23	199	183	107	4	580	504	413	589
24	194	176	103	4	580	2000	125	313
25	196	188	110	4	580	209	487	580
26	198	192	112	4	500	1005	319	492
27	200	197	115	4	500	518	357	518
28	184	183	108	4	500	201	231	402
29	167	193	114	4	500	202	176	308
30	192	176	104	5	500	198	429	624
31	202	186	109	5	500	1010	304	462
32	182	181	106	5	500	2000	116	271
33	175	170	100	5	500	519	281	403
34	173	180	105	5	580	507	484	710

Table 3 (concluded)

Run number	Electrolyte weight (mg)	Cathode			Temperature (°C)	Current (mA)	Capacity to	
		(mg VO <sub>2</sub> )	(mg ternary)	Batch			2.0 V (C/g VO <sub>2</sub> )	1.75 V (C/g VO <sub>2</sub> )
35	174	195	115	5	580	1027	432	643
36	178	176	104	5	580	205	594	692
371	185	159	94	5	580	2004	25	126
4612	300	210	90	-	580	800	290	533
4632	300	210	90	-	580	2000	57	229
5453	200	210	90	-	580	2000	314	600
5514	300	210	90	-	580	2000	200	514

Notes: 1 Poor discharge; unsteady open-circuit voltage

2 Aldrich gold label vanadium dioxide

3 VO<sub>2</sub> made by J. Knight by heating 1:1 molar V<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> at 600°C

4 VO<sub>2</sub> made by J. Knight by heating 1:1:1 molar V<sub>2</sub>O<sub>3</sub>:V<sub>2</sub>O<sub>5</sub> at 600°C

**Table 4**  
**COULOMBIC CAPACITIES FOR LVO, LiV<sub>2</sub>O<sub>5</sub> AND VO<sub>2</sub>**

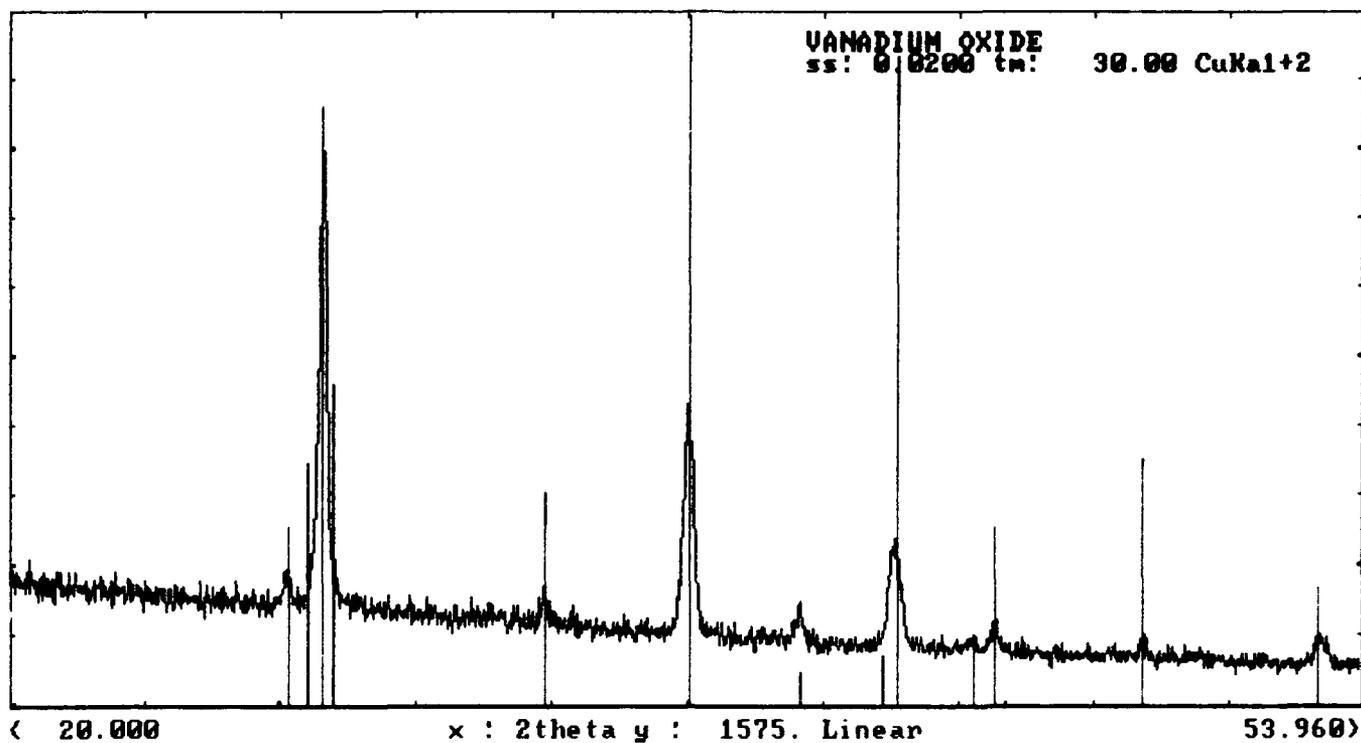
Temperature (°C)	Current (mA)	Material	Capacity (C/g) to		
			2.0 V	1.75 V	
580	200	LVO	457	706	
		LiV <sub>2</sub> O <sub>5</sub>	600	640	
		VO <sub>2</sub>	594	692	
	500	500	LVO	583	640
			LiV <sub>2</sub> O <sub>5</sub>	348	488
			VO <sub>2</sub>	484	710
	2000	1000	LVO	386	593
			LiV <sub>2</sub> O <sub>5</sub>	469	633
			VO <sub>2</sub>	432	643
		2000	LVO	233	471
			LiV <sub>2</sub> O <sub>5</sub>	398	524
	500	200	VO <sub>2</sub> batch 5	25	126
VO <sub>2</sub> batch 4			125	313	
LVO			337	514	
500		200	LiV <sub>2</sub> O <sub>5</sub>	486	643
			VO <sub>2</sub>	429	624
			LVO	386	531
1000		500	LiV <sub>2</sub> O <sub>5</sub>	457	636
			VO <sub>2</sub>	281	403
			LVO	290	457
2000		1000	LiV <sub>2</sub> O <sub>5</sub>	371	543
			VO <sub>2</sub>	304	462
			LVO	236	395
2000	2000	LiV <sub>2</sub> O <sub>5</sub>	0	255*	
		VO <sub>2</sub>	116	271	
		LVO	236	395	

\* Run number 122, no useful capacity obtained in run number 120 under same conditions

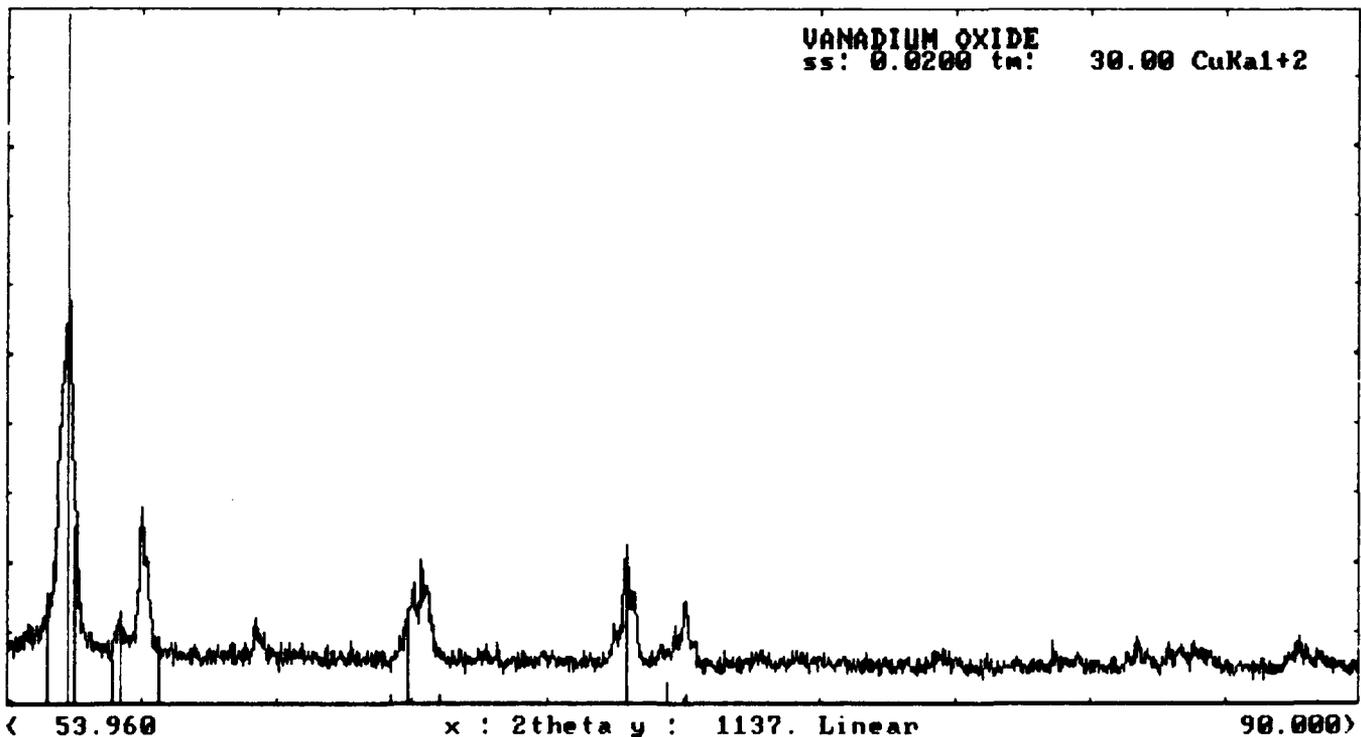
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| 7   | I. Faul<br>A.J. Golder   | <i>Electrochemical cell structures.</i><br>European Patent Application 0145261, November 1984   |
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| 11  | V.L. Volkov<br>L.L. Surat<br>A.A. Fotiev<br>I.U. Koksharova    | Russ. J. Phys. Chem., 47, 878 (1973)  |

Fig 1



9-0142 | UO2 Vanadium Oxide  
33-1441 | UO2 Vanadium Oxide



9-0142 | UO2 Vanadium Oxide  
33-1441 | UO2 Vanadium Oxide

Fig 1 X-ray diffractogram of vanadium dioxide

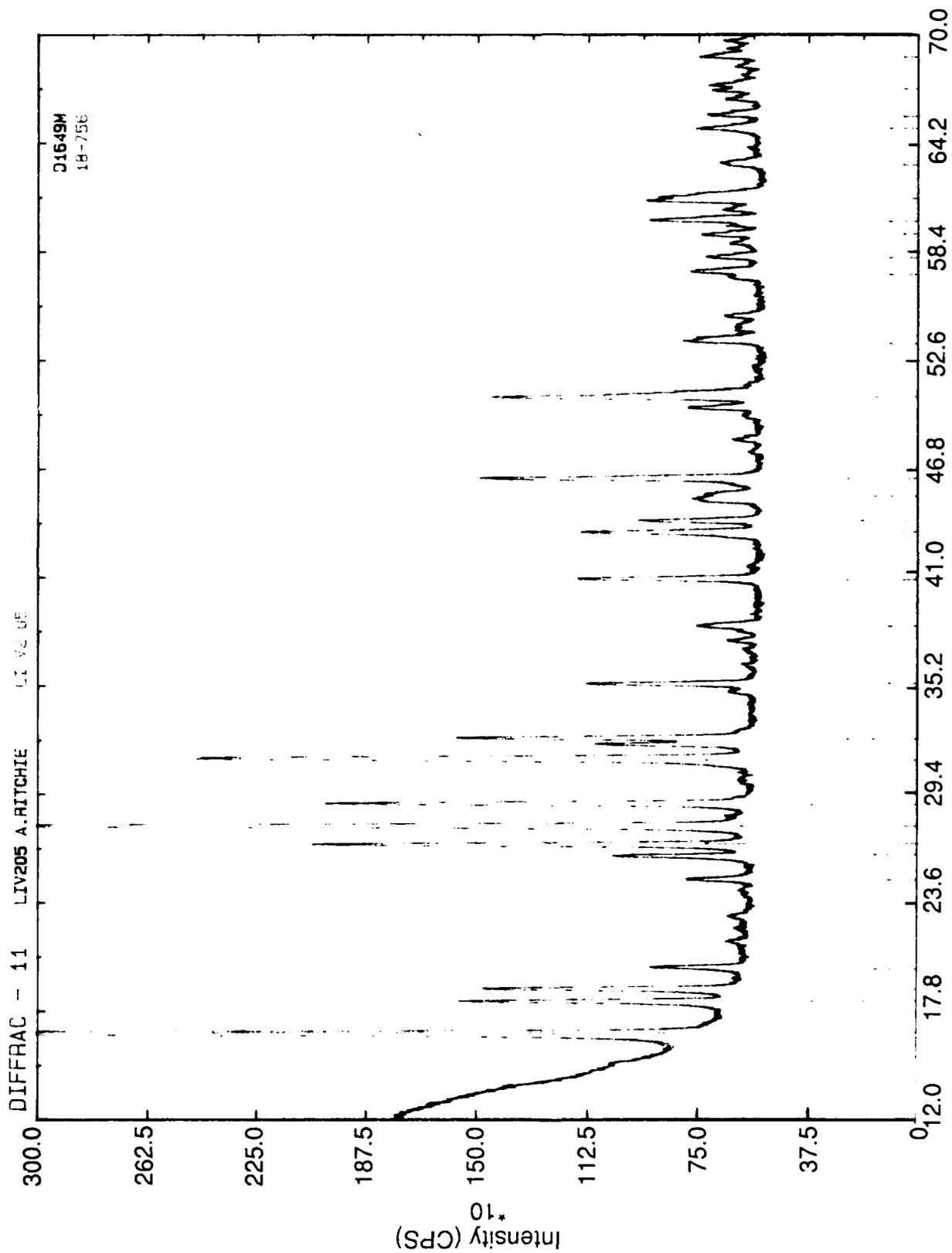


Fig 2

Two - Theta (degrees)  
 Fig 2 X-ray diffractogram of  $\gamma$ -lithium vanadium bronze

Sample ID :  $\text{LiV}_2\text{O}_5$   
 Run ID :  
 Size : 3.800 mg  
 Operator : K Warner  
 STA 1000  
 Stanton Redcroft  
 Date Run : Mar/02/1990  
 Gases : Ar  
 Source :  
 Comment : Test sample1

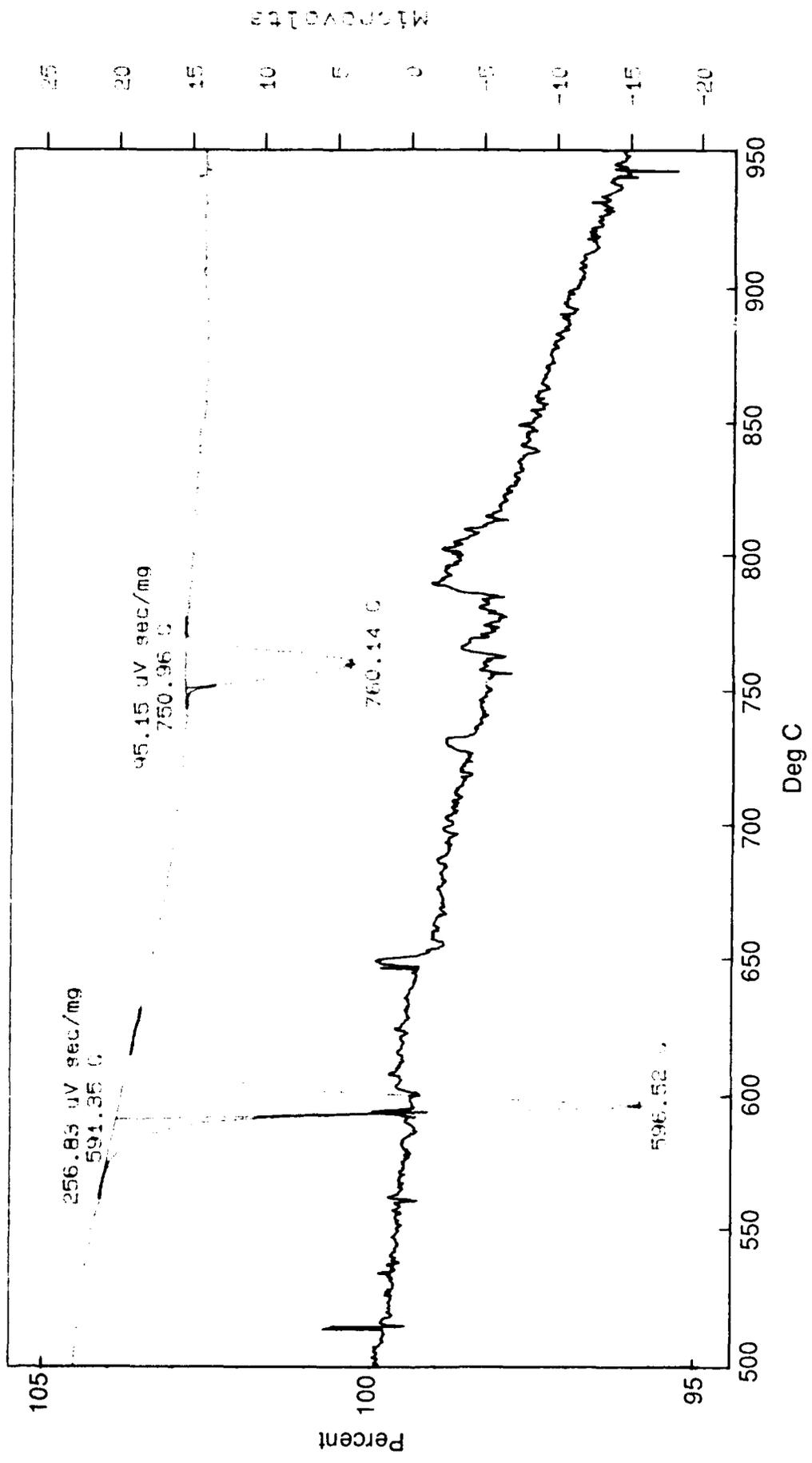


Fig 3

Fig 3 Thermal analysis of  $\text{LiV}_2\text{O}_5$

Fig 4

File: IH805.2  
Operator: AGR  
Run Date: 12/21/89 12:52

DSC

Sample :  $\text{LiV}_2\text{O}_5$   
Size : 11.3820 mg  
Method : AGR

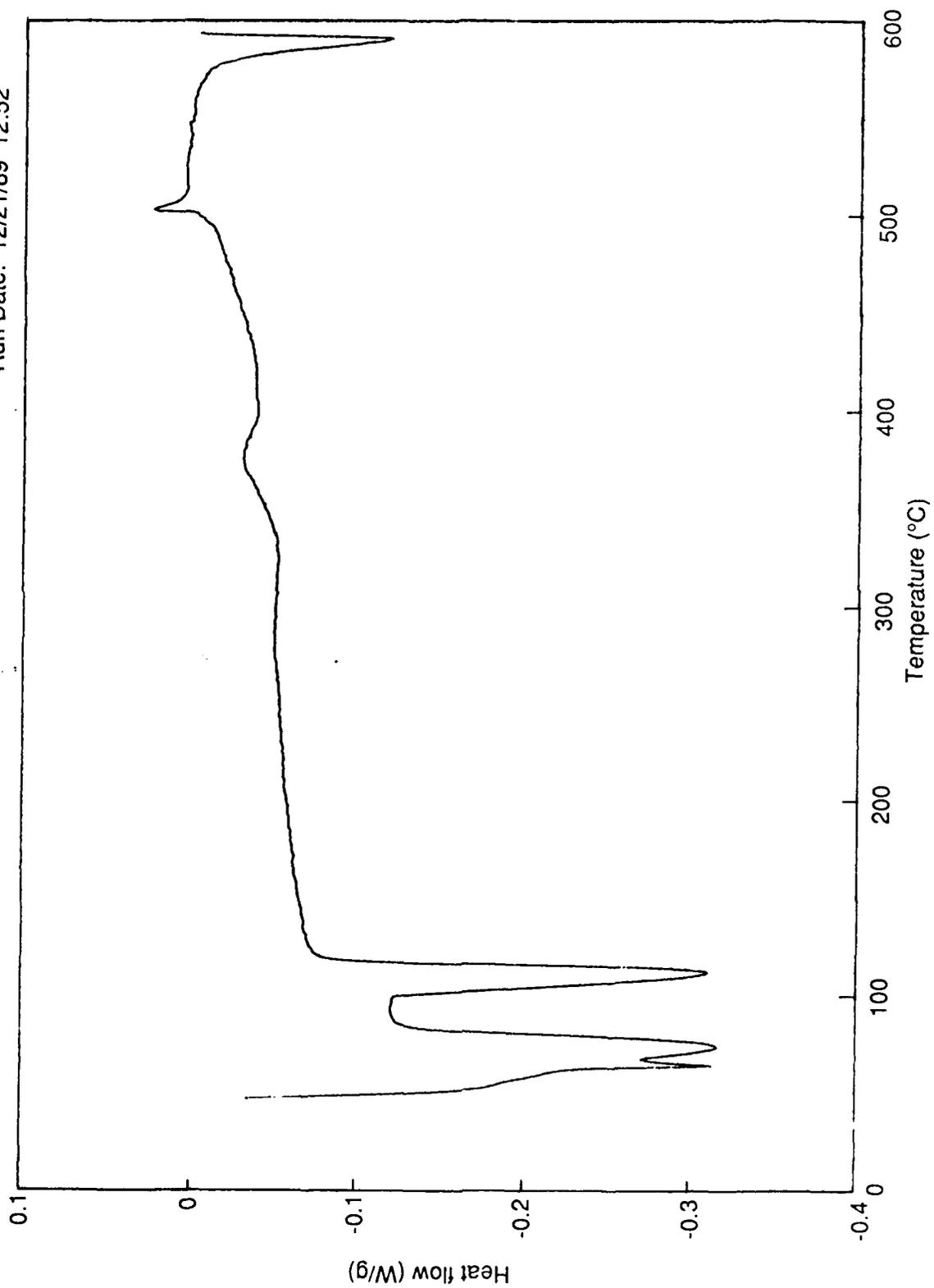
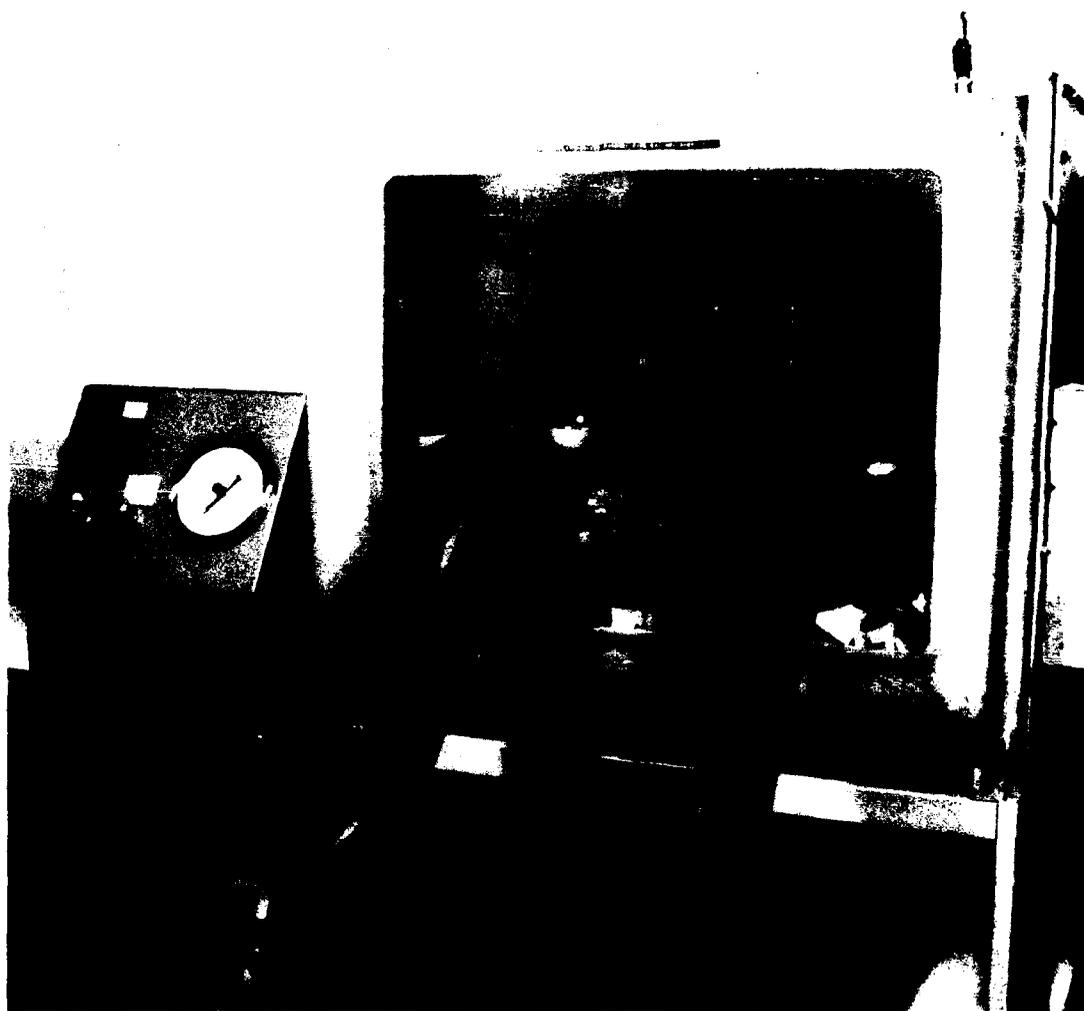


Fig 4 Thermal analysis of  $\text{LiV}_2\text{O}_5$  made by J Knight

**Fig 5**



**Fig 5 Dry-air box and press**

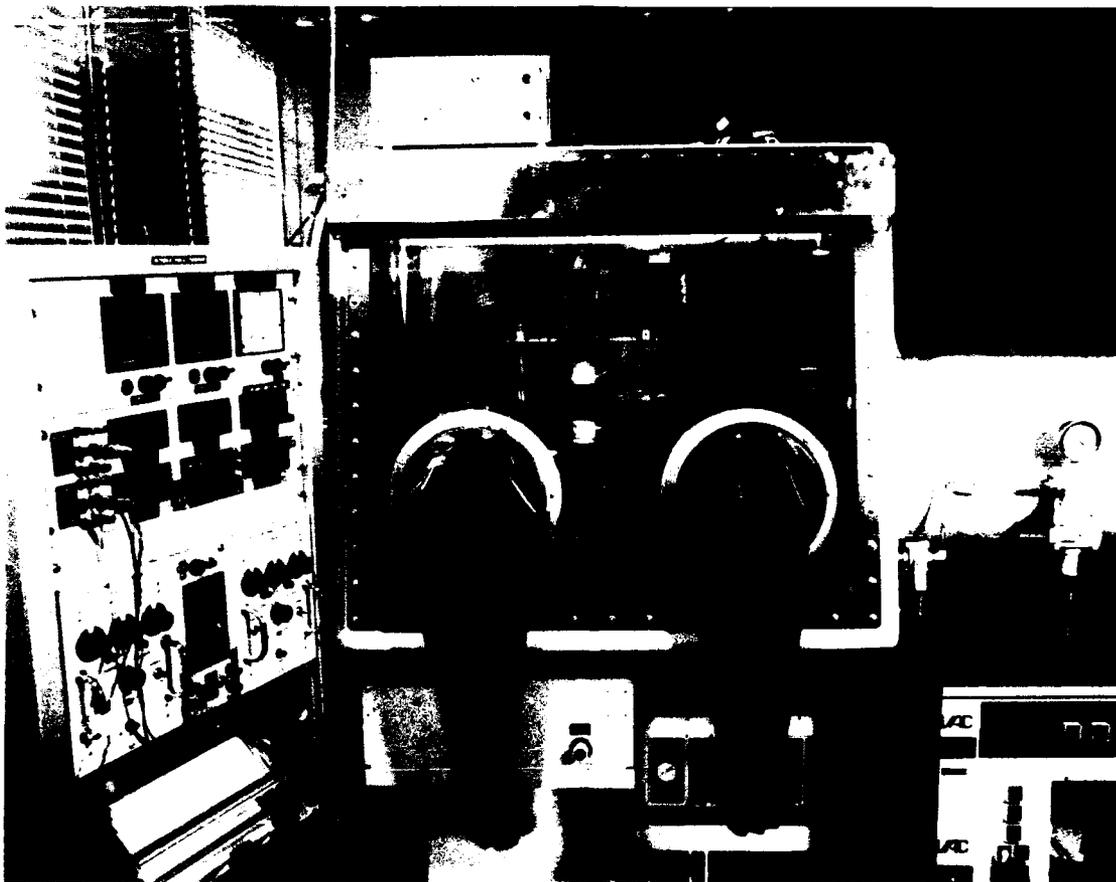


Fig 6 Argon glove box, plus electronics

Fig 7



Fig 7 The single cell tester

Fig 8

- 1 Cathode pellet
- 2 Electrolyte pellet
- 3 Anode pellet
- 4 & 5 Iron current collecting discs
- 6 Current output lead
- 7 Voltage output lead
- 8 & 9 Boron nitride platens
- 10 & 11 Pneumatic rams @ pressure  $\sim 3\text{kg cm}^{-2}$
- 12 & 13 Electrical cartridge heaters

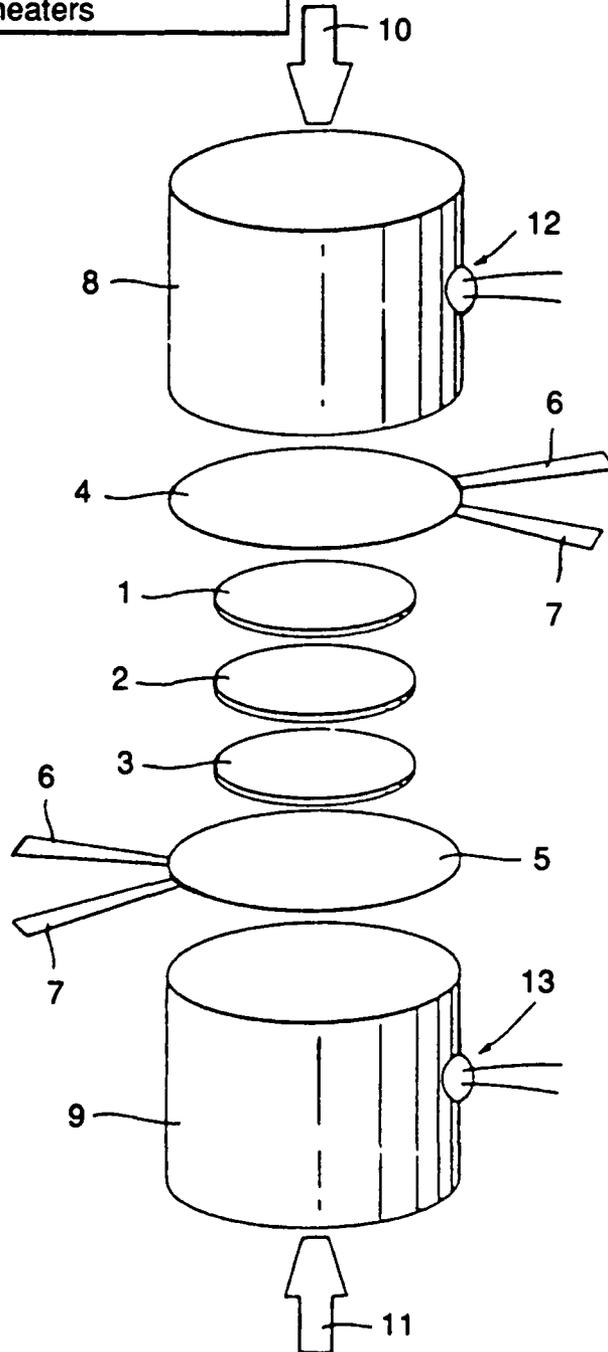
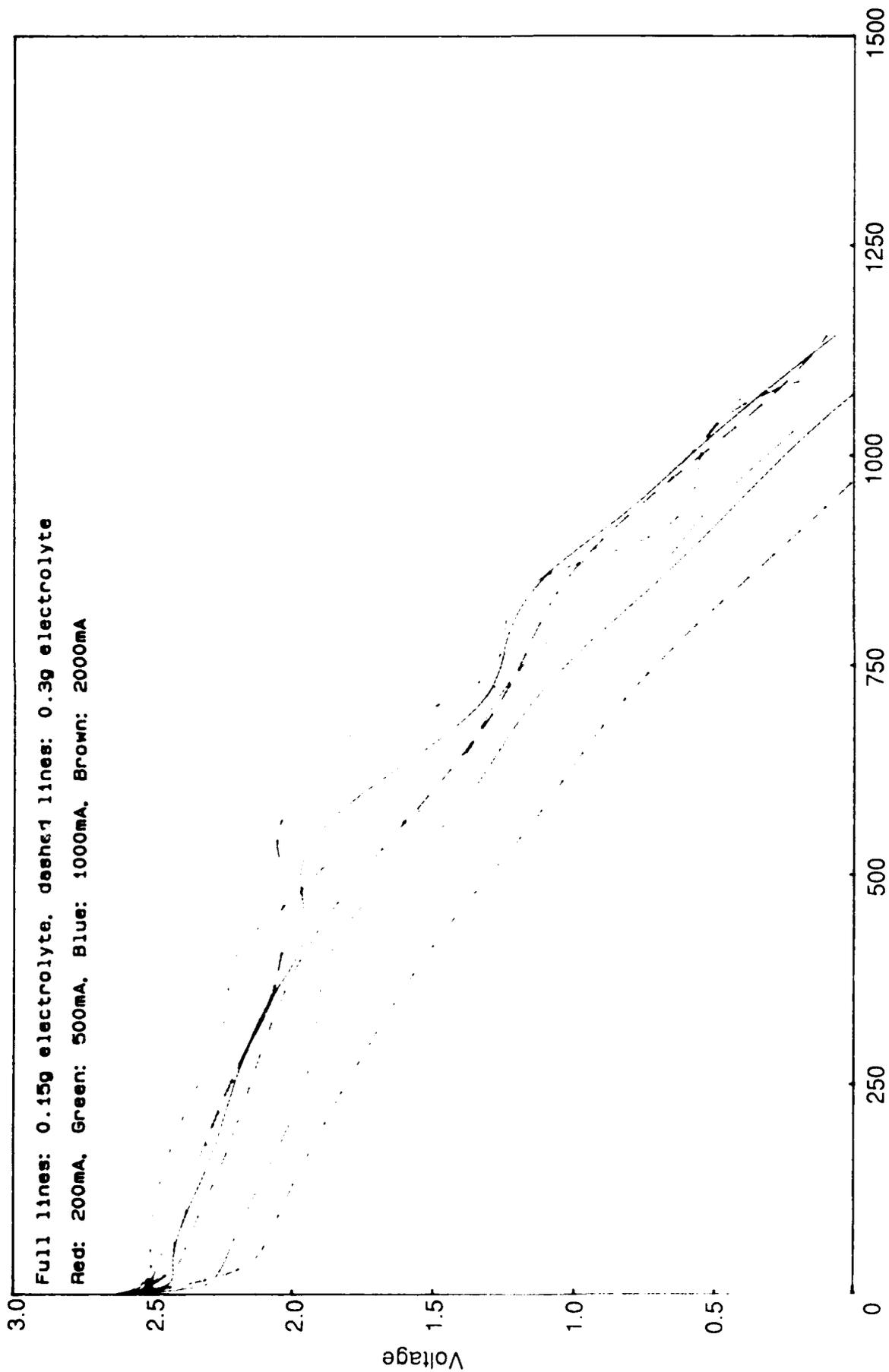


Fig 8 Simplified diagram of the single cell tester



Charge withdrawn (C/g LVO)

Fig 9 LVO 580C

Fig 9

Fig 10

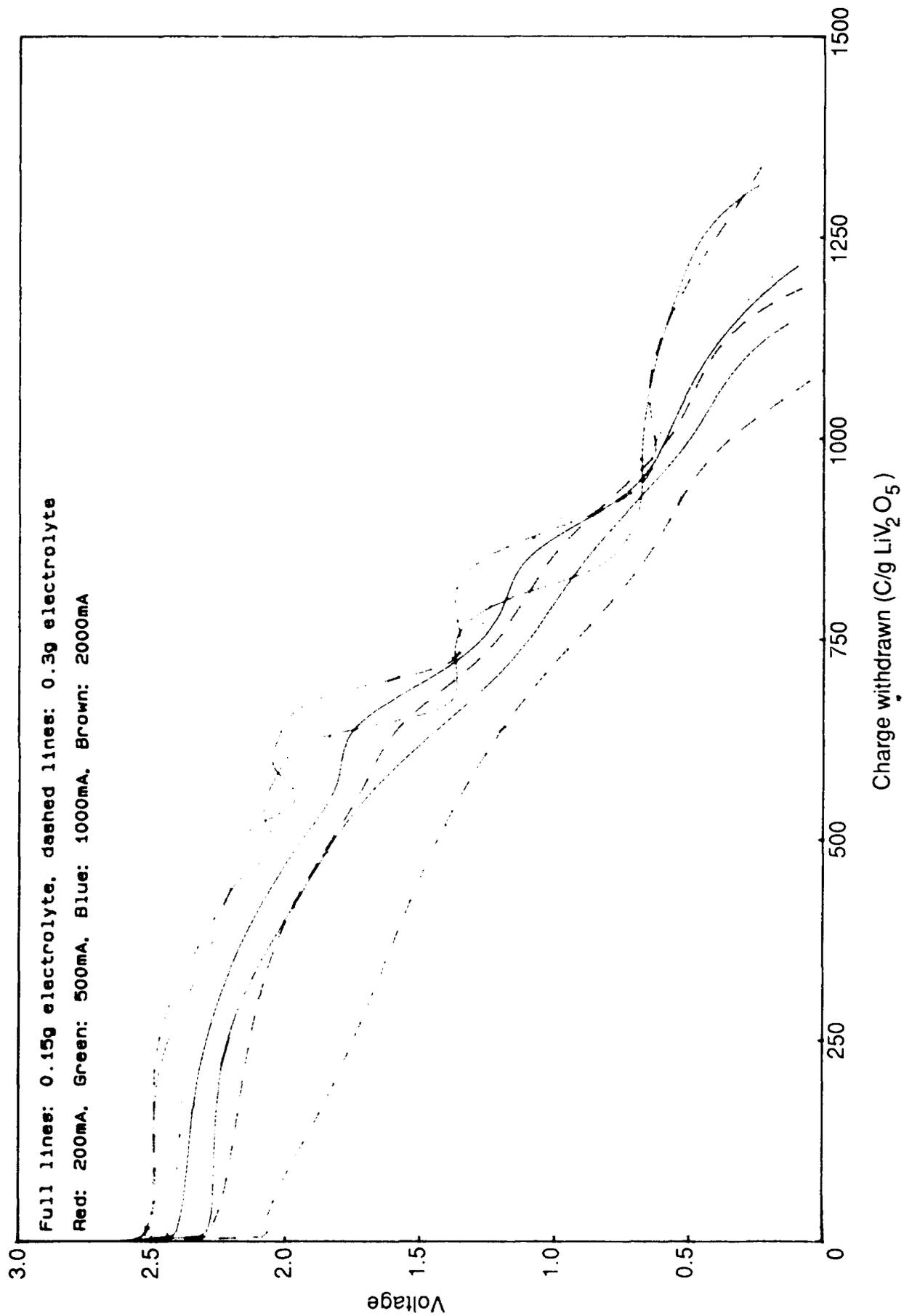
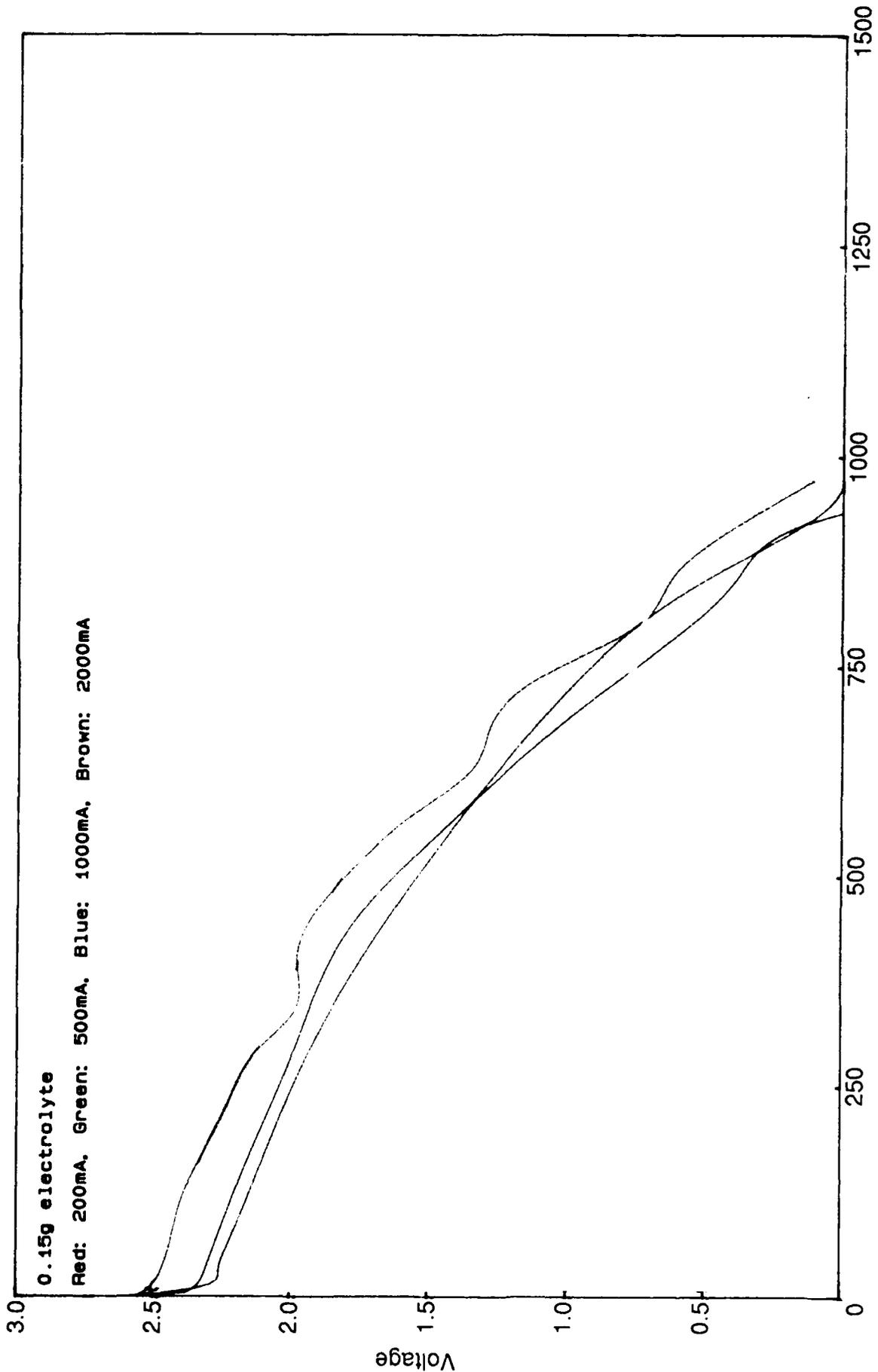


Fig 10  $\text{LiV}_2\text{O}_5$  580C



0.15g electrolyte  
Red: 200mA, Green: 500mA, Blue: 1000mA, Brown: 2000mA

Charge withdrawn (C/g LVO)

Fig 11 LVO 500C

Fig 11

Fig 12

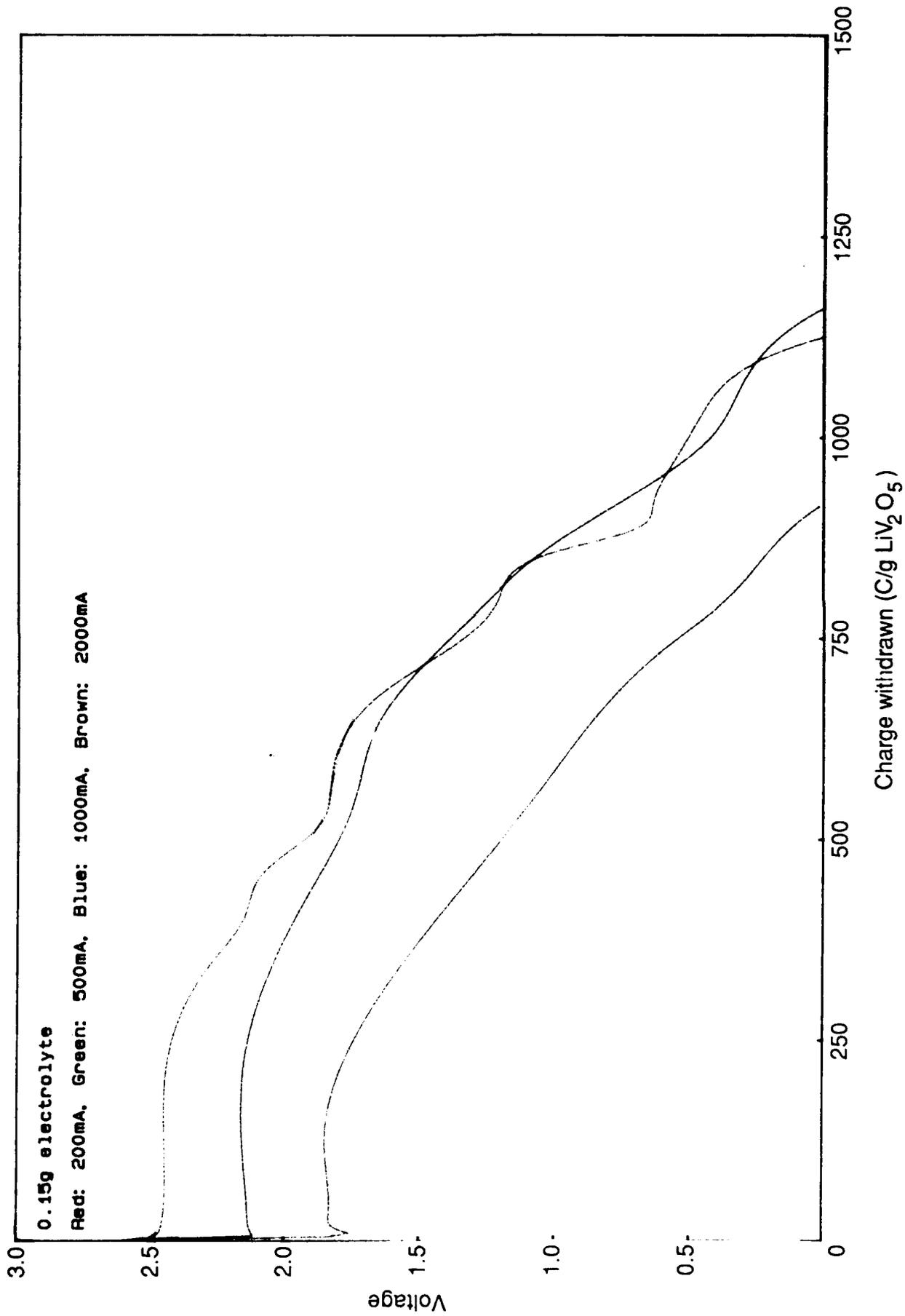
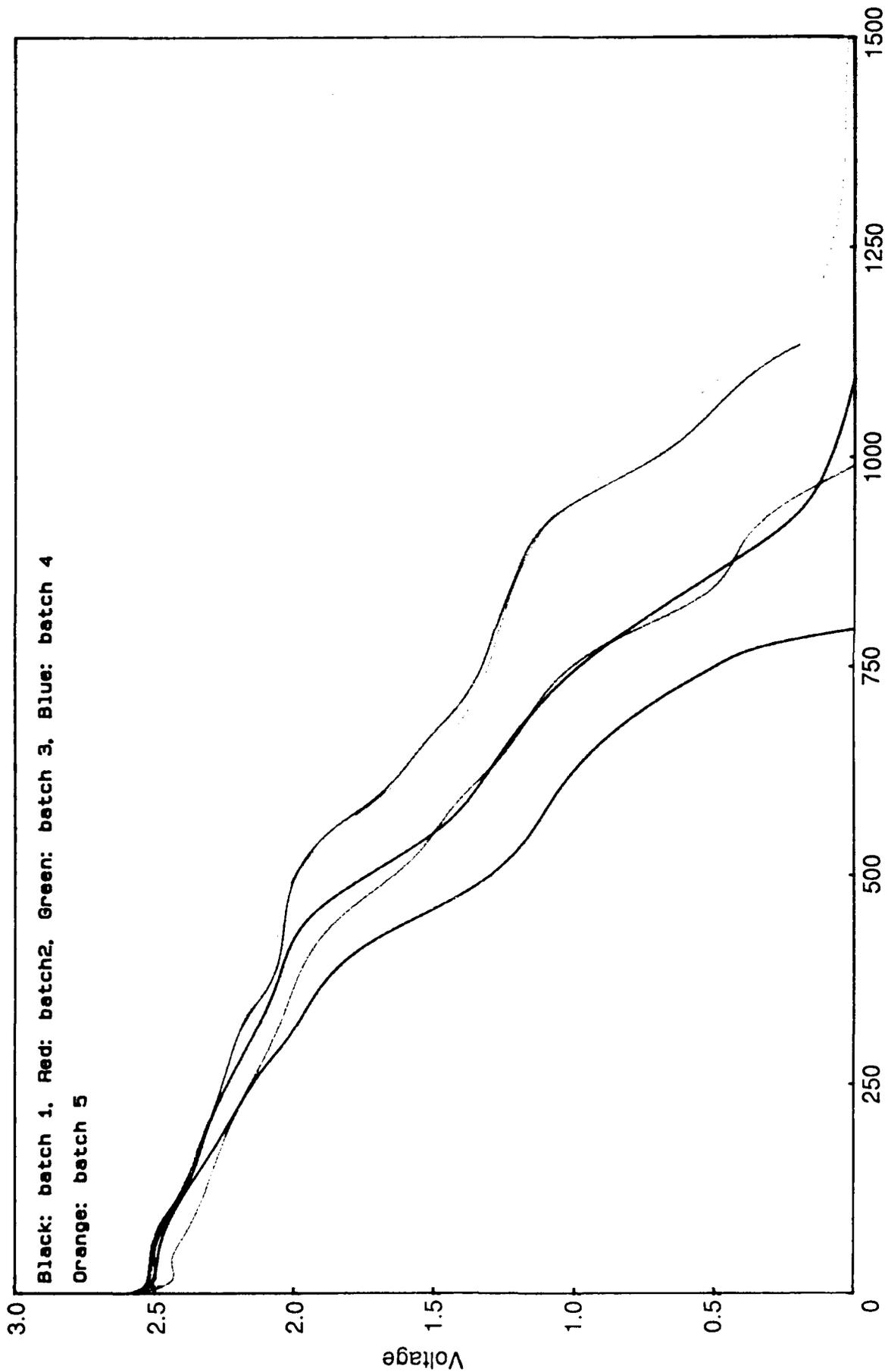


Fig 13



Charge withdrawn (C/g VO<sub>2</sub>)

Fig 13 VO<sub>2</sub> 580C 200 mA

Fig 14

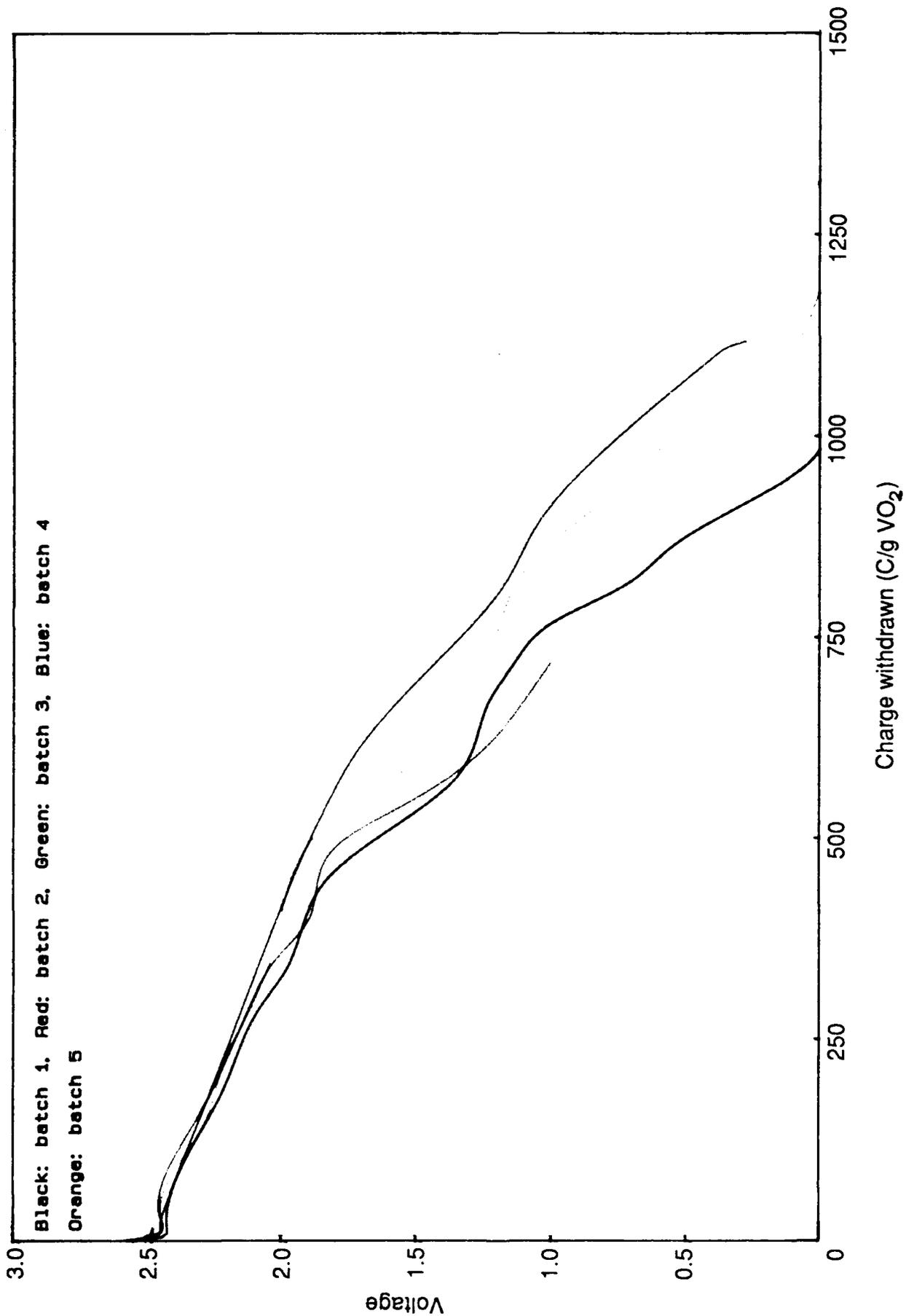


Fig 14 VO<sub>2</sub> 580C 500 mA

Fig 15

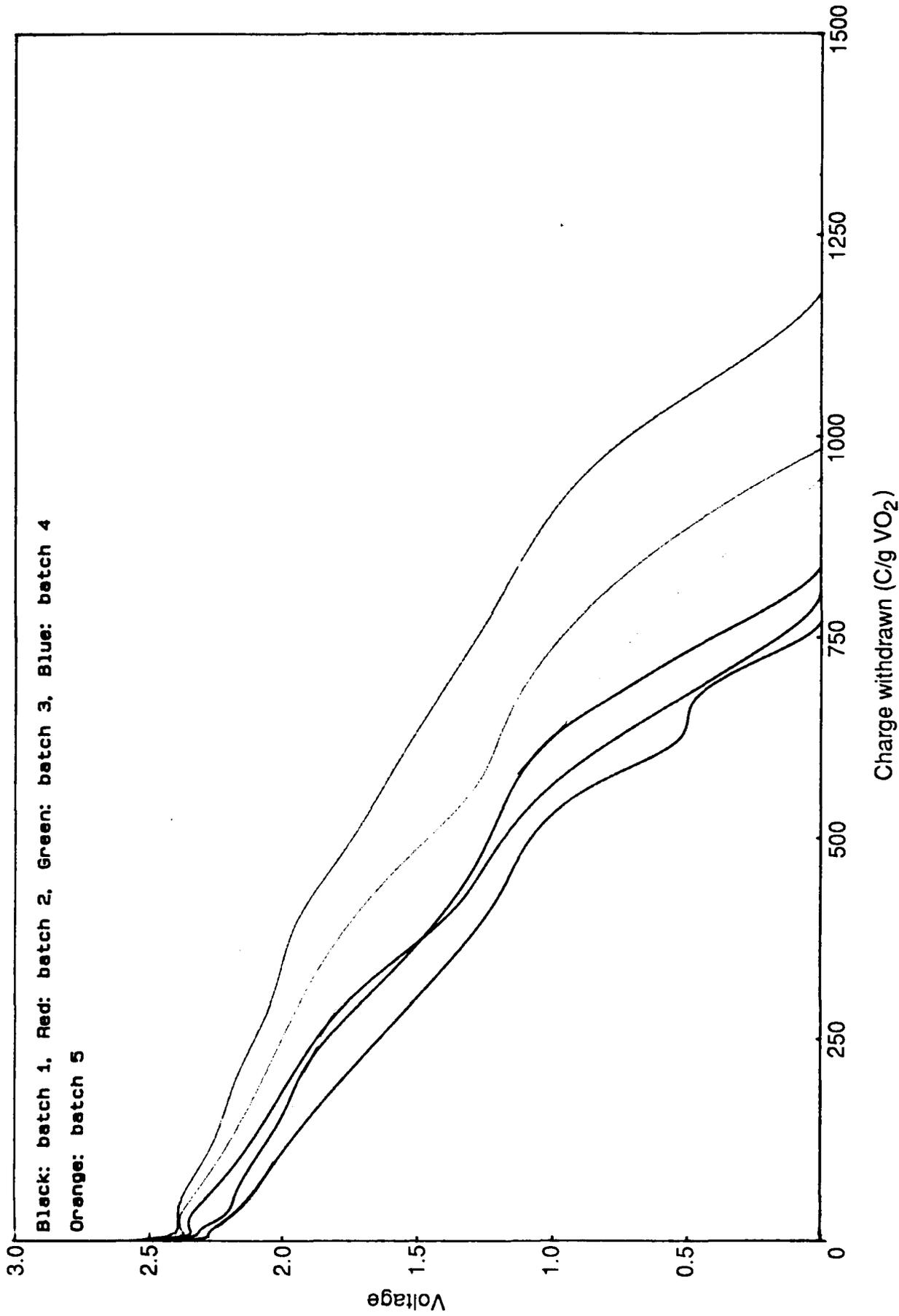


Fig 15 VO2 580C 1000 mA

Fig 16

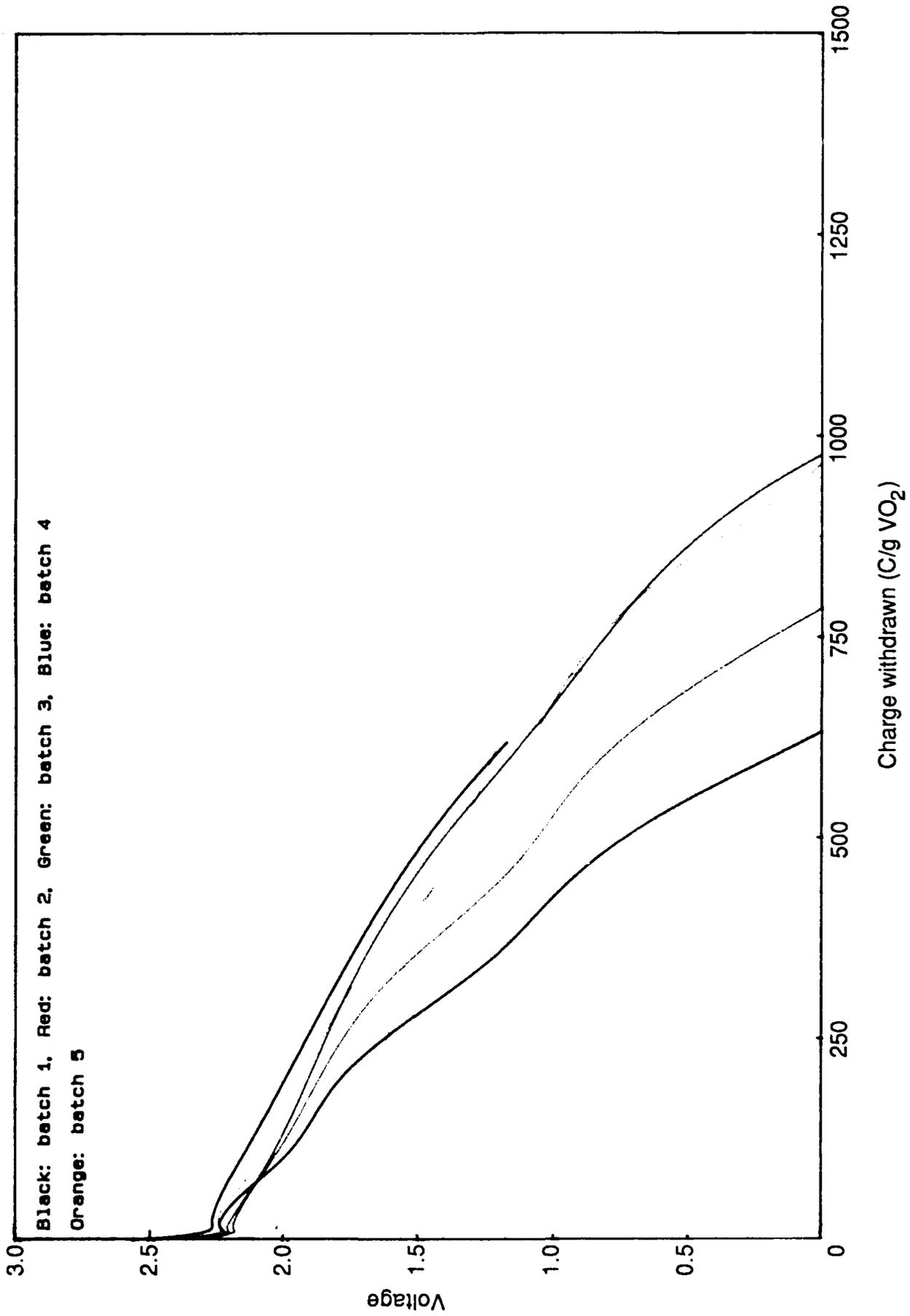


Fig 16 VO<sub>2</sub> 580C 2000 mA

Fig 17

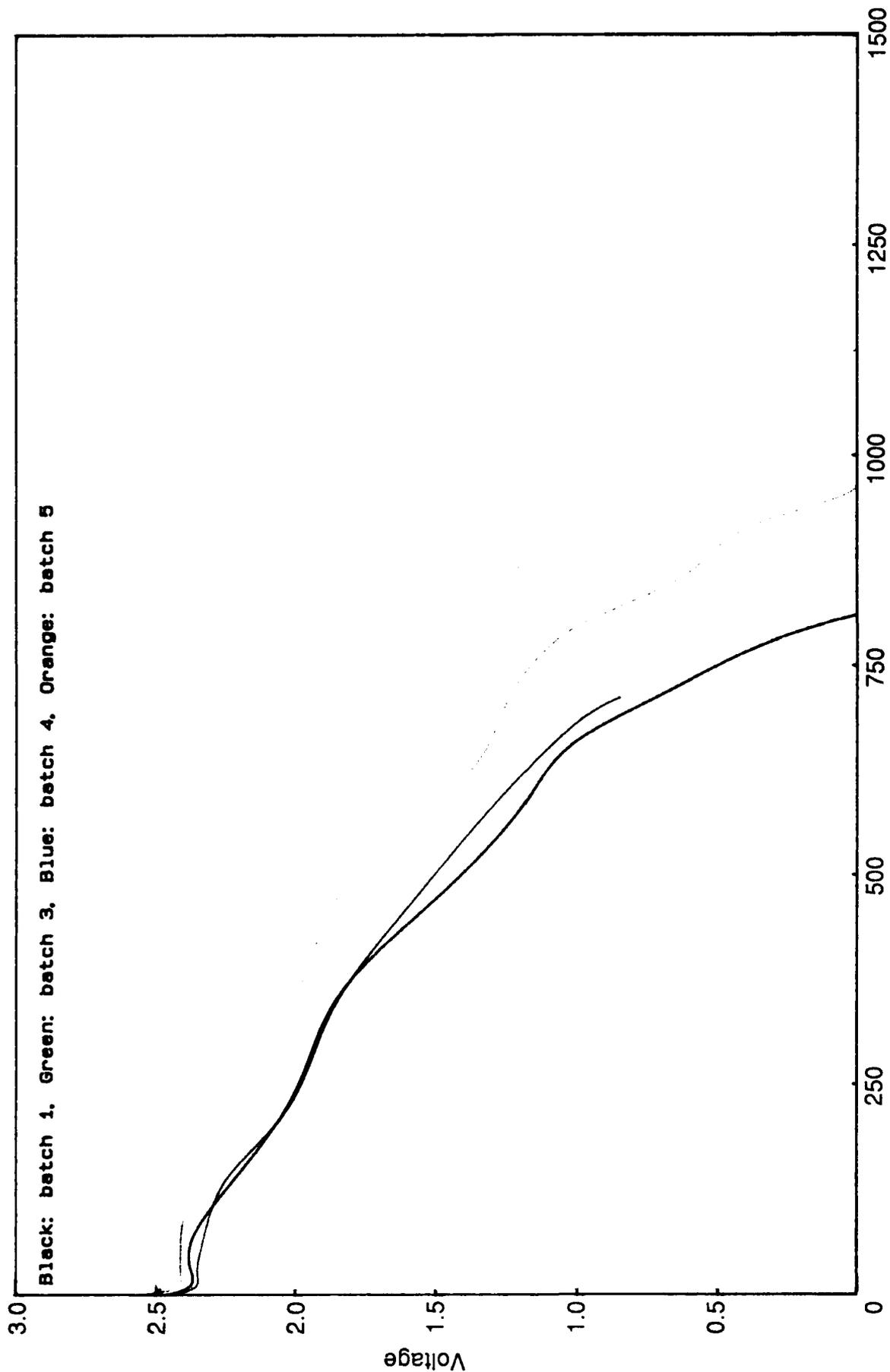
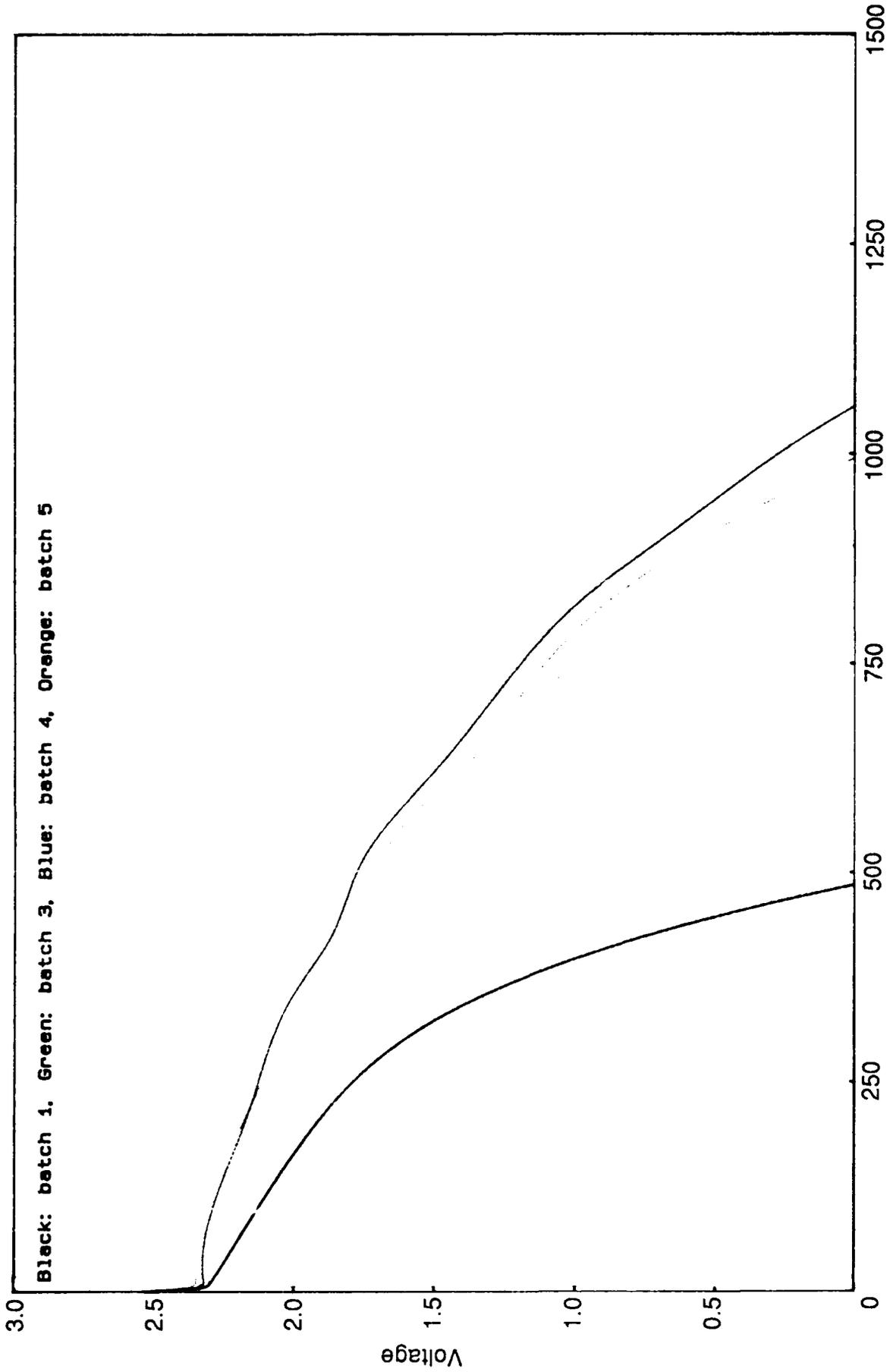


FIG 17 VO<sub>2</sub> 500C 200mA

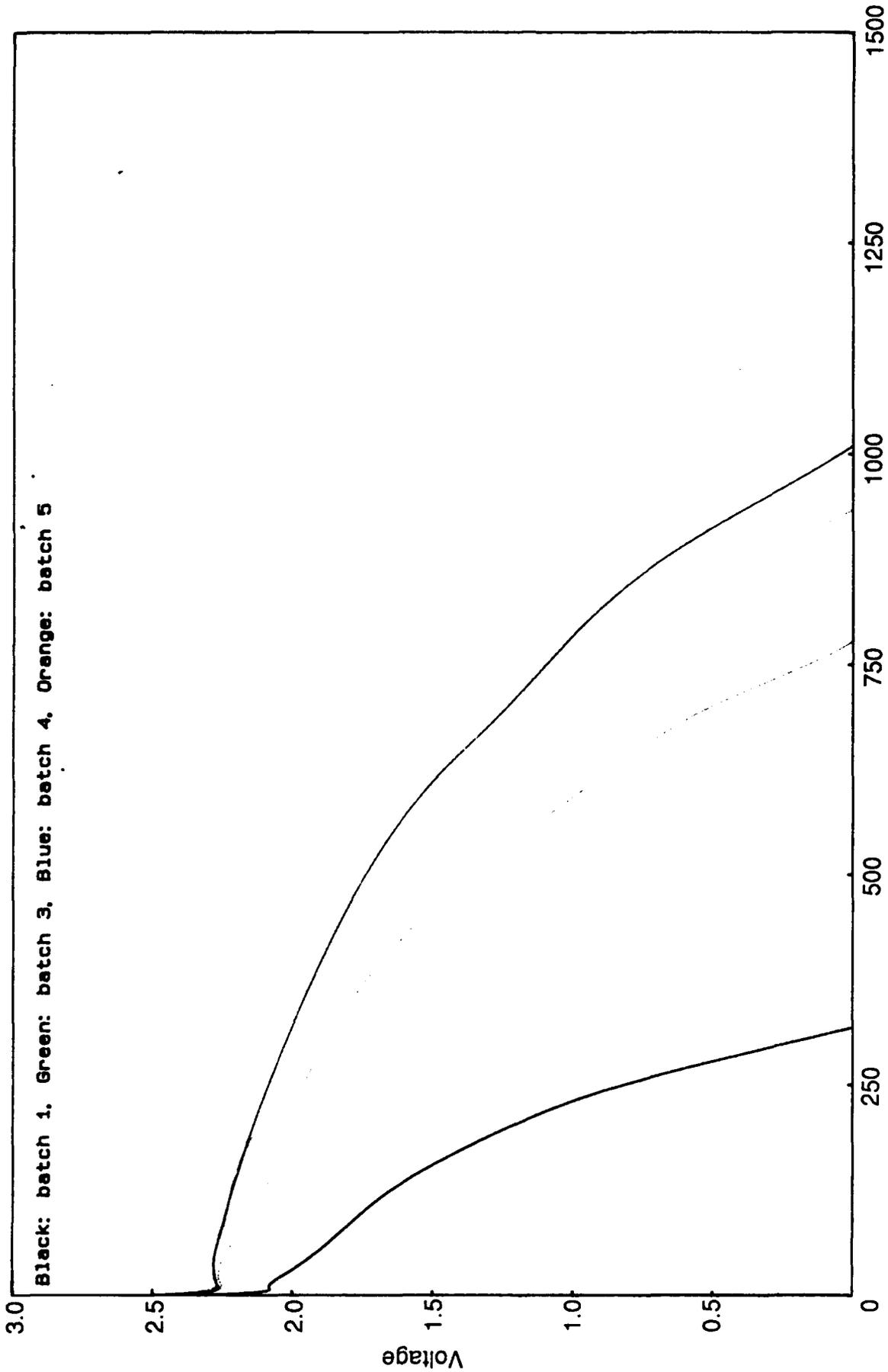
Fig 18



Charge withdrawn (C/g VO<sub>2</sub>)

Fig 18 VO<sub>2</sub> 500C 500 mA

Fig 19

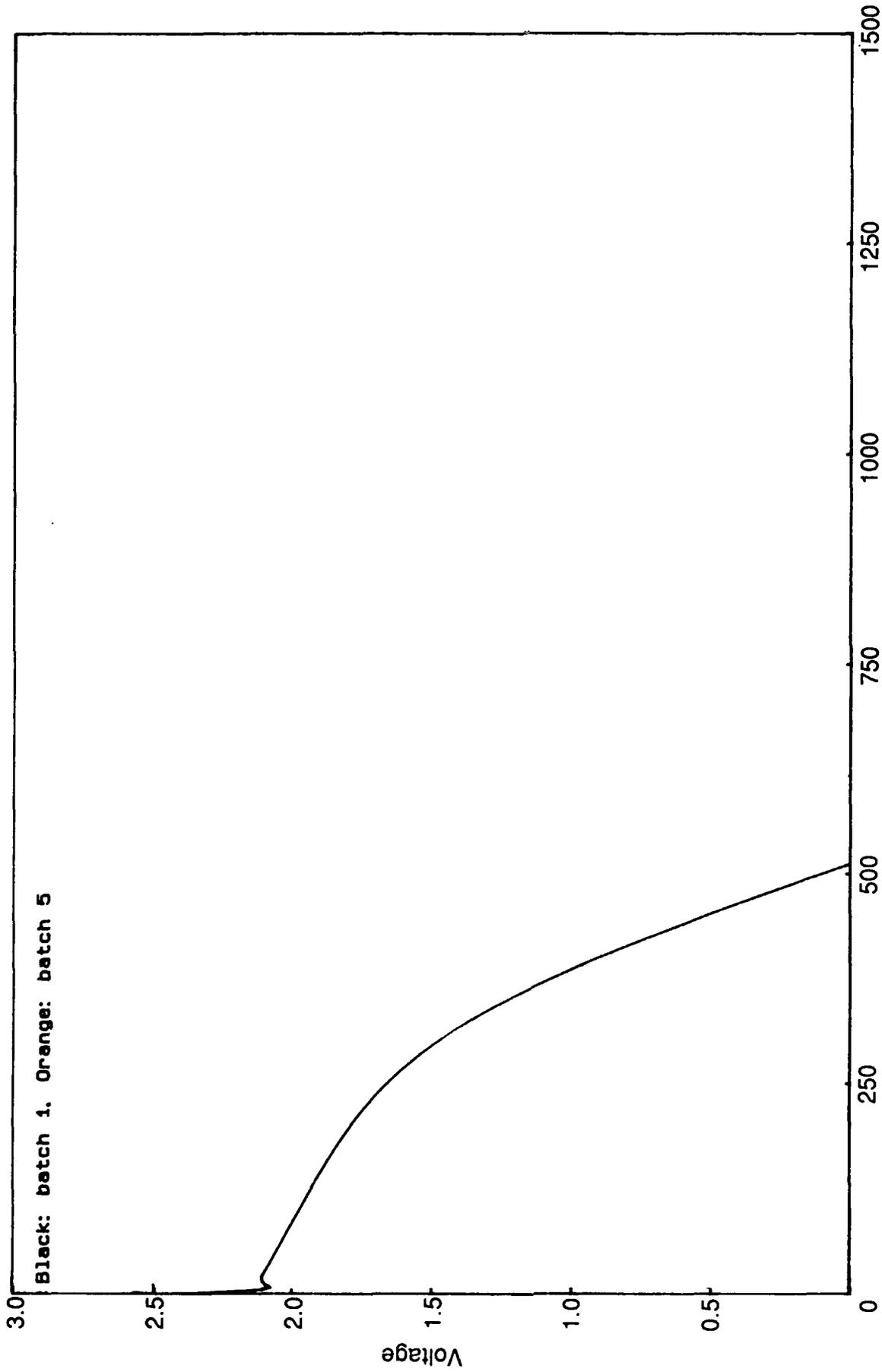


Black: batch 1. Green: batch 3. Blue: batch 4. Orange: batch 5

Charge withdrawn (C/g VO<sub>2</sub>)

Fig 19 VO<sub>2</sub> 500C 1000 mA

Fig 20



Charge withdrawn (C/g VO<sub>2</sub>)

FIG 20 VO2 500C 2000 mA

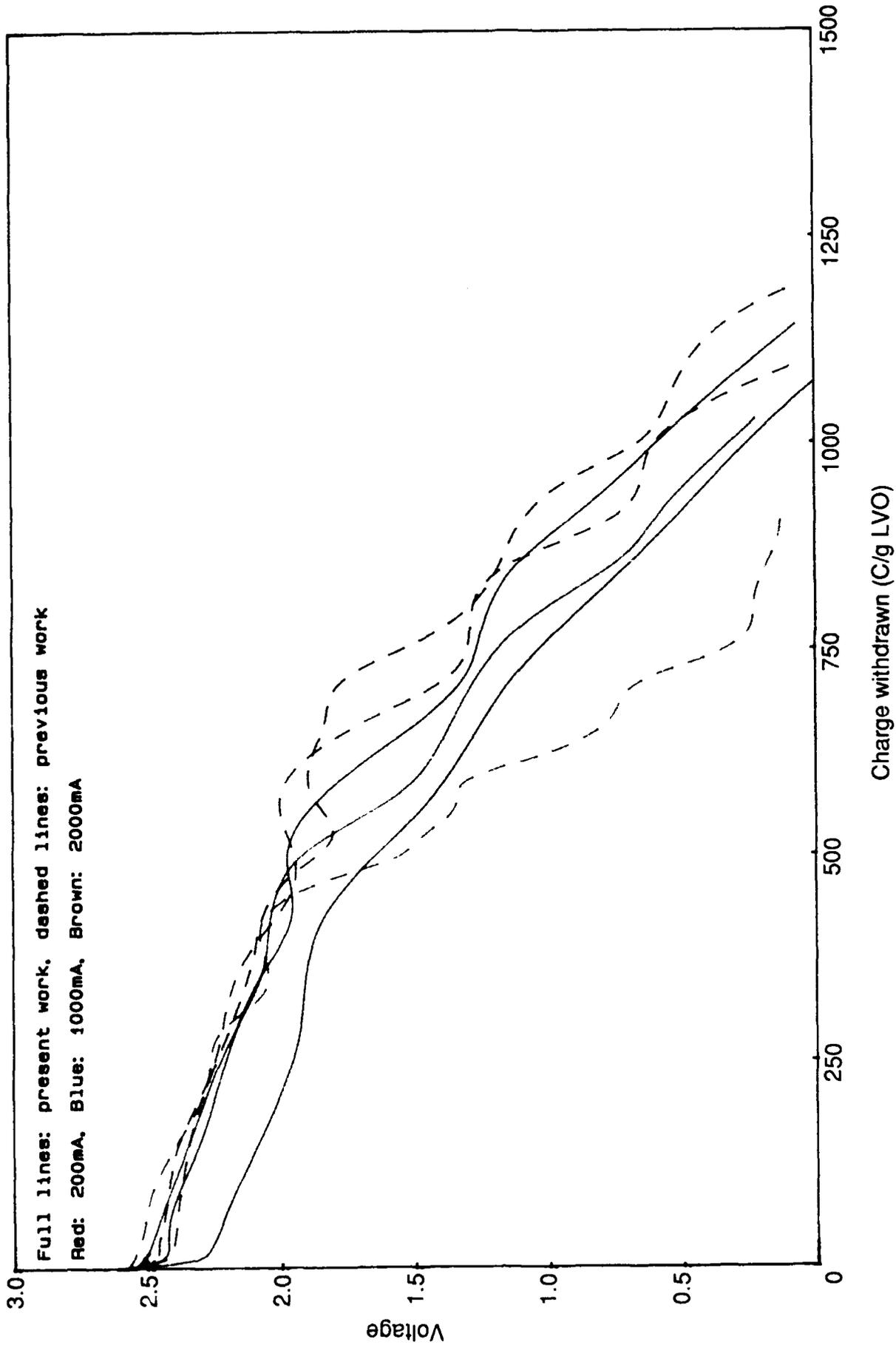


Fig 21 LVO 580C

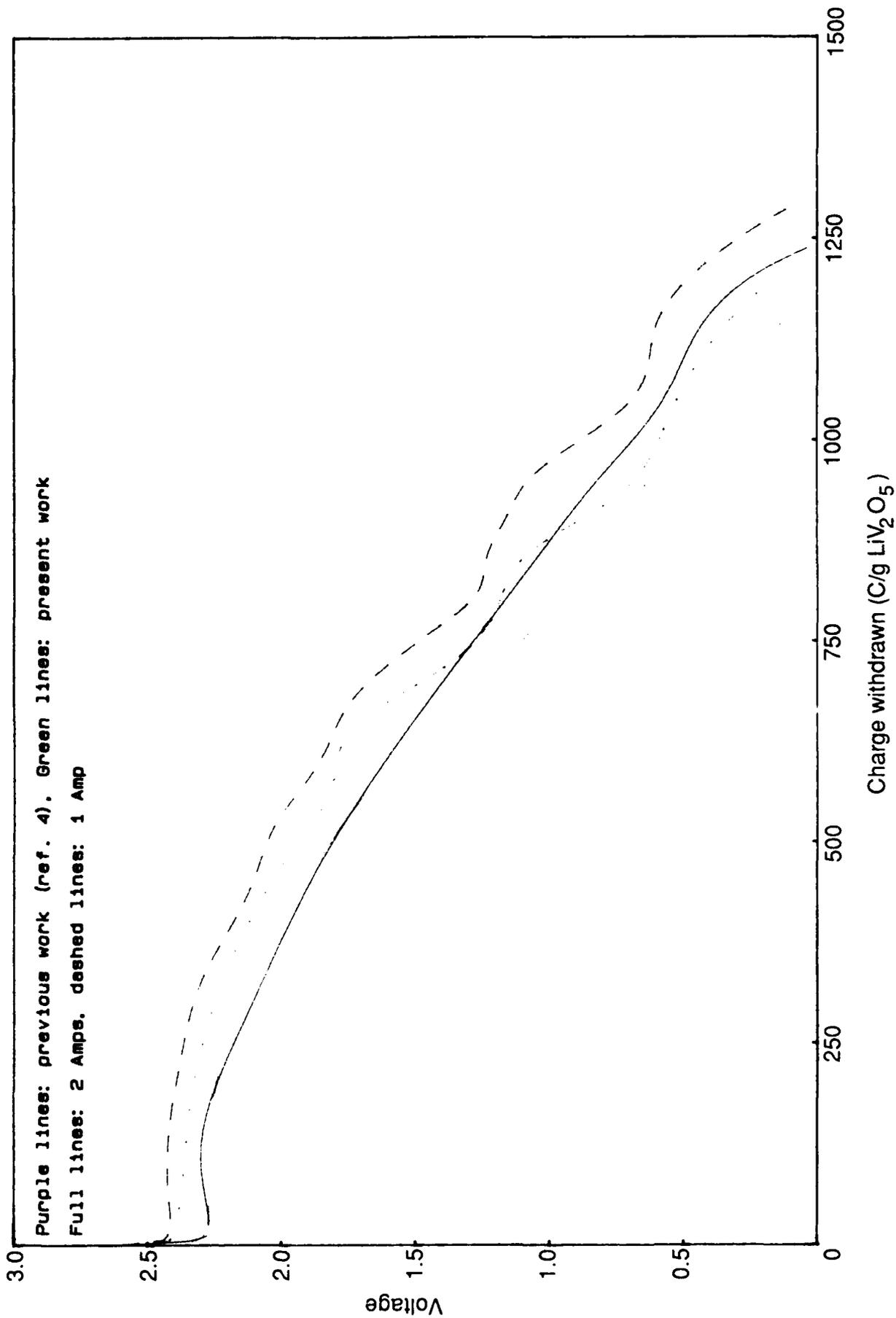


Fig 22

Fig 22  $\text{LiV}_2\text{O}_5$ : present and earlier work

Fig 23

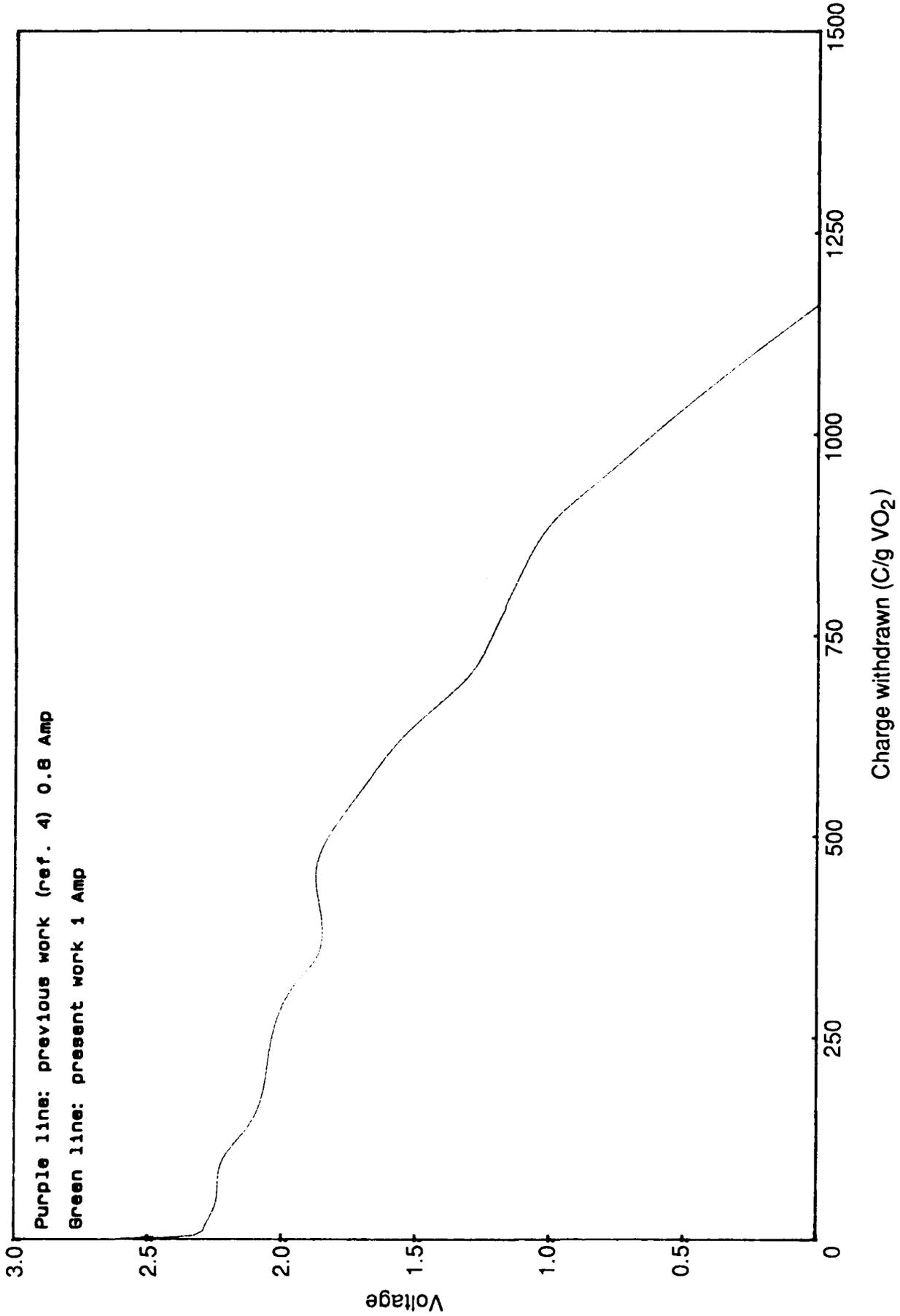
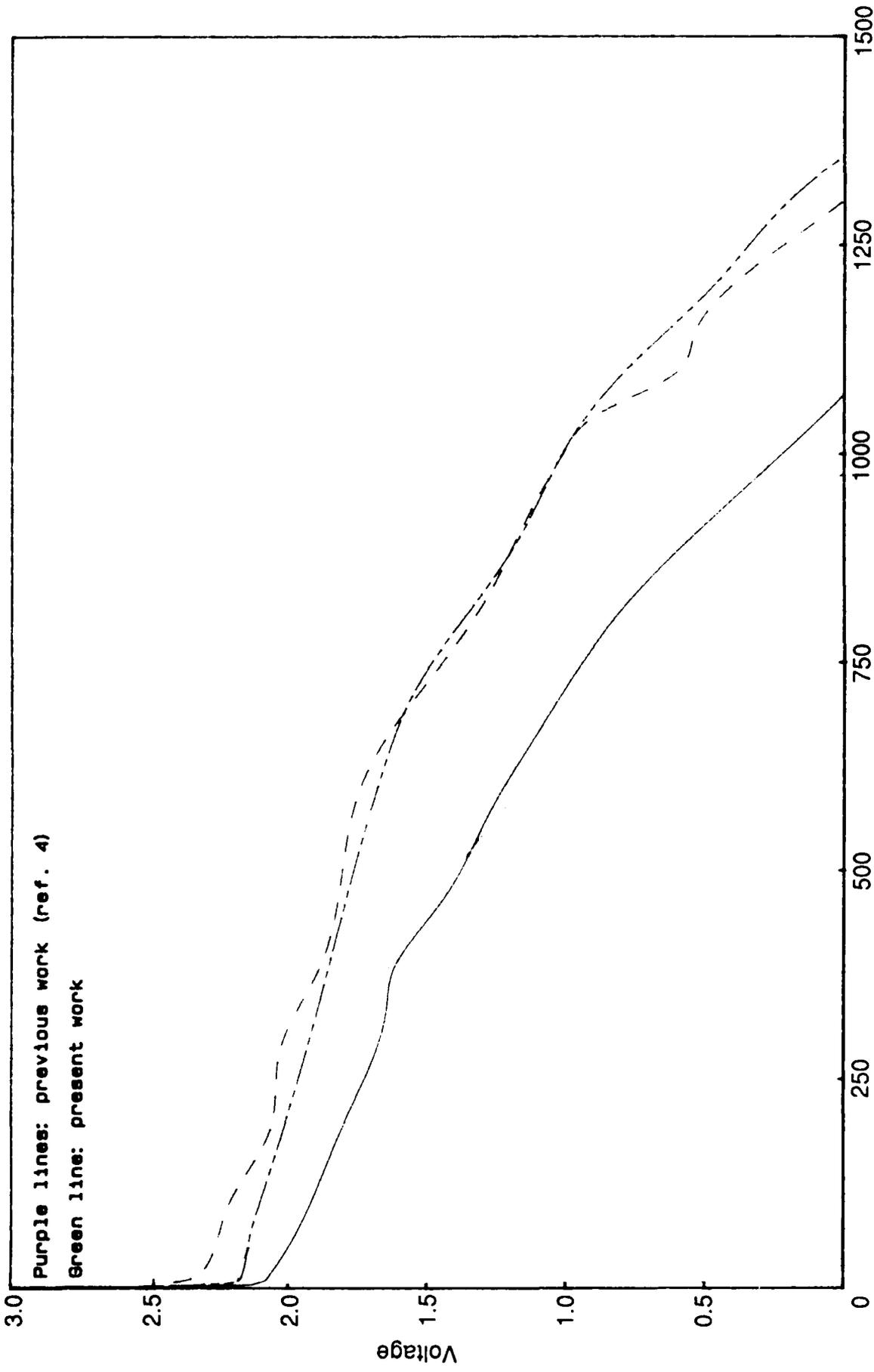


Fig 23 VO2: present and earlier work



Charge withdrawn (C/g VO<sub>2</sub>)

Fig 24 VO2: present and earlier work

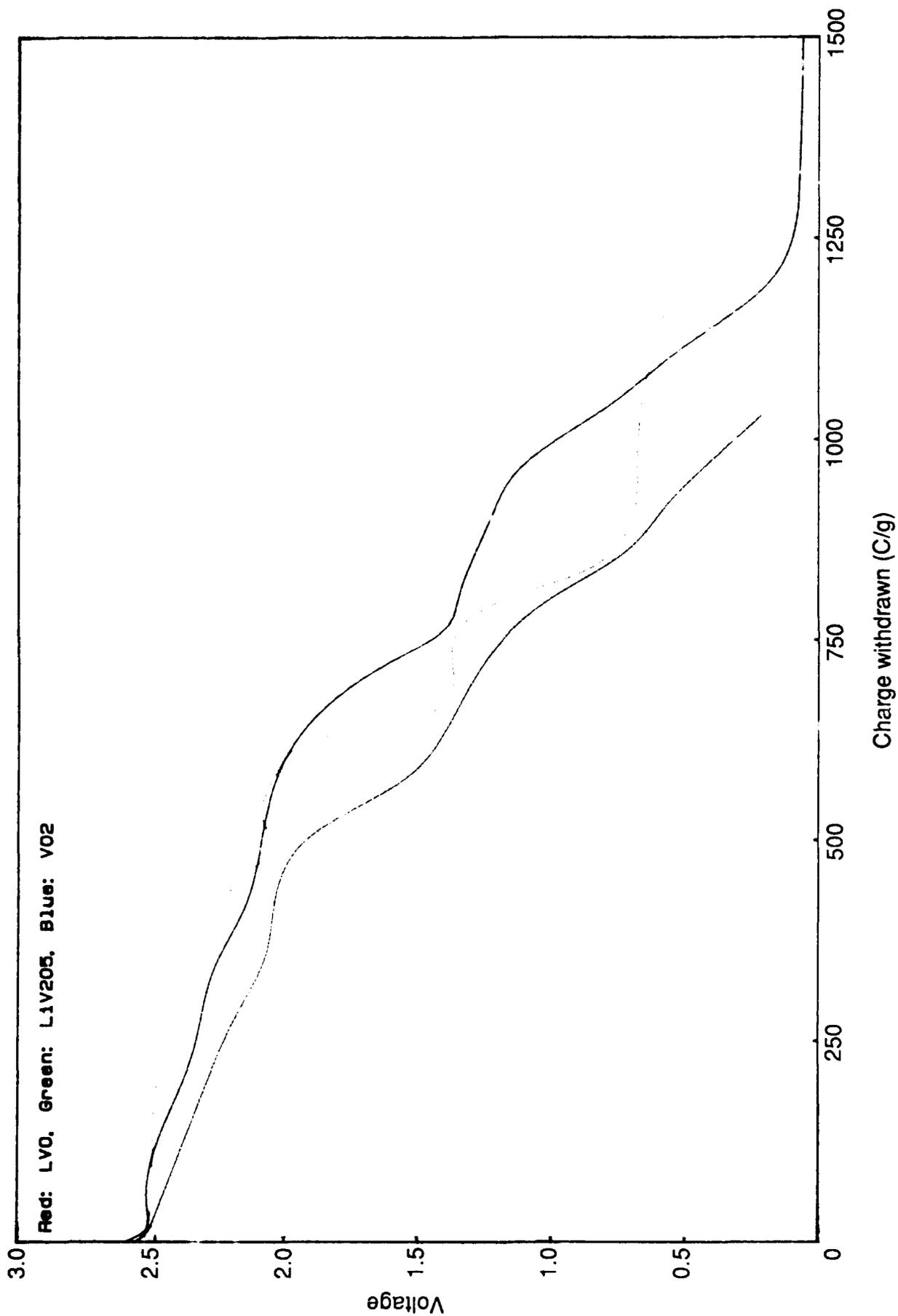


Fig 25 LVO, LIV205 and VO2 580C 200 mA

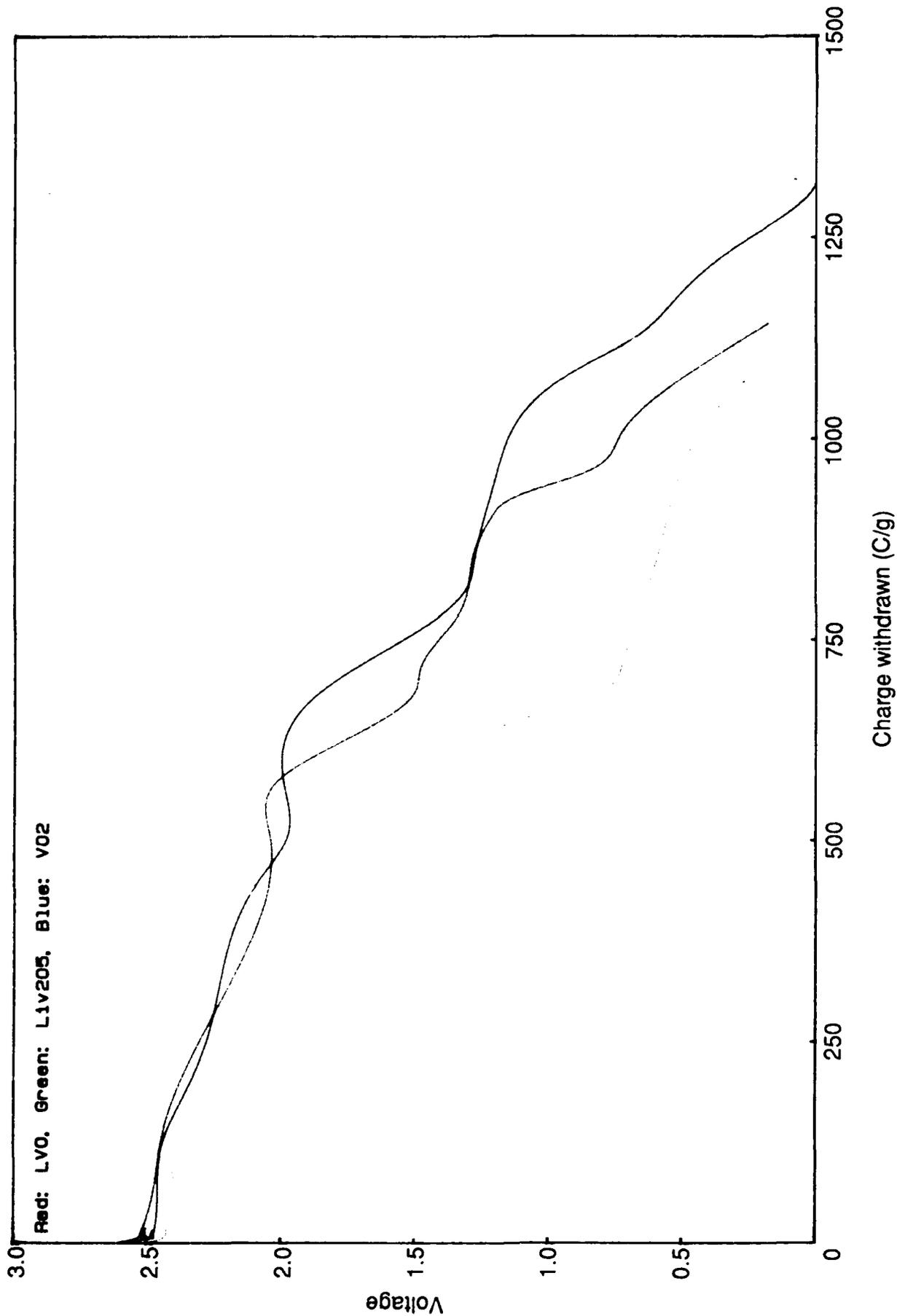


Fig 26 LVO, LIV205 and VO2 580C 500 mA

Fig 27

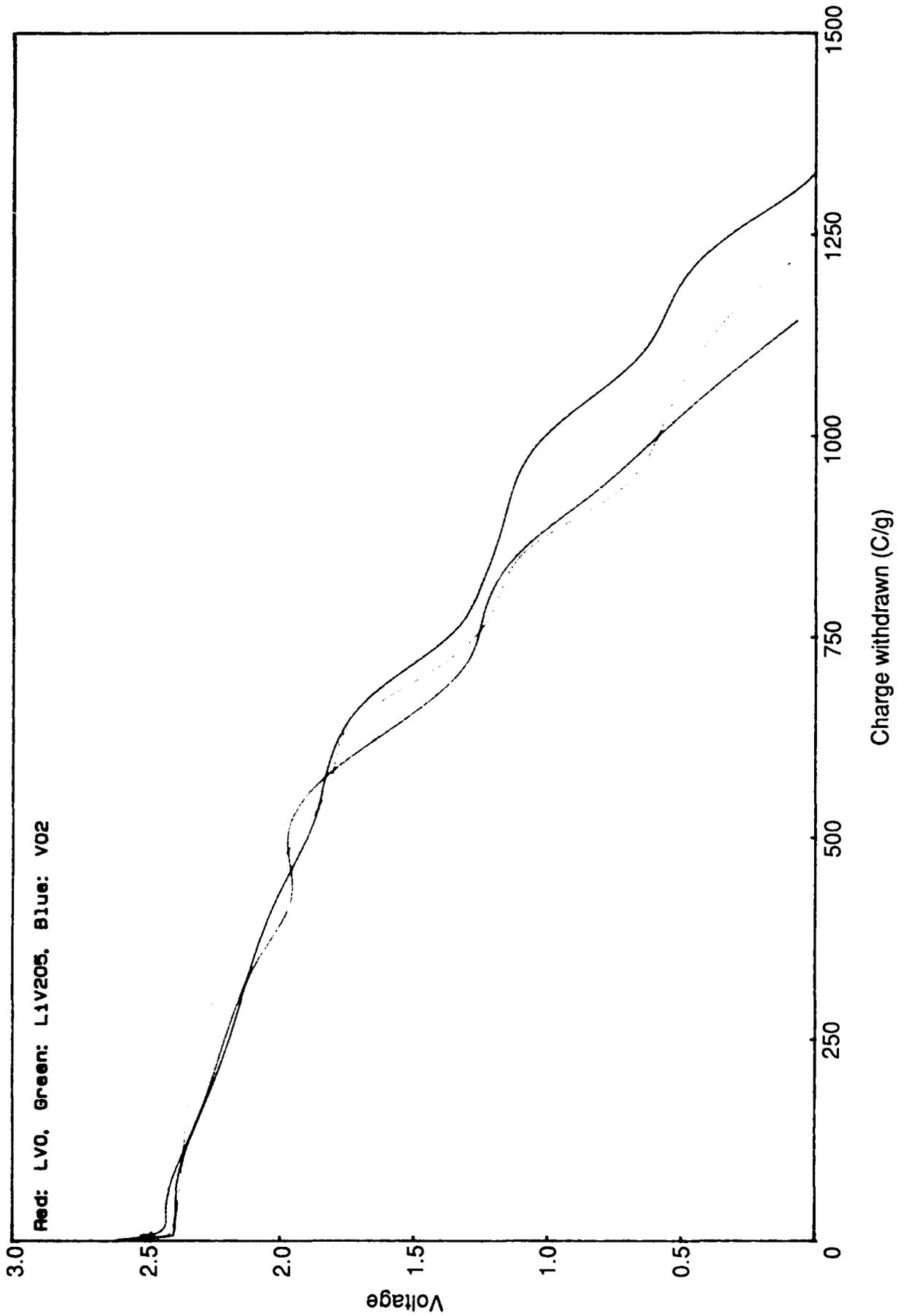


Fig 27 LVO, LIV205 and VO2 580C 1000 mA

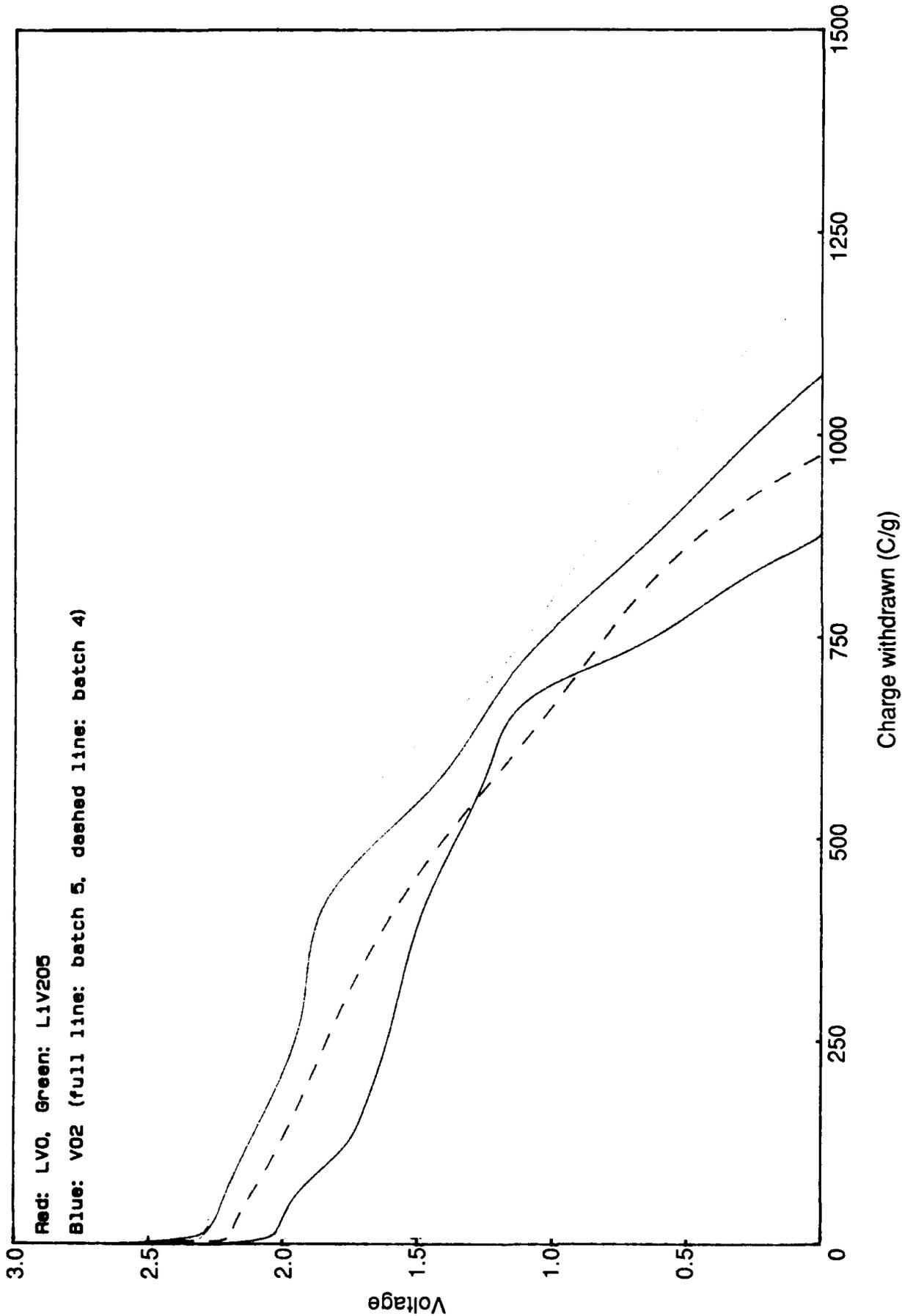
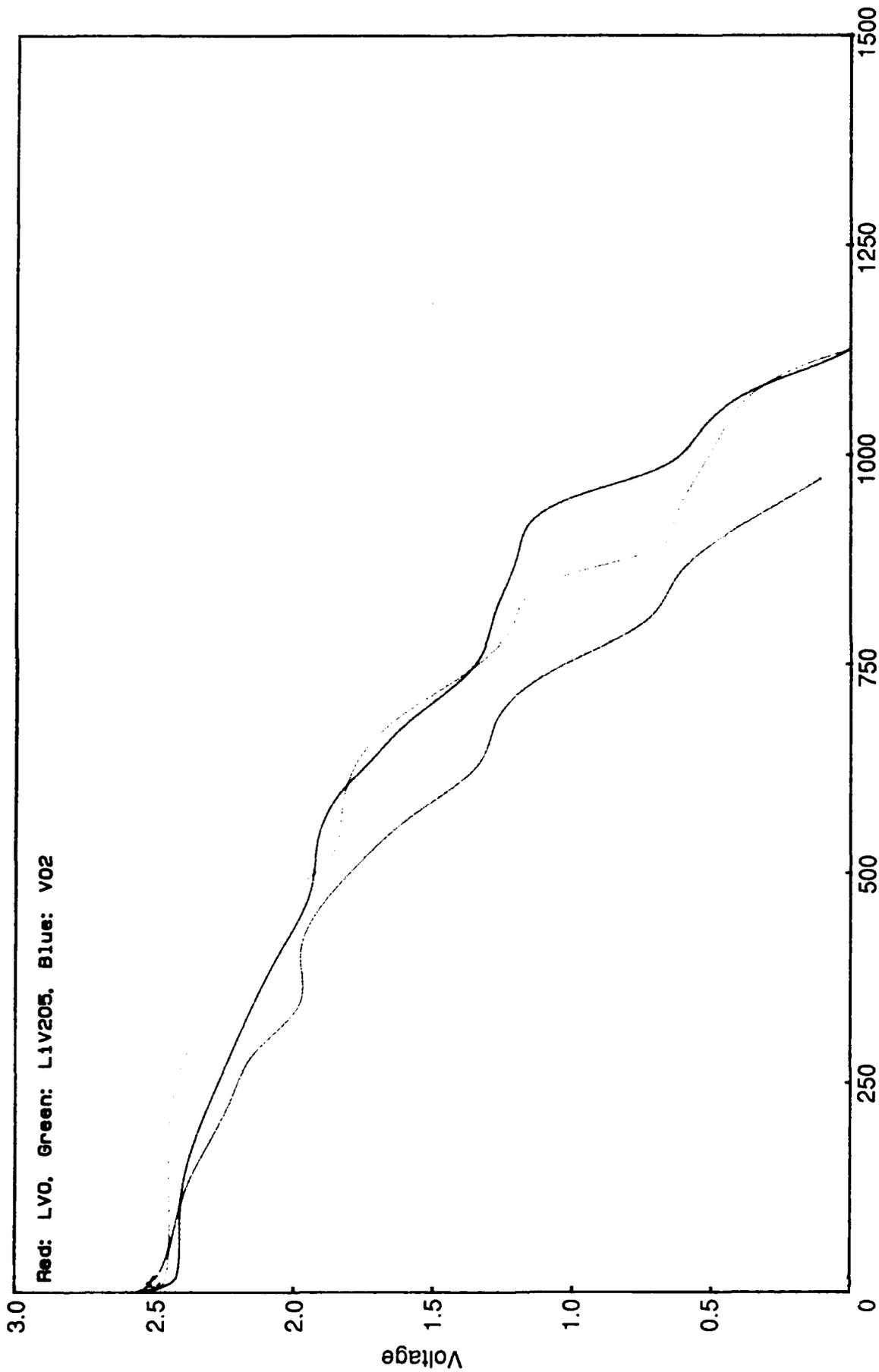


Fig 28 LVO, LIV205 and V02 580C 2000 mA



Charge withdrawn (C/g)  
Fig 29 LVO, LIV205 and VO2 500C 200 mA

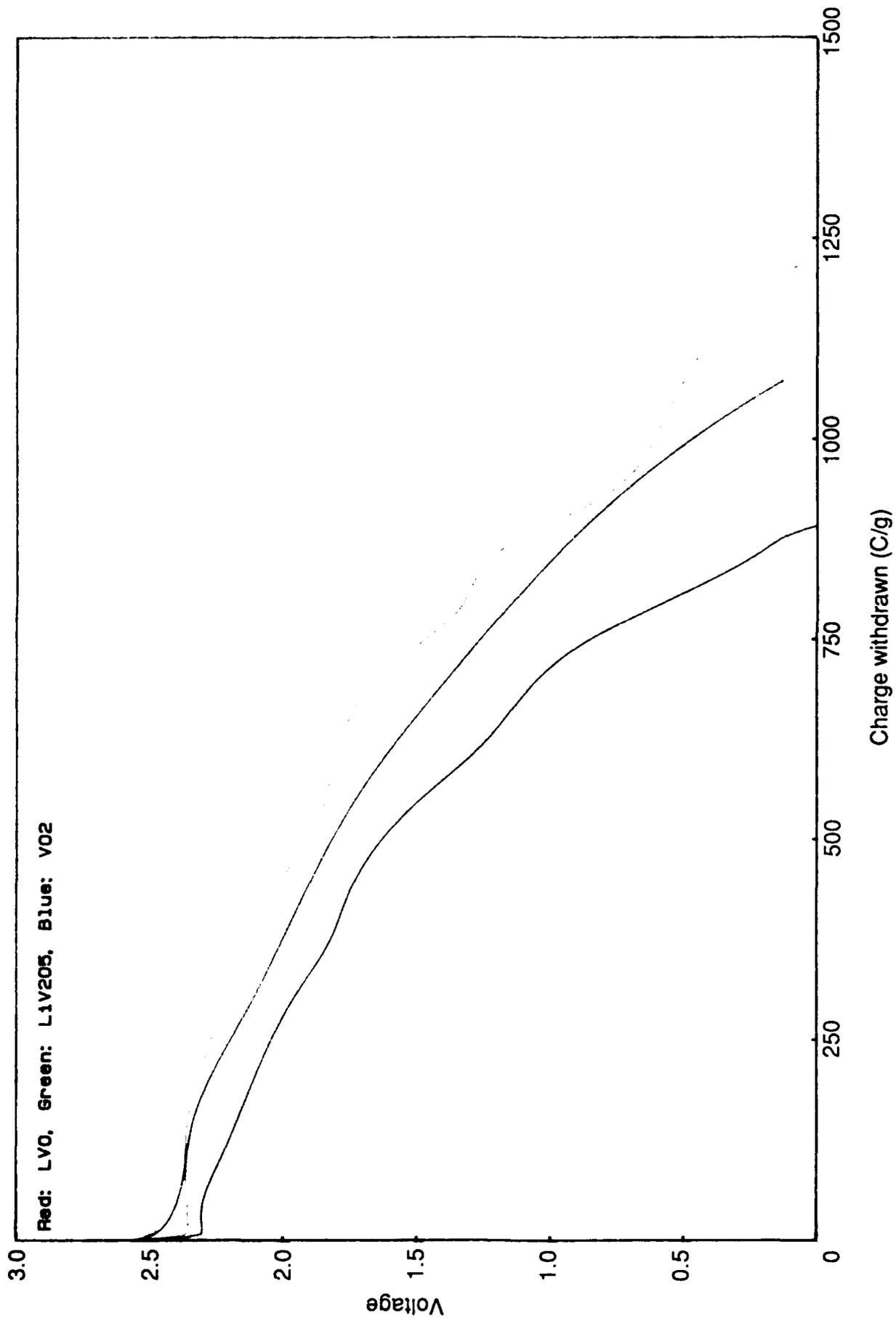


Fig 30 LVO, LIV205 and VO2 500C 500 mA

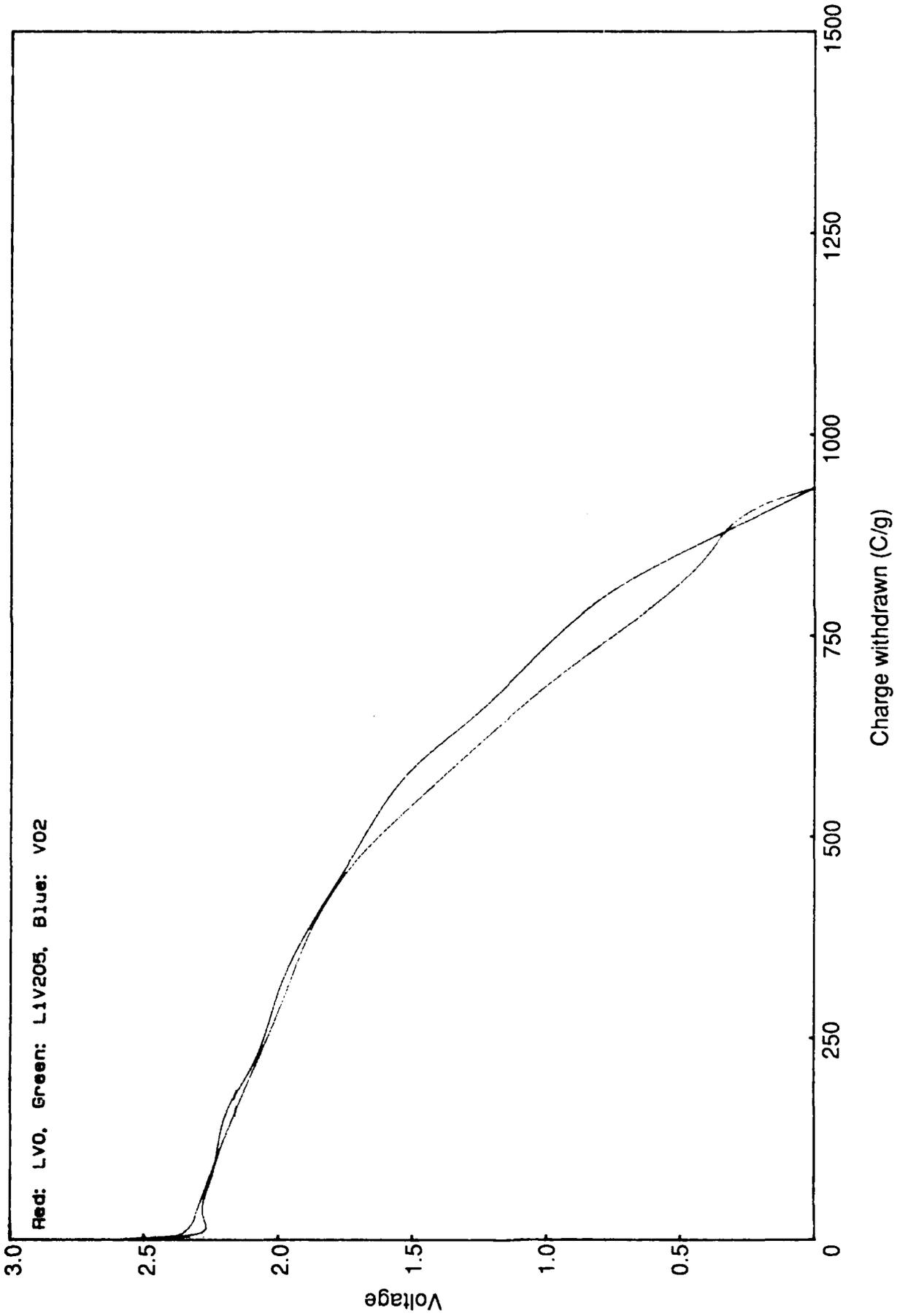


Fig 31 LVO, LIV205 and VO2 500C 1000 mA

Fig 32

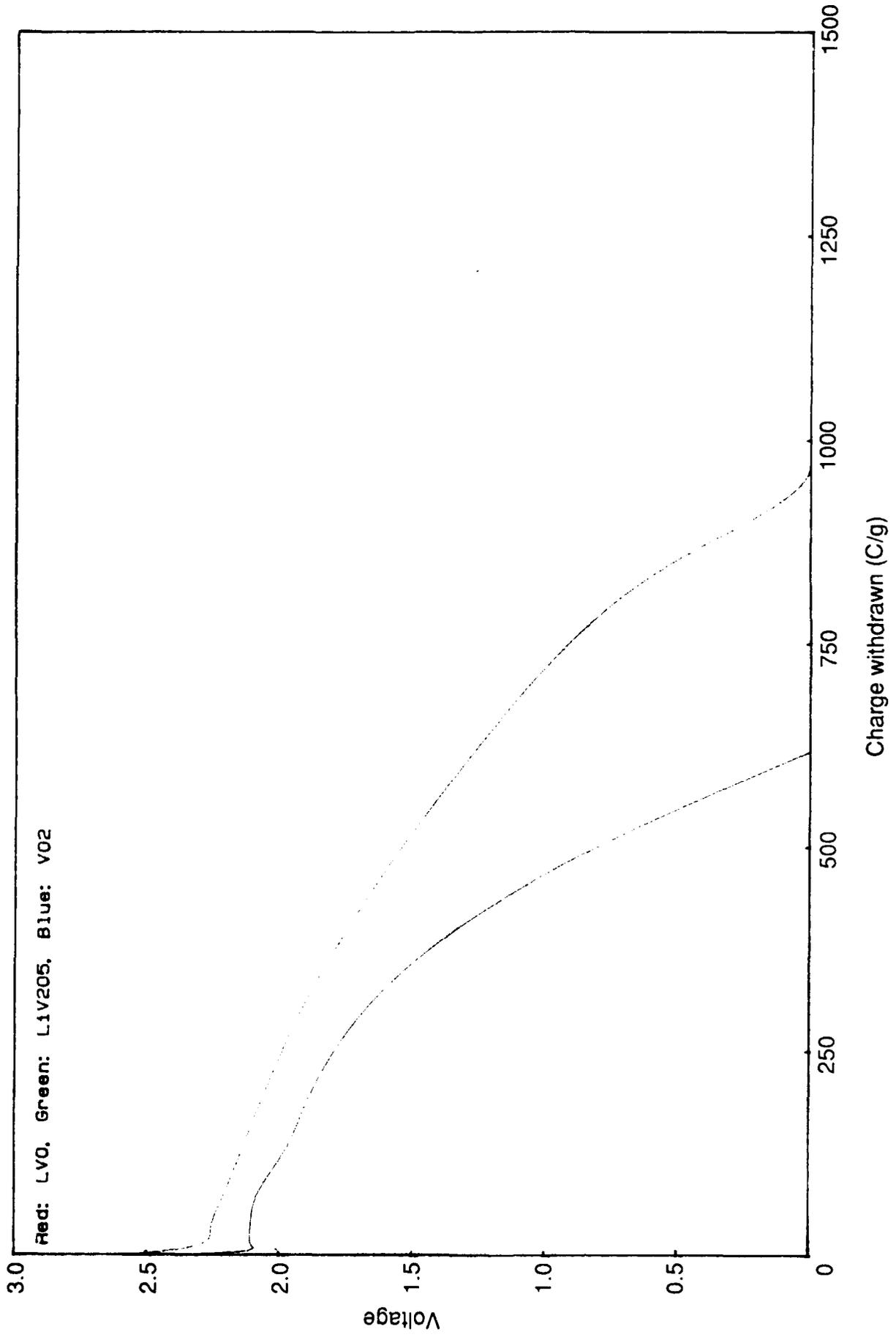
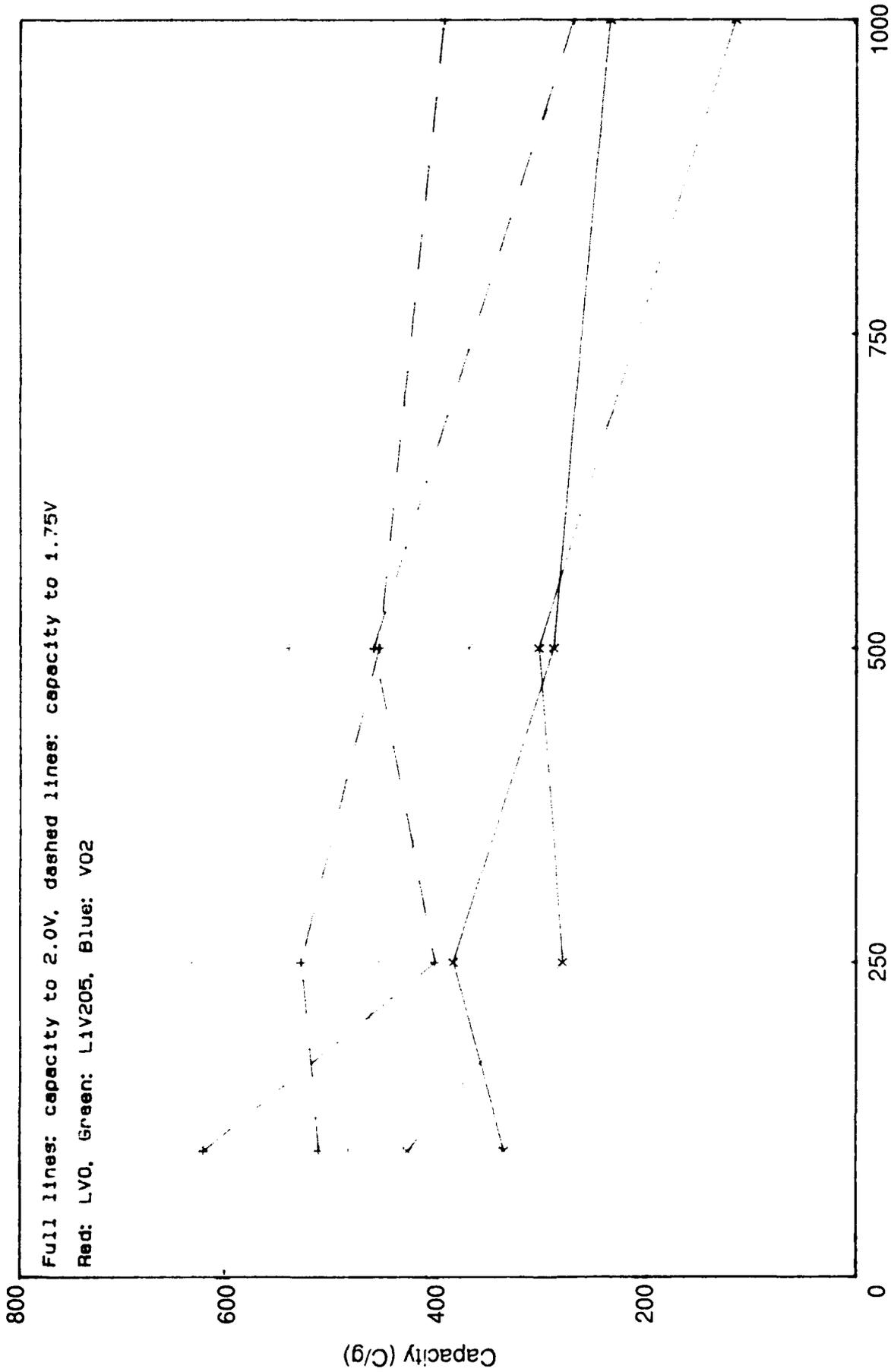


Fig 32 LVO, LIV205 and VO2 500C 2000 mA

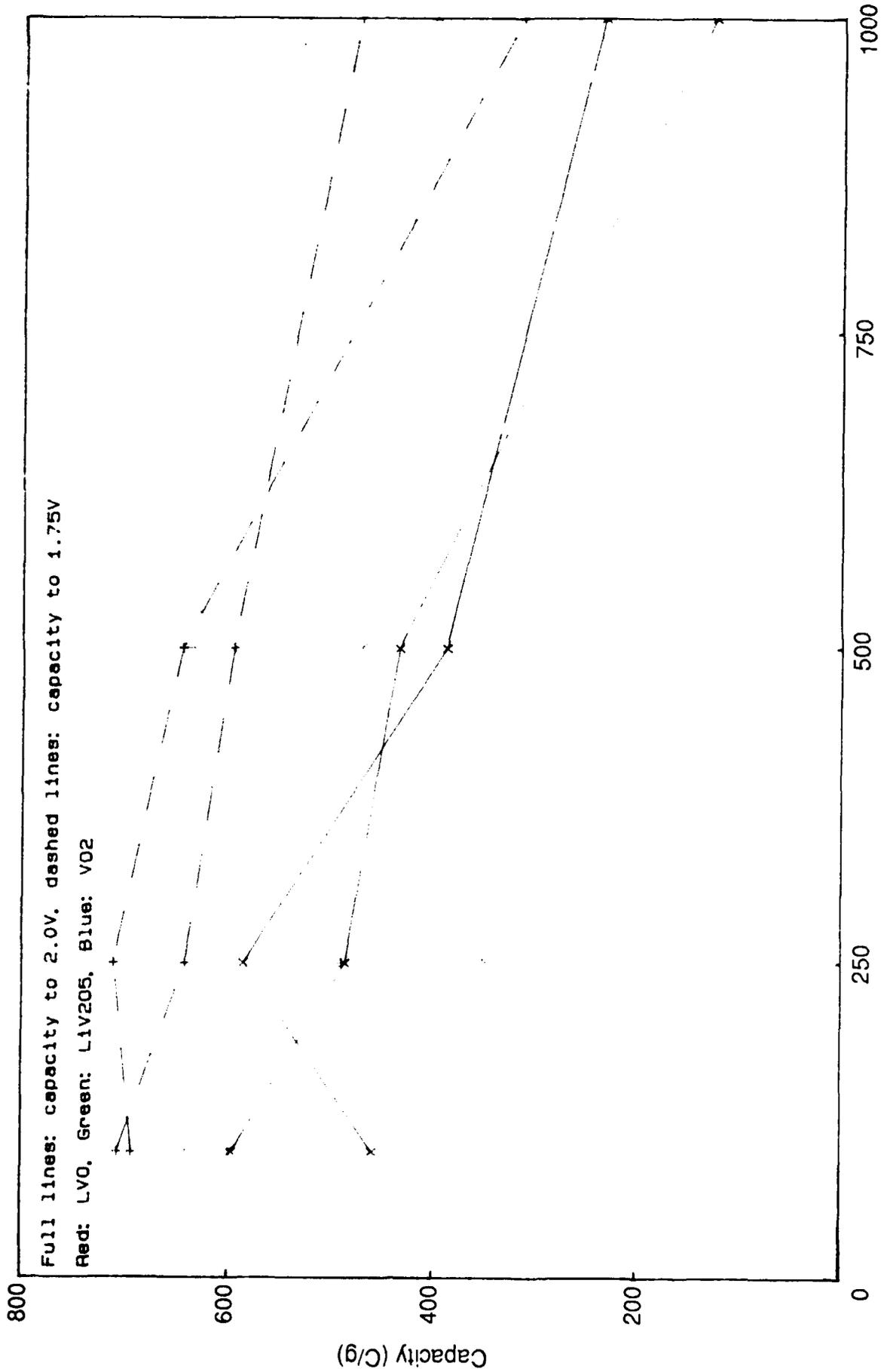
Fig 33



Current density (mA/cm<sup>2</sup>)

Fig 33 Capacities at 500C

Fig 34



Current density (mA/cm²)  
Fig 34 Capacities at 580C

**REPORT DOCUMENTATION PAGE**

Overall security classification of this page

UNLIMITED

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5. DRIC Code for Originator 7673000W	6. Originator (Corporate Author) Name and Location DRA Aerospace Division, RAE Farnborough, Hants, UK		
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7a. (For Translations) Title in Foreign Language			
7b. (For Conference Papers) Title, Place and Date of Conference			
8. Author 1. Surname, Initials Ritchie, A.G.	9a. Author 2 Warner, K.	9b. Authors 3, 4 ....	10. Date June 1991
		Pages	Ref's 11
11. Contract Number	12. Period	13. Project	14. Other Reference Nos. Materials/ Structures 322
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16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)  Thermal battery cathode materials.			
17. Abstract  Lithiated vanadium oxide (LVO), $\gamma$ -lithium vanadium bronze ( $\gamma$ -LiV <sub>2</sub> O <sub>5</sub> ) and vanadium dioxide (VO <sub>2</sub> ) have been compared as potential cathode materials for high temperature thermal batteries by electrochemical discharges in a laboratory single cell tester. The three materials showed similar performance though LVO may be superior at the highest current density (1A/cm <sup>2</sup> ). VO <sub>2</sub> has the advantage of being commercially available.			