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(54) Title: USE OF THERMAL CARBON BLACK AS ANODE MATERIAL FOR LITHIUM-ION BATTERIES		
(57) Abstract The apparatus of the present invention relates to improved lithium-ion batteries. More particularly, the present invention relates to improved electrodes in lithium-ion batteries, the improved electrodes containing specific carbon blacks, such as specific thermal carbon blacks.		

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TITLE OF THE INVENTION

USE OF THERMAL CARBON BLACK AS ANODE MATERIAL FOR LITHIUM-ION
BATTERIES

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CROSS-REFERENCE TO RELATED APPLICATIONS

Priority of U.S. Provisional Patent Application Serial No. 60/039,812, filed
February 26, 1997, is hereby claimed. That application is hereby incorporated
10 by reference.

This is a continuation of U.S. Patent Application Serial No. 08/979,533,
filed 11/26/97, and incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

15 Not applicable

REFERENCE TO A "MICROFICHE APPENDIX"

Not applicable

BACKGROUND OF THE INVENTION

20 1. Field of the Invention

The apparatus of the present invention relates to improved lithium-ion
batteries. More particularly, the present invention relates to improved
electrodes in lithium-ion batteries, the improved electrodes containing specific
carbon blacks.

25 2. General Background of the Invention

Lithium-ion batteries are well known in the art and generally comprise
features such as those described in U.S. Patent No. 5,571,638 (Sato et al,
Lithium Secondary Battery) which is hereby incorporated by reference in its
entirety.

30 Lithium-ion (Li-ion) batteries are a relatively new type of secondary
(rechargeable) battery. Until recently, Nickel-Metal-Hydride/NiMH and Nickel-

Cadmium/NiCd batteries were at the forefront of secondary battery technology for everyday applications. However, with higher energy density, more compact cells, and ability to be shaped specifically for a given device, Li-ion batteries have become the battery of choice for laptop computers, camcorders, and other portable electronic devices.

Li-ion cells are typically composed of three major components: cathode, anode, and electrolyte. The cathode is generally comprised of a Lithium-Metal-Oxide (e.g. LiCoO_2), while the anode mostly contains a carbon material capable of intercalation and release of lithium ions from and to the cathode (during the charge and discharge cycles, respectively). The carbon material used in the anode must have a low surface area, high cycling capacity, and excellent stability over extended cycling. The electrolyte serves as a conductive medium through which lithium ions can be transported to and from the electrodes. In the past, electrolytes have mainly been liquid in nature; however, new solid polymer electrolytes are also now being used for Li-ion batteries.

The present invention primarily focuses on the anode, more specifically the use of a certain carbon material as the chief anode material. This new anode material is a unique form of carbon black known as thermal black. This type of carbon black is unlike any other form of carbon black mentioned for use in Li-ion batteries in the prior art as it has a mean particle size greater than 100 nm (typically ~400 nm) and is produced by the thermal process described herein (as opposed to the furnace or acetylene process). The use of this type of carbon black in Li-ion battery anodes is also unique in that it is used in the anode for intercalation of lithium ions from the cathode, and can comprise nearly 100% of the anode. Previous inventions primarily disclose the use of carbon black in smaller percentages for conductivity purposes only.

Several groups have previously conducted work with carbonaceous materials in Lithium ion batteries for use in anodes and cathodes; however, these materials have different properties than those described for the carbon blacks of the present invention. More specifically, the prior art generally teaches the use of carbonaceous materials in lower concentrations that are

smaller in particle size or higher in surface area and higher in graphitic order than that of the present invention.

For example, Binder et al. in U.S. Patent 4,543,305, claim the use of low (60 m²/g) and high (1500 m²/g) surface area carbon blacks in cathodes of primary cells which are bonded with Teflon (5 to 10%) on a nickel support. The main claim of this work is that washing of the carbon blacks with acetone increases the operating voltage and cell life. In addition, this work teaches that higher surface area carbon blacks (>60 m²/g) are desirable. In the present invention, we have disclosed that lower surface area carbon blacks (<10 m²/g) are preferred, and they are used in the anode of secondary or rechargeable lithium ion batteries.

Another patent by Visco et al., U.S. 5,162,175 teaches the use of carbon black in a cathode in a metal-organosulfur secondary battery. In this patent, carbon black is added to the cathode in a 1 to 10 wt% basis and is used only for conductive purposes. Also, no specifications were made on the type of carbon black, and the carbon black is not used for intercalation as in the present invention.

Further work by Fauteux in U.S. Patent No. 5,219,680 teaches the use of disordered carbons selected from activated carbons, acetylene black and Shawinigan black (also an acetylene black) with surface areas greater than about 20 m²/g and preferably greater than 50 m²/g. The acetylene blacks are the preferred carbons. These workers also teach the use of more disordered acetylene carbon blacks versus that of the graphites. While the acetylene carbons are more disordered than graphite, they are not as disordered as anode carbon "A" disclosed in the present invention and the specified surface areas of these carbons are significantly higher than the carbon blacks described in the present invention. Fauteux et al. also specify the use of only 10 to 50 parts by weight of the carbon black in the anode which is significantly lower than the >85 wt% level specified in the present invention.

U.S. Patent No. 5,426,006 by Delnick et al. also teaches the use of disordered carbons in anodes of rechargeable lithium ion batteries; however,

these carbons are prepared from carbonization of "polymeric high internal phase emulsions" which in no way is comparable to carbon black in either its morphology or microstructure. It is also specified in this patent that the disordered material should have an average interlayer spacing (d_{002}) between the carbon planes of $>3.7 \text{ \AA}$, which is larger than the d_{002} of the carbon blacks specified in the present invention (d_{002} ranges from 3.390 to 3.565 $\text{\AA}$).

In another direction, Mitate et al. in U.S. Patent No. 5,478,364 teach the use of copper oxide coated graphite in the anodes of lithium secondary batteries for higher charge/discharge capacity. They teach in this patent that the use of disordered carbons is actually unfavorable and that the graphite : copper ratio should fall in the approximate range of 98 : 2 to 60 : 40. This configuration is much different than that specified in the present invention where a carbon black with moderate disorder and in a concentration of $>85\text{wt}\%$ is specified for the anode. Mitate et al. also specify the use of a conductive material at an approximately 50 wt% concentration in the cathode for conductive purposes only. These materials include carbon blacks (acetylene black, thermal black, and channel black given as examples), graphite powder, metal powder, among other materials. The present invention specifies the use of thermal carbon black in the anode at a concentration of $>85 \text{ wt}\%$ for intercalation of lithium ions. The Mitate et al. patent describes the use of thermal black in the cathode for conductive purposes only and not for intercalation.

U.S. Patent No. 5,028,500, by Fong et al. describes the use of a carbonaceous anode (or first electrode as they define it) for rechargeable lithium ion batteries. This patent teaches that a certain degree of graphitization is required for the carbonaceous materials used in the anodes as specified by the following equation:

$$g = (3.45 - d_{002}) / 0.085,$$

where g is the degree of graphitization and ranges between 0 and 1. For one composition they state that the mean g for a two phase carbonaceous composition should be about 0.4 with one phase having a g of >0.8 (i.e. highly

graphitic). This carbonaceous composition is composed of a mixture of finely milled graphite (g about 1.0) and a pitch binder which is then heated to convert the pitch to coke or a partially graphitized type of carbon (this material is referred to as isotropic graphite and preferably this material has a g above about 0.4 and is stated as being commercially available from Graphite Sales, Inc. of Chagrin Falls, Ohio, USA). Another material described as meeting the above criteria is spherical graphite that is also commercially available from Graphite Co, of Chicago, Illinois, USA. The degree of graphitization for anode carbons "A" and "B" described in the present invention have g values <0 which indicates that these carbons are significantly more disordered than that considered appropriate in the Fong et al. patent. That is, it has been implicitly assumed by Fong et al. that any carbons used in the anodes would have d_{002} values less than 3.450 Å and greater than 3.365 Å since it is clearly stated that the graphitization parameter, g , ranges from 0 to 1. As noted above, anode carbons "A" and "B" of the present invention have g values outside the range of 0 to 1. The inventors in U.S. Patent No. 5,028,500 also state that 1 to 12 wt% of a filamentous carbon black is used in the anode to reduce capacity fade during cycling of the battery and to prevent the need for applying pressure to the cell (this prevents dendritic growth of lithium metal between the anode and cathode). The filamentous carbon black is only specified by its surface area which is listed as being less than 50 m²/g and preferably 40 m²/g. These values are significantly higher than that for the carbon blacks described in the present invention. Lastly, Fong et al. describe the use of low surface area (g greater than 0.03 m²/g and less than 8 m²/g) coke and particularly petroleum coke as a carbonaceous anode material with a g value of less than about 0.4. These materials are claimed to reduce exfoliation and initial capacity loss (i.e. irreversible capacity) due to their low surface area. However, Fong et al. discloses only the use of coke rather than carbon black and does not describe or suggest the carbon black anodes of the present invention, having, for example, g values less than 0.

U.S. Patent No. 5,510,209 issued to Abraham et al., describes a

lithium/oxygen battery where the anode is lithium metal and the cathode is oxygen gas taken from the air. A carbonaceous powder is mixed with a polymer electrolyte to serve as a porous medium in which the oxygen is reduced to form Li_2O . The patent teaches the use of high surface area carbons such as acetylene blacks (about $40 \text{ m}^2/\text{g}$ surface area) at a 20 to 40 wt% level in a polymer electrolyte. They teach that higher surface area is better and mention in general that the cathode composition would be suitable with already lithiated graphitic carbons such as graphite, petroleum coke, benzene or other carbonaceous materials. The above described acetylene black, as mentioned previously, is different from the anode carbons described in the present invention, and the other carbonaceous materials are not described in detail, but would be expected to be different from those described in the present invention.

Sato et al. in U.S. Patent No. 5,571,638, teaches the use of a composite carbonaceous anode for secondary lithium ion batteries, which is composed of 70 to 99 wt% of a graphite powder and 30 to 1 wt% of a pseudo-graphitic carbon black. These carbonaceous materials are treated with a silane coupling agent to reduce the irreversible capacity. The carbon blacks in this patent are described as having a mean primary particle size of 10 to 100nm, specific surface areas (as measured by nitrogen adsorption) of 10 to $300 \text{ m}^2/\text{g}$, and a d_{002} spacing of 3.38 to $3.46 \text{ \AA}$. This patent also teaches that the carbon blacks are preferentially heat treated in the range of 1500 to 3000 °C and preferably between 2500 and 3000 °C to provide a higher degree of graphitic order, and, in fact, it is taught that the use of carbon blacks subjected to no heat treatment is unfavorable. In the present invention the specified anode carbon blacks are all larger in primary particle size, lower in surface area, and more disordered with d_{002} values $> 3.46 \text{ \AA}$ (for anode carbon blacks "A" and "B" only) than the specified carbon blacks in the Sato et al. patent. Also, the Sato et al. patent teaches that at least a 70 wt% of graphite material and a maximum 30 wt% loading of heat-treated carbon black is needed in the electrode. The present invention utilizes no graphite materials in the anode and teaches the

use of >85wt% of carbon black in the anode.

Binder et al. describes in U.S. Patent No. 5,601,948, the plasma treatment of a porous carbon black cathode in a primary battery (lithium and other metals can function as anodes). In this patent the carbon black is specified as Sharwinigan (an acetylene black) and it is used at a 90% loading (weight or
5 volume not specified) with 10% Teflon® used as binder. The application and type of carbon black are different than that described for the carbon black in the present invention.

Dasgupta et al. describes a lithium-manganese oxide electrode
10 (cathode) for a rechargeable lithium battery in U.S. Patent No. 5,601,952. They describe the use of up to 6vol% of a fine carbon compound in the cathode for conductive purposes only. The carbon compound is listed as being acetylene black, petroleum coke, or a similar high purity carbon. The application and description of the carbonaceous materials are different than that described for
15 the carbon blacks in the present invention.

Yazami et al. in U.S. Patent No. 5,605,772 describes the use of prelithiated raw coke or semi-coke in an anode for a rechargeable lithium ion battery. Additionally the anode contains an ionically conductive polymer and carbon black for conductive purposes. A typical anode was stated as
20 consisting of approximately 60% raw coke, 30% coating polymer and 10% carbon black. The advantage of this anode was that it produced significantly higher reversible capacities of about 1000 mAh/g. Clearly the primary carbonaceous materials used for intercalation in this anode are the cokes and not the carbon black. Also, the carbon black used in this anode at a 10%
25 loading is used only for conductive purposes and its properties are not specified. Thus this anode is significantly different from the one described in the present invention in which thermal carbon black is the primary carbonaceous material used in the anode for intercalation at a >85wt% loading.

30 Kaschmitter et al., in U.S. Patent No. 5,636,437, describes a general methodology of preparing electrodes from carbonaceous powders. Electrodes

prepared with low surface area ($<50 \text{ m}^2/\text{g}$) cokes and graphites were described as being useful for anodes in secondary lithium ion batteries. The specifications of these materials were not clearly defined, but they are certainly different materials compared to the carbon blacks described in the present invention.

Generally, and not in a limiting sense, the lithium-ion batteries of the present invention comprise a cathode, an anode containing or comprising a specific carbon black, an electrolyte and a separator.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to a rechargeable battery comprising a cathode, an anode comprising carbon black, an electrolyte, and a separator. The size of the carbon black particles of the anode can be greater than about 100nm and/or range in particle size between about 100nm and about 800nm.

Further, the carbon black can have an average surface area of less than about $20 \text{ m}^2/\text{g}$. The carbon black particles may be produced by a thermal process.

The anode may comprise approximately 85-95% thermal carbon black about 0-10% conductive black and about 5% binder. The separator may comprise polypropylene saturated with 1 molar Li PF_6 ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 (U/U) electrolyte. The electrolyte may comprise an organic solvent and a salt of an alkali metal. The cathode of the rechargeable battery may comprise, for example, lithium metal, alkali metal or a lithium metal oxide. The cathode may also contain up to 10% conductive black and 5% of a binder such as PVDF (polyvinylidene difluoride).

Further, the cathode and anode may each be capable of reversibly incorporating an alkali metal.

Further still, the battery cell of the present invention might comprise a rechargeable battery having an alkali metal cathode, an anode comprising a thermal carbon black having an average particle size of greater than about 100 nm, an electrolyte and a separator positioned between the cathode, which may

be lithium, and the anode.

The rechargeable battery of the present invention may also comprise a cathode of lithium metal oxide and an anode comprising a carbon black produced from a thermal process and having an average carbon black particle
5 size of greater than about 100nm.

The present invention might also include a lithium secondary battery comprising a cathode of a lithium metal oxide, an electrolyte, and an improved anode comprising at least about 85% thermal carbon black material of an average particle size of between about 100nm and about 800 nm, and having
10 a surface area of less than about 20 m²/g.

Further still, the present invention may relate to an improved rechargeable battery of the type having an anode, a lithium cathode, and an electrolyte, an improvement comprising the anode being formed in part of thermal carbon black of an average particle size of greater than about 100 nm.

15 Additionally, the present invention may relate to an improved anode for a rechargeable lithium metal oxide battery, the improved anode comprising a thermal carbon black material having an average particle size of > 100nm.

Further still and generally, the present invention relates to lithium-ion batteries comprising anodes containing carbon blacks having the properties
20 described in Table 1 herein.

TABLE 1
CARBON BLACKS FOR RECHARGEABLE BATTERY ANODES

Sample	Mean Particle Size (nm)	Heat Treatment Temperature (°C)	NSA (m ² /g)	STSA (m ² /g)	L _a (Å)	L _c (Å)	d ₀₀₂ (Å)	Hydrogen (ppm)	Carbon (%)	Sulfur (%)	Transmission (%)
Carbon A	408	none	7.0	5.4	45.8	14.1	3.565	4715	98.22	0.34	99.4
Carbon B	"	1500	6.9	5.6	73.4	27.7	3.493	372	99.45	0.04	99.7
Carbon C	"	2800	7.2	5.4	322	152	3.390	10	99.76	0.01	100

BRIEF DESCRIPTION OF THE DRAWINGS

For a further understanding of the nature, objects, and advantages of the present invention, reference should be had to the following detailed description, read in conjunction with the following drawings, wherein like reference numerals denote like elements and wherein:

Part A

- Figure 1 Cycle life curves for three different cells (la01, la17, la22) made with Carbon A.
- Figure 2 Illustrates the cycle life curve for cell la17 made with Carbon A.
- 10 Figure 3 Illustrates the cycle life curve for cell la22 made with Carbon A.
- Figure 4 Illustrates voltage curves for three different cells (la01, la17, la22) made with Carbon A.
- Figure 5 Illustrates dQ/dV vs. cell voltage curves for cell la01 made with Carbon A.
- 15 Figure 6 Illustrates dQ/dV vs. cell voltage curves for cell la22 made with Carbon A.
- Figure 7 Illustrates cycle #20 voltage curve for cell la01 made with Carbon A.
- Figure 8 Illustrates cycle #20 dQ/dV vs. cell voltage curve for la01 made with Carbon A.
- 20 Figure 9 Illustrates cycle #46 voltage curve for la22 made with Carbon A.
- Figure 10 Illustrates a signature curve for cell la21 made with Carbon A at cycles 3, 9, and 15.
- Figure 11 Illustrates a signature curve for cell la22 made with Carbon A at cycles 3, 9, and 15.
- 25 Figure 12 Illustrates cycle life curves for two different cells (ul01 and ul05) made with MCMB carbon.
- Figure 13 Illustrates dQ/dV vs. cell voltage for cell ul01 made with MCMB carbon.
- 30 Figure 14 Illustrates cycle life curves for cells ul01 and ul05 made with MCMB carbon.

- Figure 15 Illustrates cycle life curves for cells la03 & la04 made with Carbon B.
- Figure 16 Illustrates the voltage curve for cell la03 & la04 made with anode carbon B.
- 5 Figure 17 Illustrates the cycle 25 voltage curve for cell la04 made with Carbon B.
- Figure 18 Illustrates the dQ/dV vs. cell voltage for cell la04 made with Carbon B.
- Figure 19 Illustrates signature curves for cell la23 made with Carbon B.
- 10 Figure 20 Illustrates signature curves for cell la24 made with Carbon B.
- Figure 21 Illustrates a cycle life curve for petroleum coke.
- Figure 22 Illustrates voltage curves for petroleum coke.
- Figure 23 Illustrates dQ/dV vs. cell voltage curves for petroleum coke.
- Figure 24 Illustrates cycle life curves for three different cells (la06, la15, la19) made with Carbon C.
- 15 Figure 25 Illustrates a cycle life curve for cell la15 made with Carbon C.
- Figure 26 Illustrates a cycle life curve for cell la06 made with Carbon C.
- Figure 27 Illustrates a cycle life curve for cell la19 made with Carbon C.
- Figure 28 Illustrates voltage curve for three different cells (la06, la15, la19) made with Carbon C.
- 20 Figure 29 Illustrates dQ/dV vs. cell voltage for two different cells made with Carbon C (la06) and MCMB Carbon (ul05).
- Figure 30 Illustrates dQ/dV vs. cell voltage for two different cells made with Carbon C (la06) and MCMB Carbon (ul05).
- 25 Figure 31 Illustrates voltage curves for cell la19 made with Carbon C.
- Figure 32 Illustrates signature curves for cell la25 made with Carbon C.
- Figure 33 Illustrates signature curves for cell la26 made with Carbon C.
- Part B
- Figure 34 Illustrates cycle life curves for cell la31 made with Carbon A.
- 30 Figure 35 Illustrates cycle life curves for cell la32 made with Carbon A.
- Figure 36 Illustrates cycle life curves for cell la33 made with Carbon A.

	Figure 37	Illustrates cycle life curves for cell la30 made with MCMB carbon.
	Figure 38	Compares cycle life data for cell la31 made with Carbon A and cell la30 made with MCMB carbon.
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5	Figure 40	Illustrates voltage curves for cell la32 made with Carbon A.
	Figure 41	Illustrates voltage curves for cell la30 made with MCMB carbon.
	Figure 42	Illustrates signature curve data for cell ls31 made with Carbon A.
	Figure 43	Illustrates signature curve data for cell ls30 made with MCMB carbon
10	Figure 44	Illustrates cycle life curves for cell la34 made with Carbon C.
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20	Table 2	Illustrates capacity and first cycle efficiency data for three different cells (la01, la17, la22) made with Carbon A vs. one made with MCMB - all vs. Li-metal cathode.
	Table 3	Illustrates capacity and first cycle efficiency data for two different cells (la03, la04) made with Carbon B vs. one made with petroleum coke - all vs. Li-metal cathode.
25	Table 4	Illustrates capacity and first cycle efficiency data for three different cells (la06, la15, la19) made with Carbon C vs. one made with MCMB - all vs. Li-metal cathode.
	Table 5	Illustrates capacity and first cycle efficiency data for three different cells (la31, la32, la33) made with Carbon A vs. one made with MCMB (la30) - all vs. li-metal-Oxide cathode.
30		

Table 6 Illustrates capacity and first cycle efficiency data for cell la34 made with Carbon C vs. one made with MCMB (la36) - both vs. Li-metal-Oxide cathode.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

EXAMPLES

The following Examples are provided to demonstrate, via illustrative examples, aspects and embodiments of the present invention and are in no matter intended to limit the scope of the present invention.

CARBON BLACKS

The three carbon blacks of the illustrative examples of the present invention, Carbons A, B, and C, were made as follows and have the properties summarized in TABLE 1.

Sample Carbon A was produced using a conventional thermal black process. This process is described in detail in the following reference:

J.B. Donnet, et al. "Carbon Black" 2nd Edition, Marcel Dekker, Inc., 1993. pp. 59-61, which is hereby incorporated by reference in its entirety.

Samples Carbon B and Carbon C are heat treated versions of Carbon A. Carbon B was treated at 1500°C, while Carbon C was treated at 2800°C. Heat treatments were carried out in an inert atmosphere in high temperature furnaces (treatment performed by UCAR Carbon, Parma OH). In each case, the furnace was ramped to the desired temperature as quickly as possible, and held at that temperature for 30 minutes. Heating was then stopped, and the sample was allowed to cool in the inert atmosphere.

X-ray diffraction measurements (L_a, L_c, d_{002}) were conducted by Core Laboratories (Carrollton, TX) using a Philips APD 3600 x-ray diffractometer.

Hydrogen, carbon, and sulfur measurements were conducted by LECO Corportion Analytical Laboratory using a LECO Model RH-404 unit.

The remainder of the carbon property measurements were performed by Columbian Chemicals Company using tests known to those skilled in the art of carbon black testing:

- Particle Size - ASTM D3849-89 using a Philips CM12 Transmission Electron Microscope and Quantimet 970 Automated Image Analyzer.
- NSA (Nitrogen Surface Area) - ASTM D4820 using a Micromeritics Gemini 2370 Analyzer.

- STSA (Statistical Thickness Surface Area) - ASTM D5816 using a Micromeritics Gemini 2370 Analyzer.
- Transmission (Toluene Discoloration) - ASTM D1618-95.

TESTS OF ELECTRODES CONTAINING CARBONS A, B AND C

5 Part A: Testing of Carbons A, B, and C in Cathodes Versus Lithium Metal Anodes

The above-described carbons, Carbons A, B, and C, were used to fabricate electrodes which were used in a coin cell battery with lithium metal anodes and liquid organic electrolyte. As such, all voltage curves are
10 measured relative to lithium metal.

Coin Cells

The test carbons were fabricated into electrodes in the following general way. The test carbon powder was dry mixed with ca. 6% Ensagri Super S carbon black used to enhance electrode conductivity. Ensagri Super S exhibits
15 a nitrogen surface area of 44 m²/g and a mean particle size of 47 nm. The resulting dry mix was mixed with polyvinylidene difluoride (PVDF) and N-methylpyrrolidinone (NMP) to give a spreadable slurry. The slurry was doctor bladed onto copper foil and dried at 80° C. Further drying was done in a vacuum oven at 120° C for 1 hour. The composition of the resultant dry
20 electrode was ca. 6% Super S, 5% PVDF and the remainder test carbon.

Cathodes were punched from the above dry electrode spreads as 0.5" dia. disks, and in most cases and except where noted, were densified by pressing at 2500 psi. Electrode disks (0.005" thick) were fabricated into coin cells in an inert atmosphere dry box. The assembled cell stack of the coin cell
25 consisted of the carbon cathode, a 1M LiPF₆ ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 (v/v) electrolyte saturated separator, and a lithium anode disk. The carbon electrode was also saturated with electrolyte. The coin cell was sealed with a polypropylene grommet by crimping the coin cell positive to the coin cell negative. Stack pressure (ca. 250 psi) was delivered with a spacer
30 and spring assembly.

Cycling tests, voltage curves, and signature curve analysis:

Assembled coin cells were subjected to constant current discharge and charge between 0.002v and 2.0 v at room temperature or taper discharge under the same conditions. Between discharge and charge and subsequent discharge, cells were open circuited for 1000 sec. Current used for the tests ranged from C/50 to 2C. A C rate means that all the nominal capacity (mahr.) is delivered in one hour. Thus C/50 is all capacity in 50 hours and 2C is all capacity in 1/2 hour. In some cases the current is expressed as D/5 to indicate a cell discharge (lithium incorporated into the carbon). This is only done when the discharge and charge (lithium removed from the carbon) are at different current. If the rates for charge and discharge are the same then they are expressed as C rates. Taper discharges were done by discharging at a constant current of C/2 or C followed by holding the cell at 0.002v for three hours during which time the current decreased from an initially high value (less than C rate) to near zero ma. Taper charging (removal of lithium from the carbon) is a favorite charging method for commercial lithium ion cells.

A signature curve analysis was performed in addition to the above described cycling tests where voltage curves (cell voltage plotted versus time or capacity) and cycle life plots (capacity plotted versus cycle number) were recorded. In the signature curve analysis, the coin cell is, after fully charging, subjected to a large constant current discharge to 0.002v, open circuited for 1000 sec, subjected to a smaller constant current discharge, open circuited, subjected to a smaller current and etc. This is done until the last discharge to 0.002v is at ca. C/40. Accumulated discharge capacity is plotted versus discharge rate to give a signature curve. The plot is constructed such that the capacity at a particular rate is a summation of all the capacities for the previous higher rates. It is generally found that the capacity from the plot at the lowest rate represents all the capacity the cell would have delivered if discharged only at the lowest rate and represents its nominal capacity. The plot gives a very good indication of the rate capability of the test material.

As well as the cycle life, voltage curve, and signature curve plots described above, an additional plot is used for analysis. The dQ/dV versus voltage plot is an essential equation of state indicator. In this plot, peaks represent voltage plateaus in the voltage curve where for example first order phase transformations occur. This can be seen for graphite where stages are observed. Sloping dQ/dV vs V curves are indicative of a continuous distribution of energy states within the test material. DQ/dV curves for taper discharged cells are not given as the decreasing current and subsequent increase in voltage makes the differential plots confusing to view.

A certain amount of electrode fabrication, cell fabrication, and rate and method of discharging optimization was done on the three carbon materials so that as near complete as possible characterization of the materials could be determined. The variations in testing will be described below for the individual cases.

All tests were done on duplicate coin cells so that reproducibility was within 5% in capacity. Data for duplicate cells are not always shown.

Example 1:

Carbon A

Carbon A was the non-heat treated carbon as described above. Figure 1 shows cycle life curves for three different sets of cells made with this carbon. La01 was initially discharged and charged at a C/50 rate followed by a cycle at C/12 then 3 cycles at d/7 and C/2 then cycled at d/2 and C/6 until the end of test. Figure 2 shows la17 where the first 5 cycles were with a d/2 taper discharge and a C/10 charge. Cycles 6 to 24 were at C/15 constant current discharge and charge then back to taper discharge and constant current charge at d/2 and C/10 until end of test. Figure 3 shows data for la22 which was a signature curve test where the first two cycles were taper discharge at a d rate and constant current charge at C/12. Cycle 3 was a signature discharge with C/12 charging., as were cycles 9 and 15. All other cycles were as for cycles 1 and 2. What can be seen from Figures 1 to 3 is that the first cycle irreversible, Qirrev and reversible, Qrev capacities are dependent upon the first discharge

rate, and the first cycle charge efficiencies, (1st discharge capacity/1st charge capacity x 100%) are independent of the first discharge rate. Delivered discharge capacity at a d/2 or better rate is increased by a faster first cycle discharge. Moreover if the first cycle is done at a fast rate this increased capacity is not lost by lower rate cycling as shown by the data of 1a17, Figures 1 and 2. The first cycle discharge results in not only reversible incorporation of lithium into the carbon but also irreversible consumption of lithium most of which is associated with the passivation of the carbon surface to further electrolyte cathodic decomposition. This is quantified by the first cycle efficiency which is tabulated below. Additionally, first cycle irreversible and reversible specific capacities are listed along with high and low rate reversible cycling specific capacities. For comparison purposes to commercial MCMB carbon where the average cell voltage is different from that of the carbons used, the specific energy densities are listed in brackets. These values are computed assuming the carbons are matched as anodes in an ion cell with a LiCoO_2 cathode.

Table 2

Cell #	1st cycle efficiency %	first cycle irreversible capacity, Q_{irrev} mahr/g, (mWhr/g)	first cycle Reversible Capacity, Q_{rev} mahr/g, (mWhr/g)	high rate Reversible Capacity, Q_{rev} mahr/g, (mWhr/g)	low rate Reversible Capacity, Q_{rev} mahr/g, (mWhr/g)
la01	78	102 (342)	361 (1209)	240 (804)	280 (938)
la17	79	77 (258)	291 (975)	305 (1022)	355 (1189)
la22	79	87 (291)	325 (1089)	340 (1139)	390 (1306)
MCMB*	88	43 (166)	313 (1205)	295	320 (1232)

*MCMB commercial mesophase microbeads heat treated to 2500 C.

10 The reversible capacity increase appears to depend upon the residence time for the formation of the passivation film. The fade rate, ie. loss of capacity per cycle, is low although la17 has a somewhat higher fade rate perhaps due to the period of slow cycling. Additionally for this cell a charge imbalance has formed where the charge is longer than the discharge. This could be an effect of
15 cycling against lithium metal and needs to be verified in lithium ion cells.

Figure 4 depicts the voltage curves for the above three cells. The discharge and charge curves are sloping with an average voltage of ca. 0.65 volts vs lithium. For cells la17 and la22 one can see the voltage drop with the taper discharge followed by the voltage rebound when the constant voltage
20 discharge takes over for the last three hours. La22 shows a rapid dip in voltage followed by a recovery during the d/I constant current discharge part of the first cycle. It's companion cell showed the same feature although not as pronounced. This could be a lithium ion electrolyte starvation effect.

Figure 4 shows some hysteresis between charge and discharge. This is
25 most pronounced for la01 and shows up as a bump in the charge curve at ca. 1.0 - 1.2 volts. This is less apparent in la17 and la22. This effect can be seen better in Figures 5 and 6 where the dQ/dV vs V curves for the first charge of la01 and la22 are shown. The peak at ca. 1.0 - 1.2 volt can clearly be seen and is more evident for the cell discharged at the lower rate, la01. This feature is still

present at later cycle numbers as is shown by Figures 7 and 8 which are for cycle # 20 for la01. Figure 7 shows the reversibility of la01. The ca. 1.0 - 1.2 volt peak in the dQ/dV vs v curves could indicate some phase change or ordering or lithium association with some "special carbons" or heteroatoms, ie., H, S, or O.

Figure 9 shows the voltage curve for la22 at cycle 46. The feature at 1.0 - 1.2 volts is there.

Figures 10 and 11 show signature curves for la21 and 22 at cycle 3, 9 and 15. Both cells were cycled the same way with a first cycle taper discharge at $d/1$ constant current followed by constant voltage discharge for three hours at 0.002v. Charging was at a constant current of $C/12$. Both cells show quite a strong dependence of capacity on rate and small loss of rate capability with cycle number.

The rate capability of la21 and 22 is as good or somewhat better than for commercial MCMB over the range $C/10$ - $C/3$. For la22, capacity at $C/3$ is 82% of that at $C/10$. For commercial MCMB as shown in Figure 12 the same value is 74%. Data from Table 2 and Figures 12 and 13 where the cycle life and voltage curve of commercial MCMB carbon are shown indicate that the cycle life, reversible capacity and rate capability of Carbon A compare favorably with commercial MCMB. The latter does have a somewhat better first cycle capacity efficiency and relatively flat voltage curve, Figure 13, with a lower average voltage, however, Carbon A has a larger reversible capacity. The specific energy densities of la22 compare quite well with those of the MCMB. Carbon A does have a larger first cycle irreversible specific energy density and a smaller first cycle reversible specific energy density but its low rate reversible specific energy density is larger, 1308 compared to 1232 mWhr/g. High rate ($d/2$ or better) reversible cycling data for MCMB is not currently available but based on the low rate data it is expected that Carbon A will compare well.

Figure 14 shows the staging of the graphitic MCMB. Figures 12 - 14 show the sensitivity of the MCMB to electrode fabrication. Cell ul01 had an electrode densified at 1250 psi while ul05 had no densification.

This means that Carbon A in anodes (tested versus Li-metal cathode) can provide superior reversible capacity to commercial MCMB (first cycle, high rate, and low rate with minimal fade upon extended cycling); although, its 1st cycle efficiency is slightly lower.

5 Example 2:

Carbon B

Carbon B was heat treated at 1500° C as described above. Figure 15 shows cycle life data for two companion cells la03 and la04. Both were cycled at C/30 for ten cycles then d/2 and C/5 for ca. 50 cycles then d6 and C/2 until

10 end of test. Fade rates are very low but capacities are also low.

Table 3

Cell #	1st cycle efficiency %	Irreversible capacity, Q _{irrev} mahr/g, first cycle	Reversible Capacity, Q _{rev} mahr/g first cycle	Reversible Capacity, Q _{rev} mahr/g high rate	Reversible Capacity, Q _{rev} mahr/g low rate
la03	79	54	204	165	190
la04	78	57	201	172	190
15 pc01*	81	50	219	160	225

*commercial petroleum coke.

Figure 16 shows the first voltage curve for these two cells. The voltage curves are sloping with an average voltage near 0.65v.

20 Figure 17 shows the cycle 25 voltage curve while Figure 18 shows the dQ/dV vs v curves for the cycles of Figure 16 and 17 for la04. As for the non-heat treated carbon, Carbon A discussed above, there is a feature in the dQ/dV vs v curve on the first cycle but for the 1500°C heat treated material it is at 0.8V, is predominantly in the discharge and it is not present at later cycles. In this

25 case, this voltage feature is associated with the formation of the passivation film.

Figures 19 and 20 show signature curve data for cells la23 and la24 which were cycled at C/10 for ten cycles then a signature curve was obtained at cycle 11. After more C/10 cycling signature data was obtained at cycles 17

and 23. From cycle 24 on, cycling was at C/10. There is a fairly strong dependence of capacity with rate but little loss of rate capability with cycle number. Comparison data is available for a commercial petroleum coke as shown in Table 3 and Figure 21 for cell pc01. At C/20, C/3, and a C rate the
5 relative normalized capacities are 1, 0.82, and 0.65. For la23 these values are 1, 0.85, and 0.72.

For comparison, Figure 22 shows the voltage curves for the first and 30th cycles of cell pc01 with commercial petroleum coke while Figure 23 shows the companion dQ/dV vs v curves.

10 The 1500°C heat treated carbon Anode Carbon B essentially behaves like commercial petroleum coke.

This means that Carbon B in anodes (tested versus Li-metal cathode) can provide nearly comparable reversible capacity and 1st cycle efficiency relative to petroleum coke. Comparatively, the reversible capacity of Carbon
15 B is much lower than Carbon A. Therefore, the heat treatment at 1500°C significantly diminished Carbon A anode performance.

Example 3:

Carbon C

Carbon C was heat treated at 2800°C as described above. Figure 24
20 shows cycling data for three representative cell sets made with this carbon material. The cells were cycled in different ways. The cycling regimes are shown better in Figures 25, 26, and 27. To summarize, la06 was cycled at C/10 for 9 cycles then at d/3 and C/5 and finally at d/6 and C/3. Fade rates were low under these conditions but reversible capacity was lower than commercial
25 MCMB. La15 used electrodes that were fabricated in a different way to that described above. The cell was cycled at C/10 then d/1 and C/5 with periodic C/5 cycling. La19 was taper discharged at d/2 and charged at C/10. This first cycle treatment has resulted in the best performance for this material. Quantitative data for the cells are summarized in Table 4. The highest
30 reversible capacity was achieved when the first discharge was done as a taper discharge, although at an expense of some first cycle charge efficiency. At a

d/l taper discharge the material may be better. 1st cycle efficiencies compare fairly well with commercial MCMB but the low rate reversible capacity is smaller.

Looking at Figure 28 where the first cycle voltage curves of all three cells are shown and comparing this to Figure 13 for MCMB one can see that they are similar and for all purposes appear to be the same type of carbon.

Table 4

Cell #	1st cycle efficiency %	first cycle Irreversible capacity, Q _{irrev} mahr/g,	first cycle Reversible Capacity, Q _{rev} mahr/g,	high rate Reversible Capacity, Q _{rev} mahr/g,	low rate Reversible Capacity, Q _{rev} mahr/g,
la06	85	42	230	195	235
la15	88	27	194	175	205
la19	82	39	180	250	250**
MCMB*	88	43	313		320

*MCMB commercial mesophase microbeads heat treated to 2500 C.

**Data from signature curves

15

The question is then, what causes the lower capacity with the Carbon C? The similar first cycle irreversible capacities suggest that the surface area of both are similar. The voltage curves suggest the carbon structure is similar yet the Carbon C carbon material does not intercalate lithium to the same extent. Examining Figures 29 and 30 where dQ/dV plots of la06 and a MCMB cell, ul05, are shown one can see that the intercalation and de-intercalation of lithium for the first and seventh cycle is not as structured or staged for the Carbon C as for the MCMB. It is not clear if this means that the Carbon C has a higher or lower degree of graphitization. The dQ/dV plots suggest the Carbon C is less graphitized but it has been heat treated to 2800°C while the MCMB was treated to 2500°C. Perhaps the Carbon C has residual heteroatoms that cause it to be less structured. It is possible that over-heat treating could cause the observed result.

Figure 31 shows a comparison of cycle 1 and cycle 10 for la19. The charge efficiency for cycle 10 is near 100% and the cell impedance has decreased. Figures 32 and 33 show signature curve data for la25 and 26 where signature data are collected at cycles 3, 9 and 15. Cycling was at C/10 for all other cycles. Data are similar for both cells except for the 3rd cycle curve of la26. This cell performed better at later cycles. The capacity is strongly dependent upon rate but little rate capability is lost with cycling. To compare to MCMB, capacity at C/3 is 90% of that at C/10 for la25 and 82% for MCMB.

Summarizing all collected data, this means that Carbon C in anodes (tested versus Li-metal cathode) provides lower reversible capacity and 1st cycle efficiency relative to commercial MCMB. In this case, the higher temperature heat treatment of 2800°C slightly improved the 1st cycle efficiency of Carbon C versus Carbon A; although the reversible capacity was noticeably reduced (though not as much as with the 1500°C treatment).

Part B: Testing of Carbons A and C in Anodes Versus Lithium Metal Oxide Cathode (Li-ion cell)

Carbons A and C were used to fabricate electrodes which were used in coin cell hardware as anodes with LiCoO₂ cathodes and liquid organic electrolyte. All voltage curves are cell voltages and are not referenced to lithium metal.

The test carbons were fabricated into electrodes in the following general way. The test carbon powder was dry mixed with ca. 6% Super S carbon black used to enhance electrode conductivity. The resulting dry mix was mixed with polyvinylidene difluoride (PVDF) and N-methylpyrrolidinone (NMP) to give a spreadable slurry. The slurry doctor bladed onto copper foil and dried at 80°C. Further, drying was done in a vacuum oven at 120°C for one hour. The composition of the resultant dry electrode was ca. 6% Super S, 5% PVDF and the remainder test carbon.

LiCoO₂ cathodes were fabricated in a similar way. Here the Super S carbon content was 10%.

Anodes were punched from the above dry electrode spreads as 0.5" dia. disks and in most cases and except where noted were densified by pressing with 2500 psi. Anode electrode disks (0.001" thick) and cathode electrode disks (0.003" thick) were fabricated into coin cells in an inert atmosphere dry box.

5 Cathode electrodes this thin were required to allow C rate charging, consequently the anode electrodes are thinner than used in the previously reported carbon evaluations versus lithium electrodes. The assembled cell stack of the coin cell consisted of the carbon anode, a 1M LiPF_6 ethylene carbonate (EC)/dimethyl carbonate(DMC) 1:1 (v/v) electrolyte saturated

10 separator, and a LiCoO_2 cathode. The carbon and LiCoO_2 electrodes were also saturated with electrolyte. The coin cell was sealed with a polypropylene grommet by crimping the coin cell positive to the coin cell negative. Stack pressure (ca. 250 psi) was delivered with a spacer and spring assembly.

It was anticipated that for the test cells to work at high rates the LiCoO_2 cathodes would have to be kept thinner than 0.004". To balance the capacity of the anode and cathode so that the cell was anode limited, anodes of ca. 0.001" were used.

15

Lithium ion cells as opposed to lithium metal cells are constructed in the discharged state. The cathode, LiCoO_2 is fully lithiated and has an open circuit potential versus lithium metal of ca. 4.0 volts. The anode, in this case carbon,

20 is fully de-lithiated and has an open circuit voltage of between 2 and 3 volts versus lithium metal. Consequently the open circuit voltage of a lithium ion cell before charging is less than 2 volts, the difference between the voltage of each electrode relative to lithium metal. The first charge of the lithium ion cell de-

25 lithiates the cathode producing $\text{Li}_{1-x}\text{CoO}_2$ and lithiates the anode. The material balance of the cell is chosen so that the carbon is fully lithiated on charge to near LiC_6 and the cathode is de-lithiated so that x is less than 0.5. Removal of more lithium than this will result in rapid cathode failure. To achieve these lithium balances on the first charge one must know the reversible and

30 irreversible capacities of the anode. These values were approximated by previous tests in lithium ion cells.

Assembled coin cells were subjected to constant current discharge and charge between 2.0v and 4.0v at room temperature or taper charge under the same conditions. Between discharge and charge and subsequent discharge, cells were open circuited for 1000 sec.

5 Based on the results of the Carbon A tested in lithium metal cells the first batch of ion cells were taper charged at a C rate for 1 hr then at variable current and constant voltage of 4.0 v. It was found that virtually all the anode capacity (>96%) was realized during the C rate constant current charge part of the taper charge. For this reason all subsequent charges were done at
10 constant C rate with no taper charge.

For both types of charges there is a difficulty in establishing the upper charge limit. This is because the voltage curves established for the anode material in lithium metal cells are not exactly the same as what could be found in lithium ion cells. The anode could deliver more capacity at a particular rate
15 in an ion cell as opposed to a lithium metal cell where the lithium anode could be limiting, especially at high rates. For this reason, the anode results for the ion cell may not be fully optimized. To do this a three electrode reference cell is required. In this cell, the voltage curve of both the anode and cathode versus lithium metal can be determined without any lithium metal limiting electrode.
20 Results for the Carbon A material are obtained with this cell. The difficulty of obtaining the exact voltage curve for the anode and cathode without the reference cell also means that there can be a lot of variation in capacity and performance of two electrode ion cells. More than three cells were made of each carbon anode material.

25 Example 4:

Carbon A

Figure 34 presents cycle life data for the best performance ion cell, la31, charged at a C rate and discharged at a D/5 rate. Except for the first cycle the charge capacity has been limited to ca. 330 mahr/g. This corresponds to an ion
30 cell voltage of 4.0 v. This limit has been imposed to ensure that the anode does not go below 0.0 v versus lithium and deposit lithium metal. The first few cycles

of the cell were used to establish this limit. From the figure one can see the fade rate is extremely low. Over the first twenty cycles the discharge capacity of the cell increases and eventually is larger than the charge capacity.

Figures 35 and 36 present similar data for two other lithium ion cells made with this carbon as an anode, la32 and la33. Here the charge and discharge capacity are the same and capacity fades with cycle number.

Figure 37 presents similar data for a mesophase microbead anode lithium ion cell, la30.

Figure 38 presents discharge cycle life data as a comparison between Carbon A carbon anode and mesophase microbead anode lithium ion cells. Over the first 100 cycles the capacities of both cells were similar. After 100 cycles the microbead cell began to fade. For this cell, la31, the cycle life is longer than for the microbead anode.

Table 5 summarizes the cycle life data.

Table 5

Cell #	1st cycle efficiency %	1st cycle Irreversible capacity, Q _{irrev} mahr/g, (mWhr/g)	1st cycle Reversible Capacity, Q _{rev} mahr/g, (mWhr/g)	high rate Reversible Capacity, Q _{rev} mahr/g, (mWhr/g)	low rate Reversible Capacity, Q _{rev} mahr/g, (mWhr/g)
la31	65	149 (447)	274 (882)	340 (1020)	N/A
la32	65	147 (441)	276 (828)	318 (954)	N/A
la33	65	147 (441)	276 (828)	315 (945)	N/A
MCMB* la30	76	93 (334)	292 (1051)	335 (1206)	N/A

*MCMB commercial mesophase microbeads heat treated to 2500°C.

The first cycle efficiencies are lower than found in the lithium metal cell. To some extent, this is due to the difficulty in setting the cell upper voltage and capacity limit. There is no reason to expect this irreversible capacity to be different from that found in the lithium metal cell.

Comparing the microbead cell to the inventive carbon cells, Table 5, the discharge capacities at high rate are similar. Due to the microbead cell having

a higher average voltage ca. 3.6 v and the inventive cells, 3.0 v, the former has a higher energy density in mWhr/g. The cell voltages can be seen in Figures 39 to 41. For the inventive carbon cells la31 and la32 the voltage curves show capacity evenly from 2.0 to 4.0 volts while the microbead cell, la30, Figure 41, has most of the capacity near 3.8 volts with some down to 2.5 volts. With these cells the cell impedance increases with cycle number as the capacity decreases.

Figures 42 and 43 present signature curve data for inventive carbon cell la31 and microbead cell la30 respectively. Signature curve data are collected at cycle 205, 220 and 240 for each cell. The rate performance of the inventive carbon cell la31 is excellent. The charge cycle before the signature cycle was ca. 340 mahr which is delivered on the subsequent discharge steps at rates greater than C/2. The signature data is collected by charging the cell followed by discharge steps at rates of 2C, C, C/1.25, C/1.5, C/2, C/3, etc. down to C/40. The signature curve for rates of 2C to C/2 or C/3 is correct, for rates lower than this it may be suspect. This indicates that the rate capability of the inventive Carbon A in a lithium ion cell is excellent. Figure 43 shows similar data for the microbead cell. Here the rate capability is also excellent in that all the available capacity is delivered at high rates, however the overall delivered capacity is lower than for the inventive carbon cell.

Example 5:Carbon C

Carbon C was heat treated at 2800°C. Lithium ion cells were charged at constant current at a C rate and discharged at a D/5 rate. Figures 44 and 45 present data for Carbon C lithium ion cells. Capacity is low under this cycling regime and some cell shunting occurred, presumably lithium metal was deposited. Figures 46 and 47 present data for microbead lithium ion cells. Capacity is higher but at later life shunting occurs. Figure 48 presents comparison discharge cycle life data. Here it can be seen that the microbead anode gives higher capacity. Comparative cycle life data are presented in Table 6.

Table 6

Cell #	1st cycle efficiency %	1st cycle Irreversible capacity, Q _{irrev} mahr/g,	1st cycle Reversible Capacity, Q _{rev} mahr/g,	high rate Reversible Capacity, Q _{rev} mahr/g	low rate Reversible Capacity, Q _{rev} mahr/g,
1a34	60	125	190	140	N/A
MCMB* 1a 36	76	93	292	230	N/A

*MCMB commercial mesophase microbeads heat treated to 2500°C.

Figures 49 and 50 present cell voltage plots of the inventive carbon anode and mesophase microbead anode cells respectively. Here again as was found with the lithium metal cells the voltage plots for both materials is similar. With cycle life the cell impedance increases leading to capacity loss. With 1a37, Figure 50 at cycles 60 and 115 one can see the cell shunting on charge.

Conclusions

The low temperature carbon, Carbon A, performs as well in the lithium ion cell as it does in the lithium metal cell.

CLAIMS

- 1 1. A rechargeable battery, comprising:
 - 2 a) a cathode;
 - 3 b) an anode comprising carbon black of average particle size
4 greater than 100nm;
 - 5 c) an electrolyte;
 - 6 d) a separator.
- 1 2. The rechargeable battery in claim 1, wherein the size of the
2 carbon black particles range between 100nm and 800nm.
- 1 3. The rechargeable battery in claim 1, wherein the carbon black
2 has an average surface area of less than 20m²/g.
- 1 4. The rechargeable battery in claim 1, wherein the carbon black
2 particles are produced from a thermal process.
- 1 5. The rechargeable battery in claim 1, wherein the anode
2 comprises approximately 85-95% thermal carbon black, 0-10% conductive black
3 and 5% binder.
- 1 6. The lithium rechargeable battery in claim 1, wherein the separator
2 comprises polypropylene saturated with 1M Li PF₆ ethylene carbonate
3 (EC)/dimethyl carbonate (DMC) 1:1 (V/V) electrolyte.
- 1 7. The rechargeable battery in claim 1, wherein the cathode
2 comprises a metal selected from the group consisting of alkali metal, lithium
3 metal, and lithium metal oxide.
- 1 8. The rechargeable battery in claim 1, wherein the cathode and
2 anode are each capable of reversibly incorporating an alkali metal.

1 9. The rechargeable battery in claim 7, where the electrolyte
2 comprises an organic solvent and a salt of said alkali metal.

1 10. A rechargeable battery, comprising:
2 a) an alkali metal cathode;
3 b) an anode comprising a thermal carbon black of average particle
4 size greater than 100nm;
5 c) an electrolyte; and
6 d) a separator positioned between the cathode and the anode.

1 11. A rechargeable battery, comprising:
2 a) a cathode of lithium metal oxide;
3 b) an anode comprising a carbon black produced from a thermal
4 process, the average particle size of the carbon black greater than 100 nm.

1 12. A lithium secondary battery comprising a cathode of a lithium
2 metal oxide; an electrolyte; and an improved anode comprising at least 90%
3 thermal carbon black material of average particle size between 100 nm and
4 800 nm, and a surface area of less than 20m²/g.

1 13. An improved rechargeable battery, of the type having an anode,
2 a lithium cathode, and an electrolyte, wherein the improvement comprises the
3 anode formed in part of thermal carbon black of average particle size greater
4 than 100nm.

1 14. An improved anode for a rechargeable metal oxide battery, the
2 anode comprising a thermal black material having an average particle size of
3 greater than 100nm.

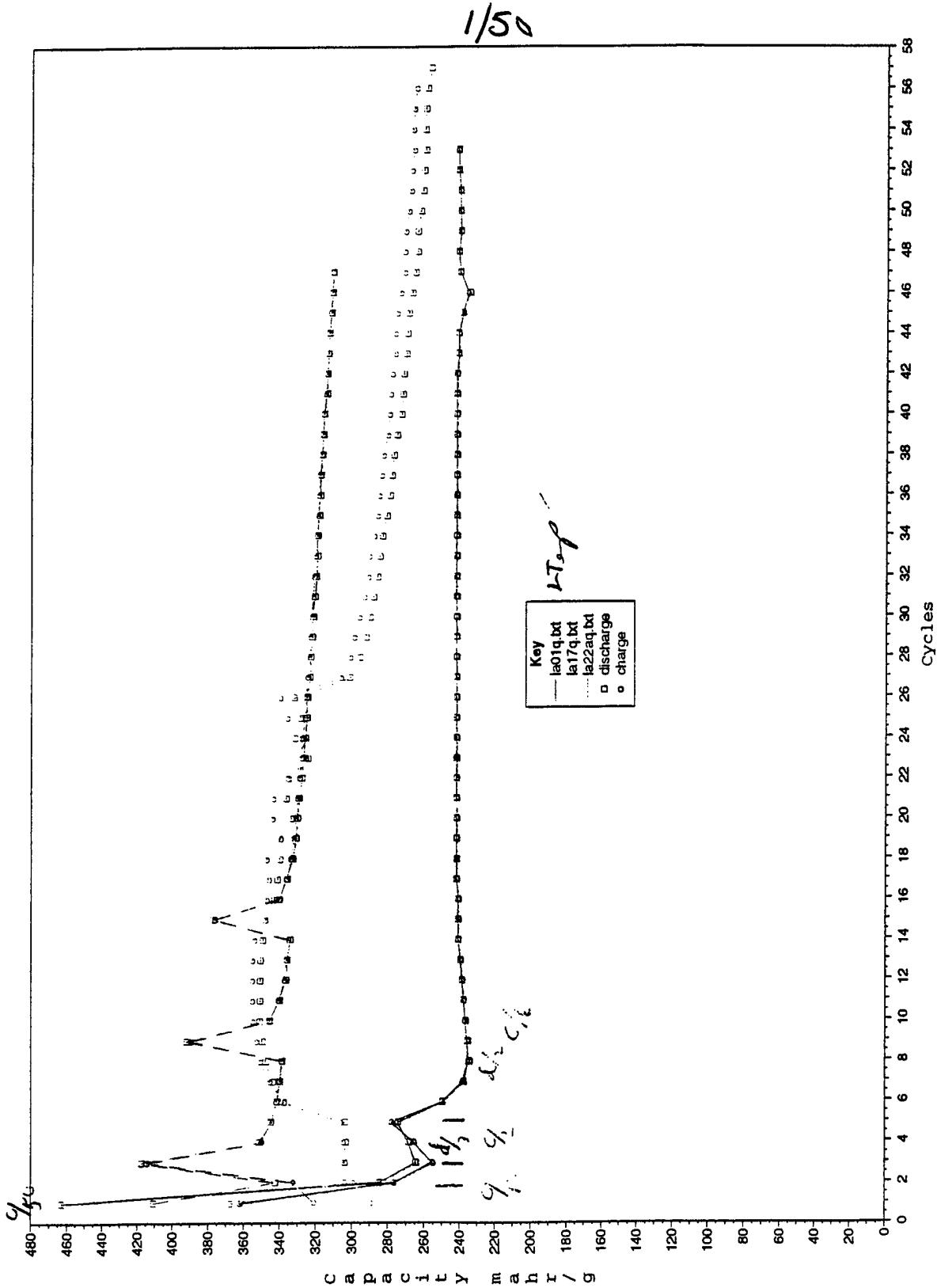


Figure 1

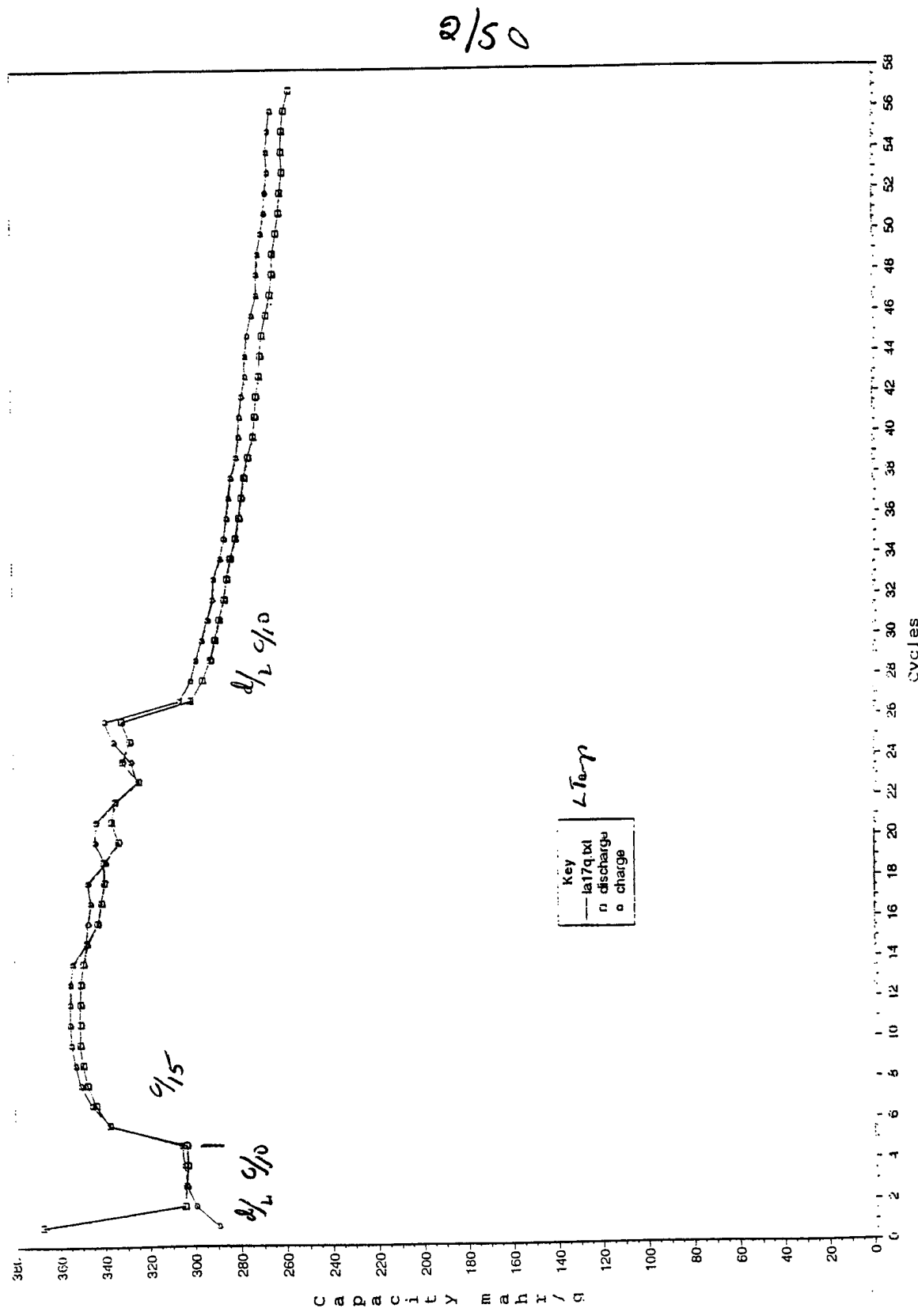


Figure 2

3/50

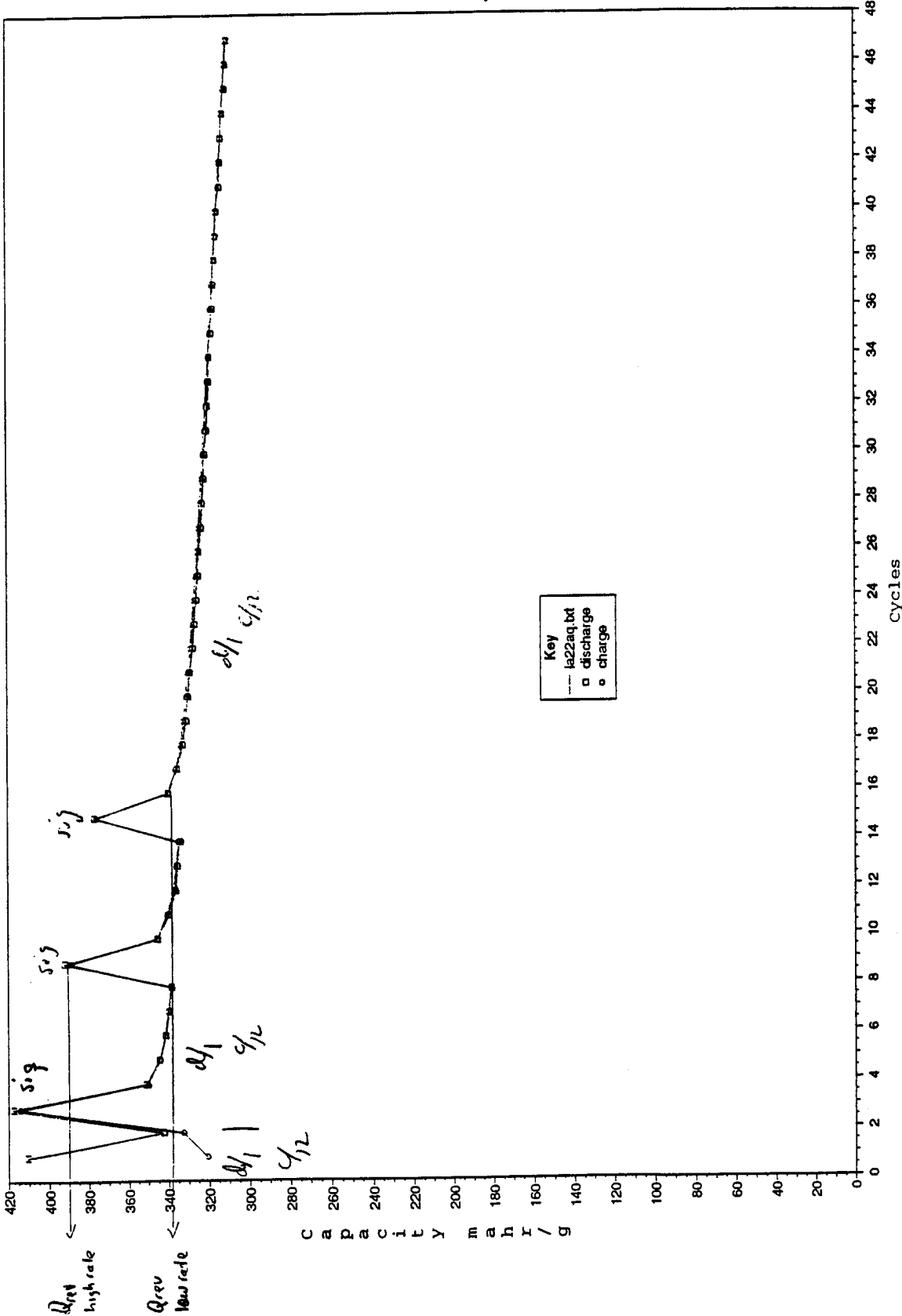


Figure 3

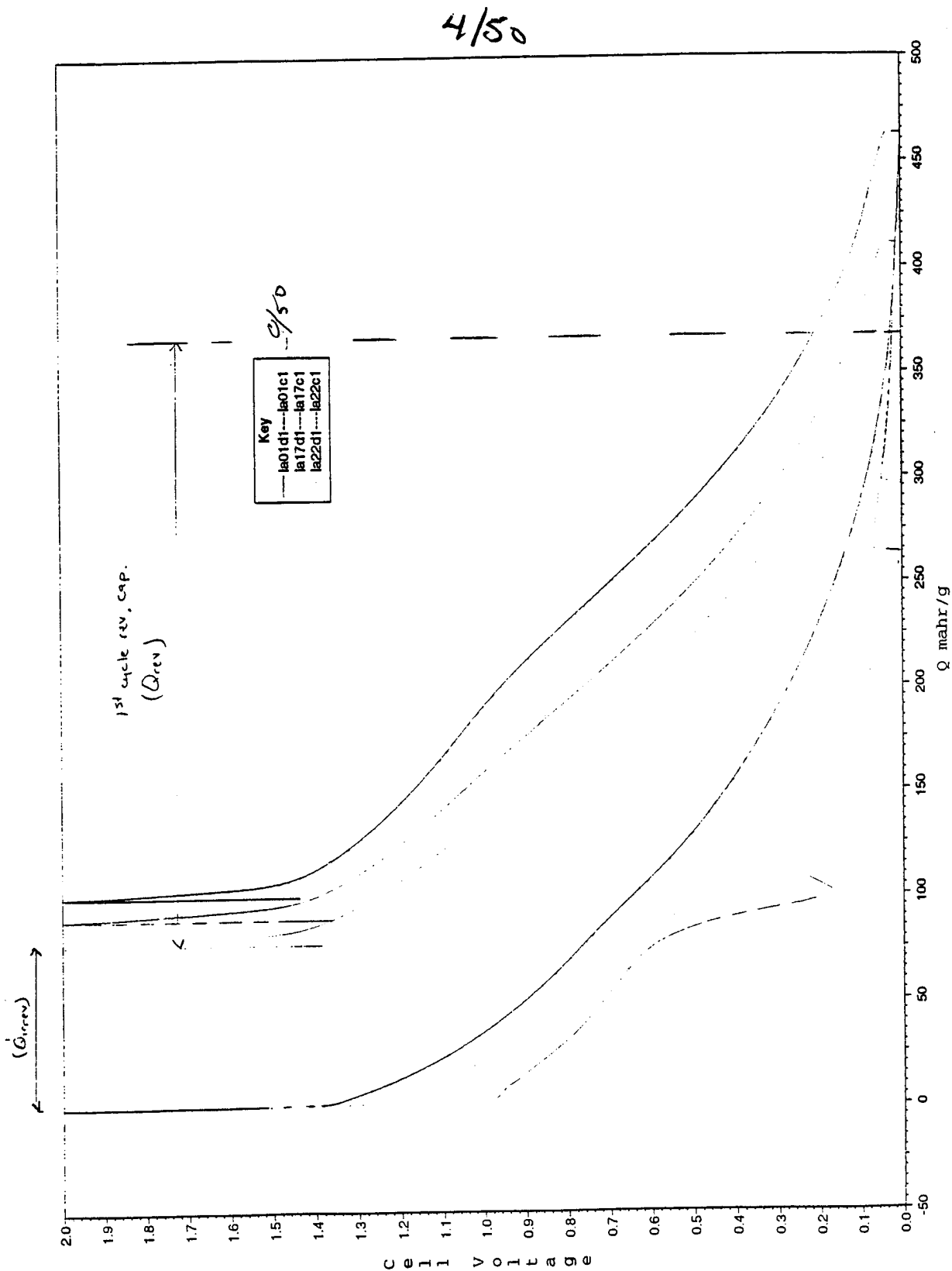


Figure 4

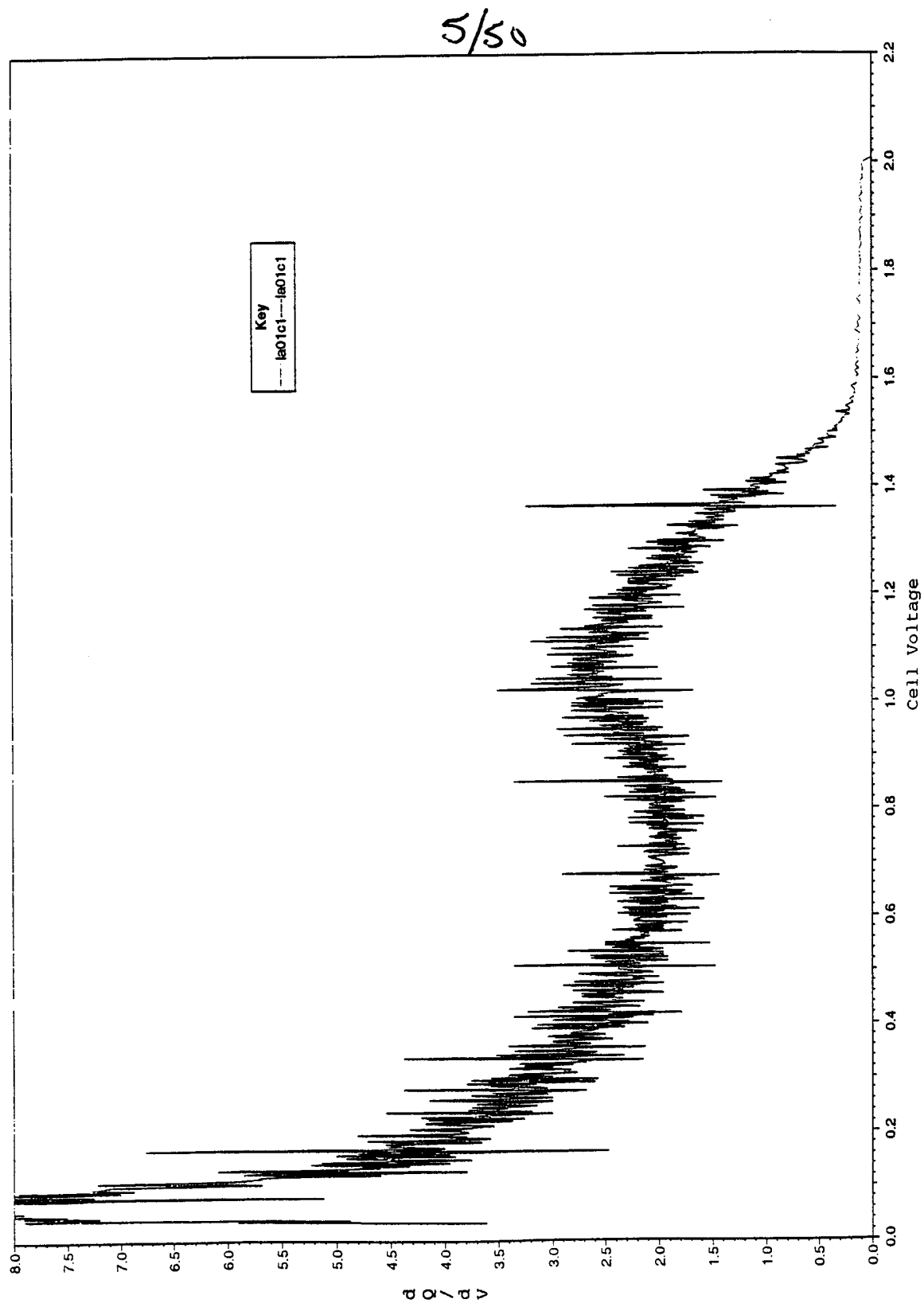


Figure 5

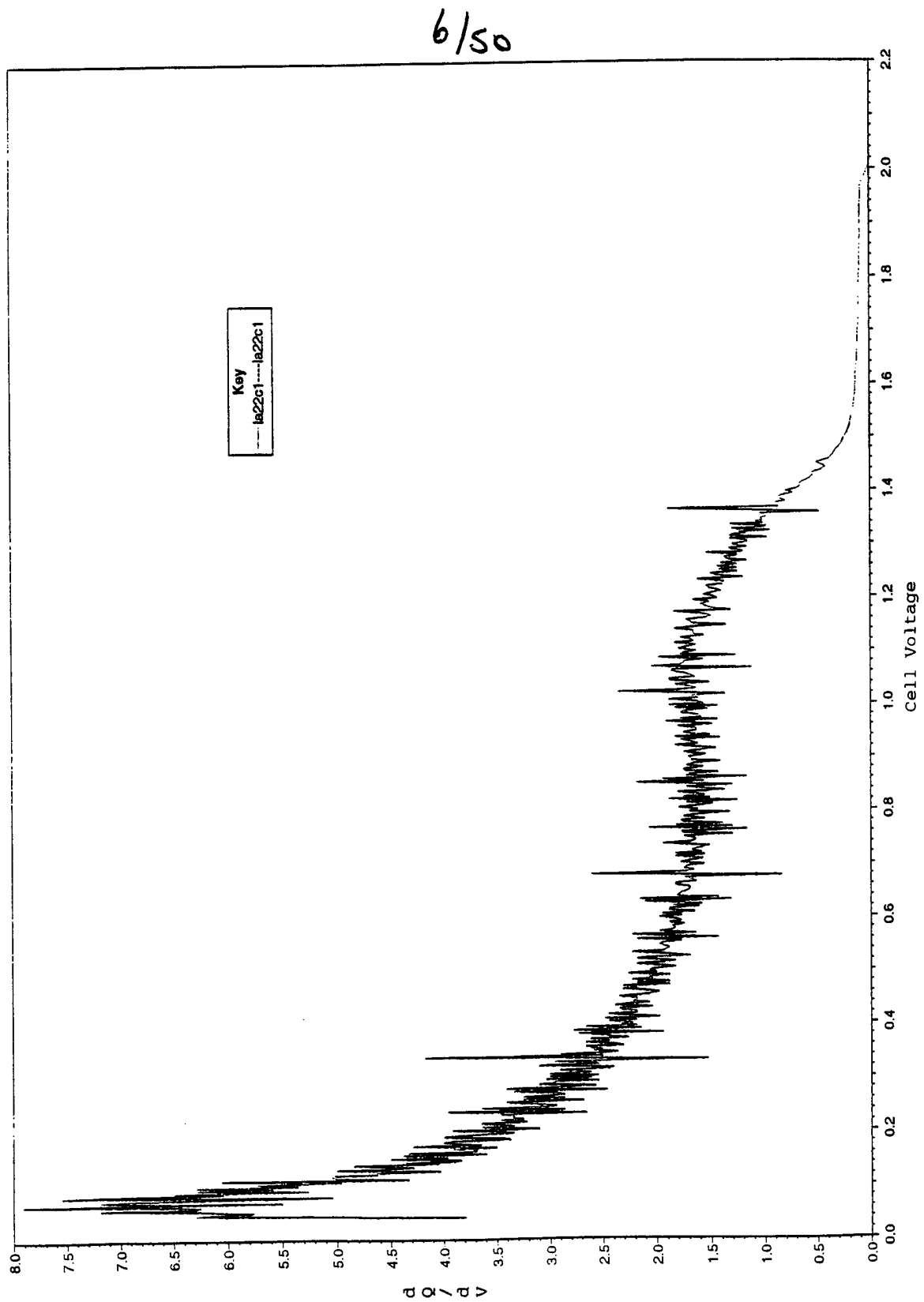


Figure 6

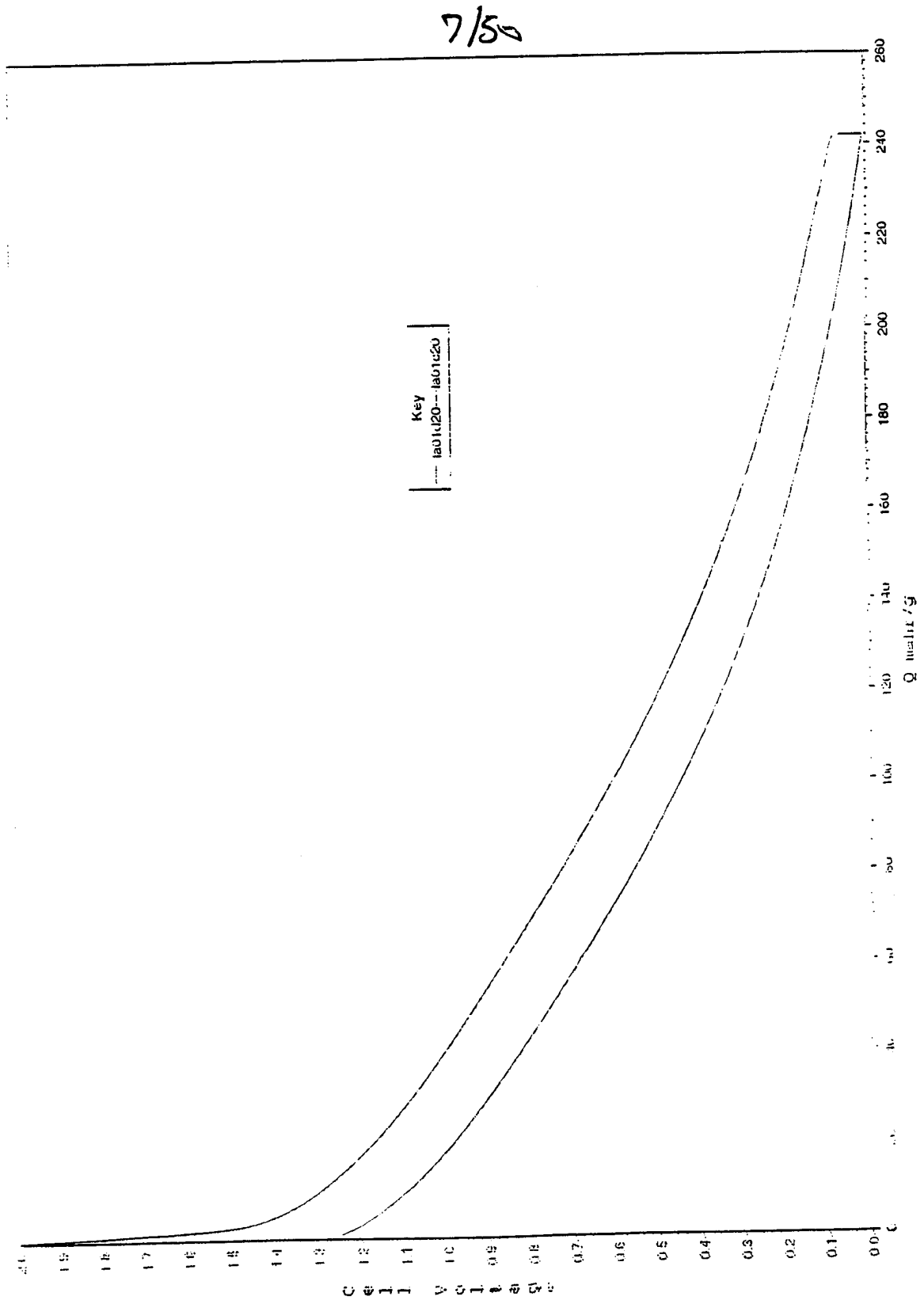


Figure 7

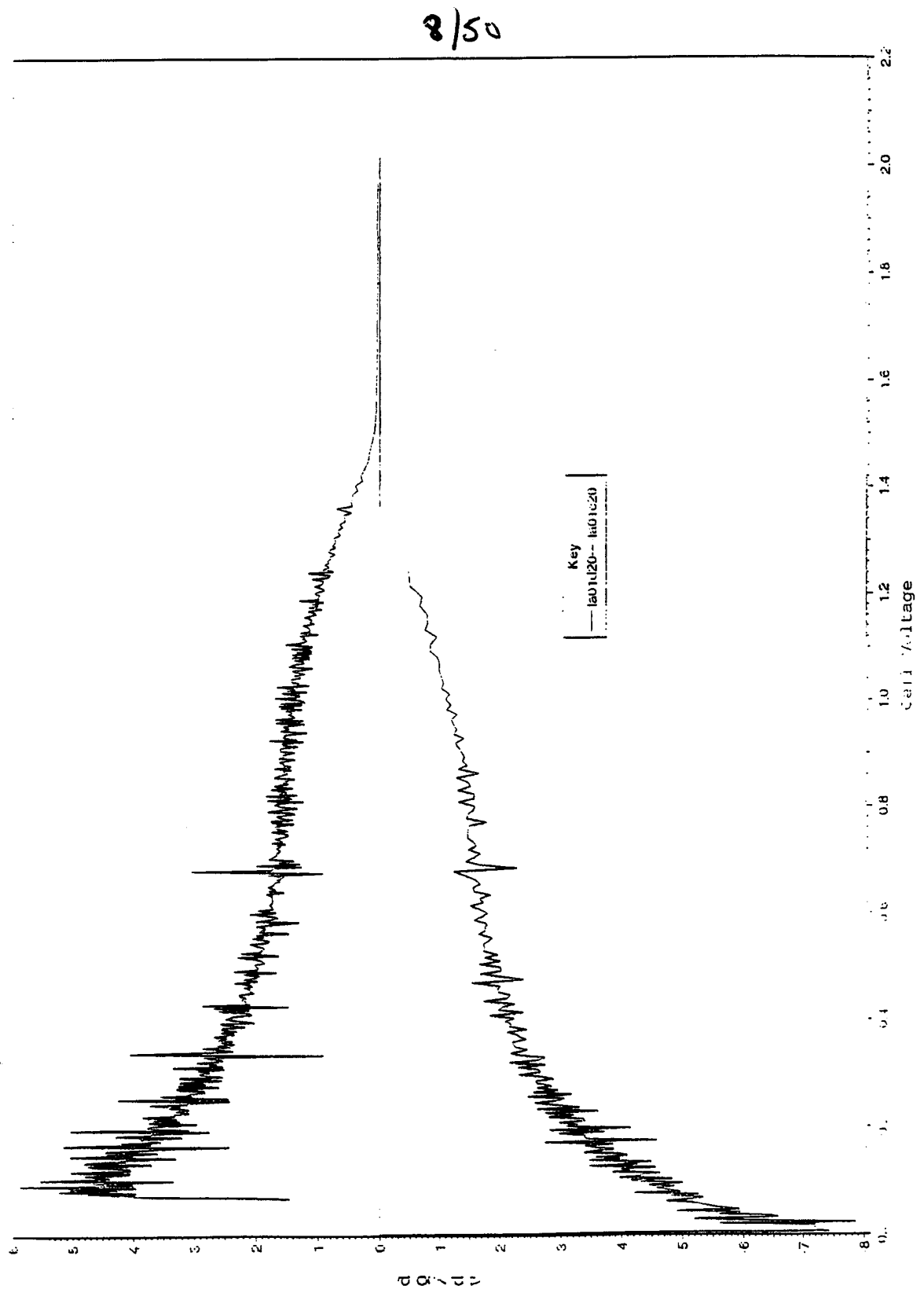


Figure 8

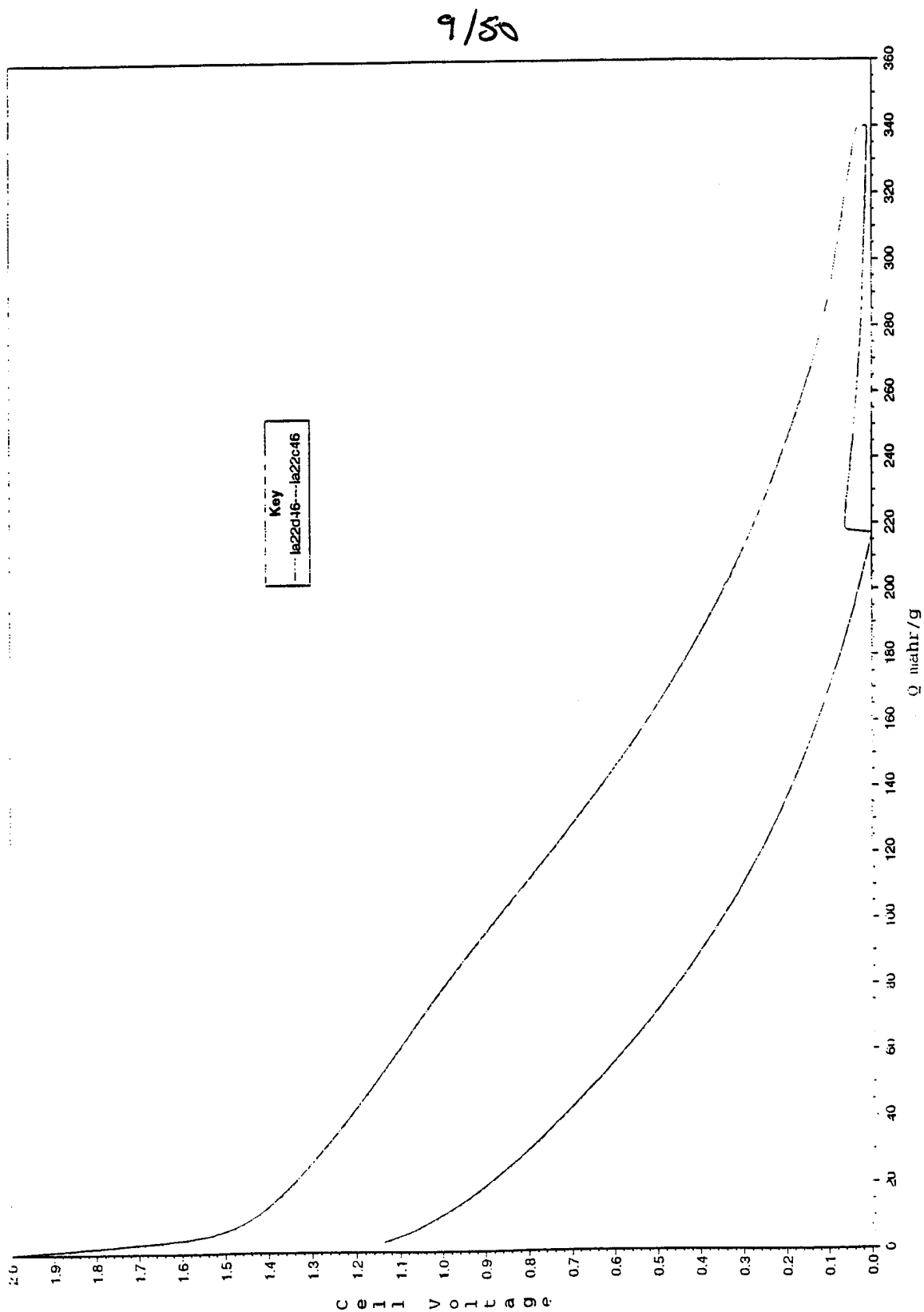


Figure 9

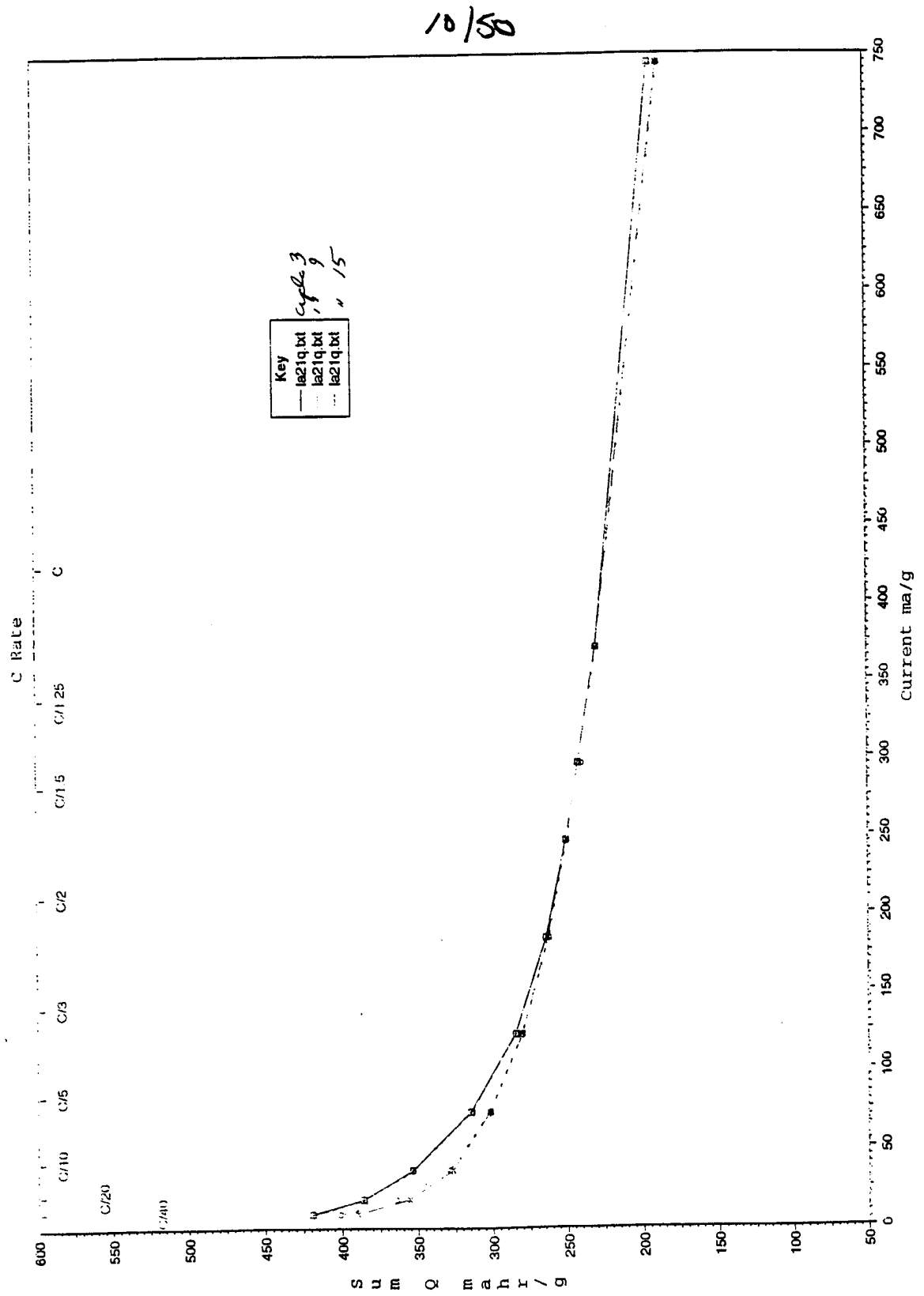


Figure 10

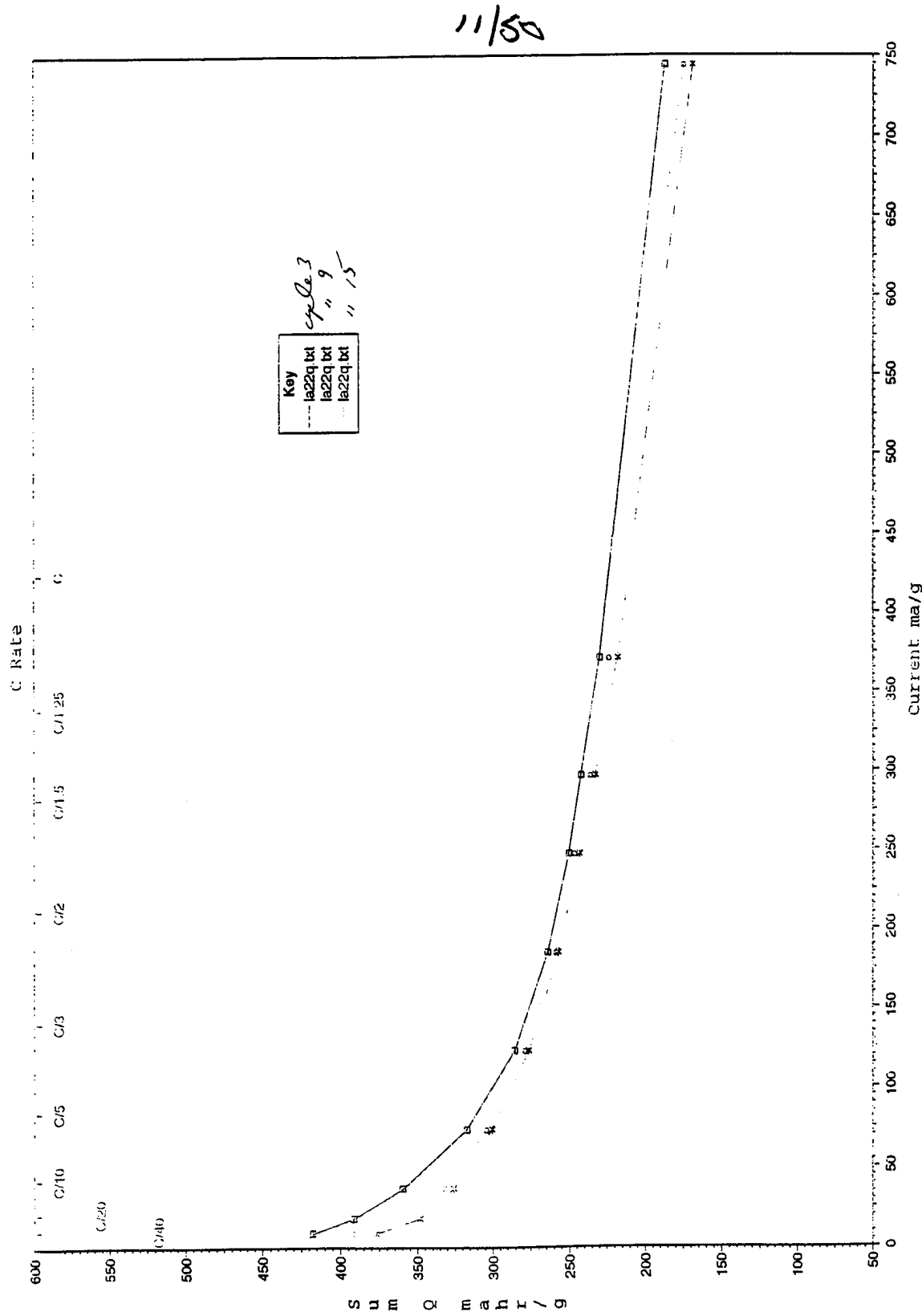


Figure 11

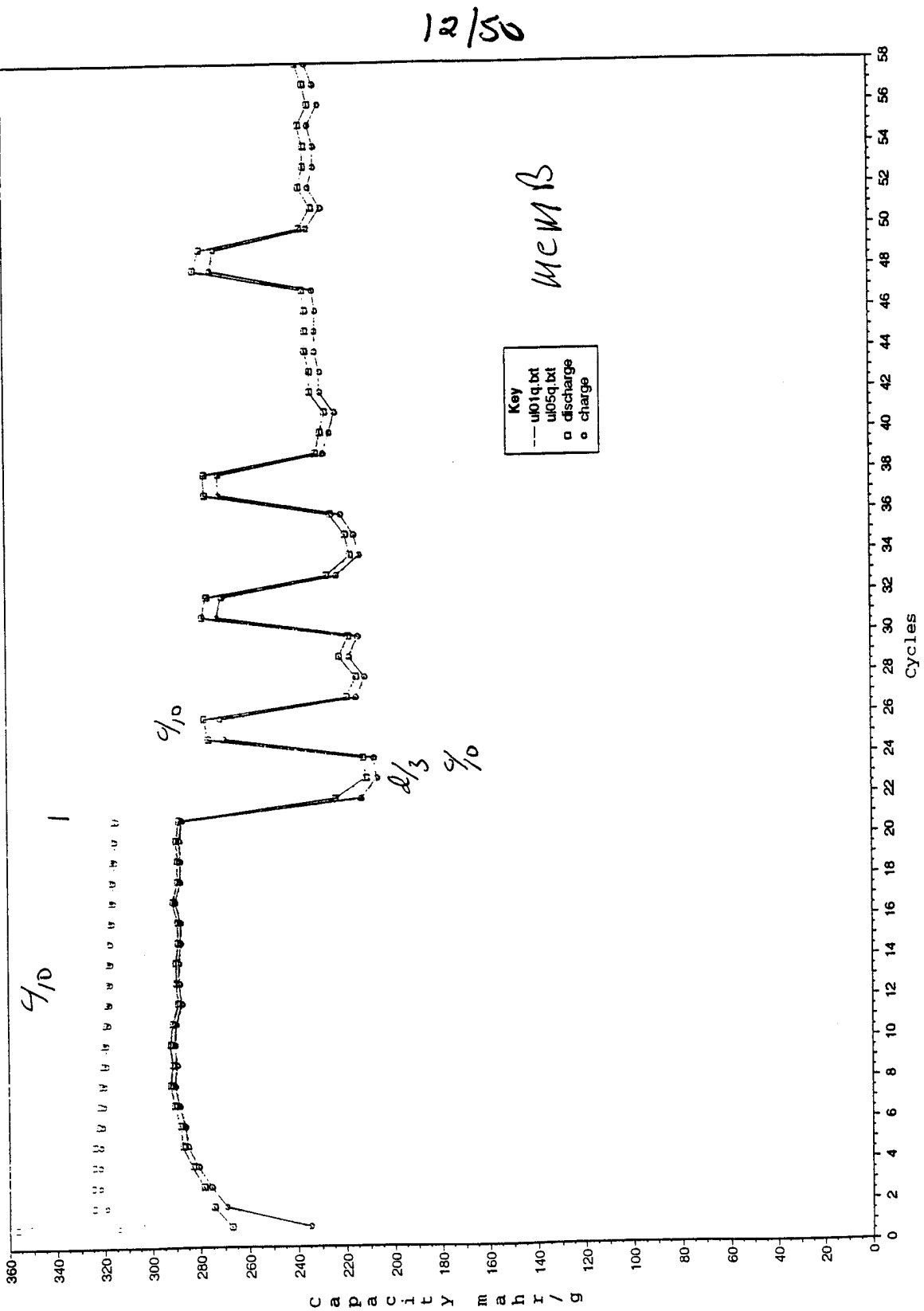


Figure 12

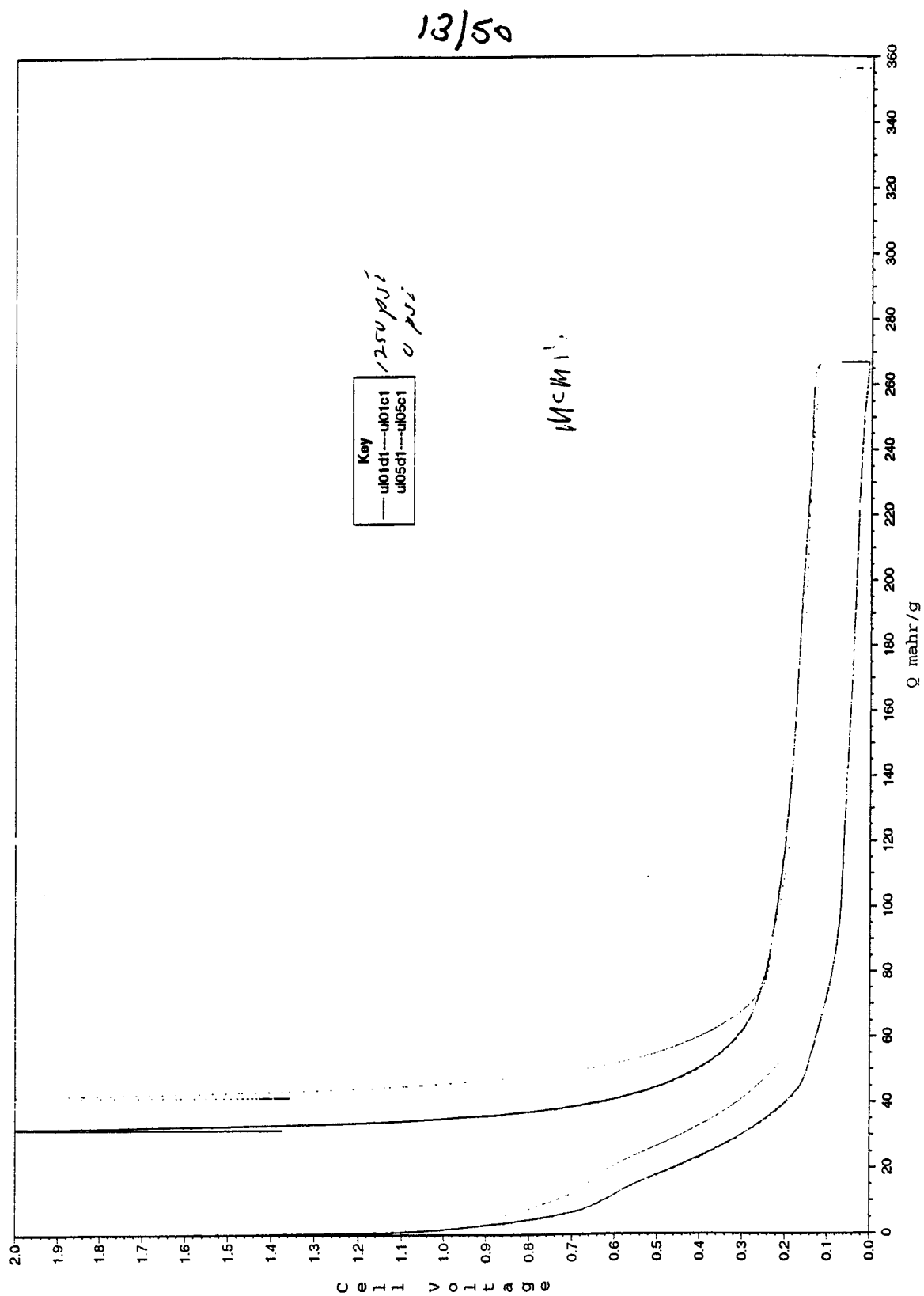


Figure 13

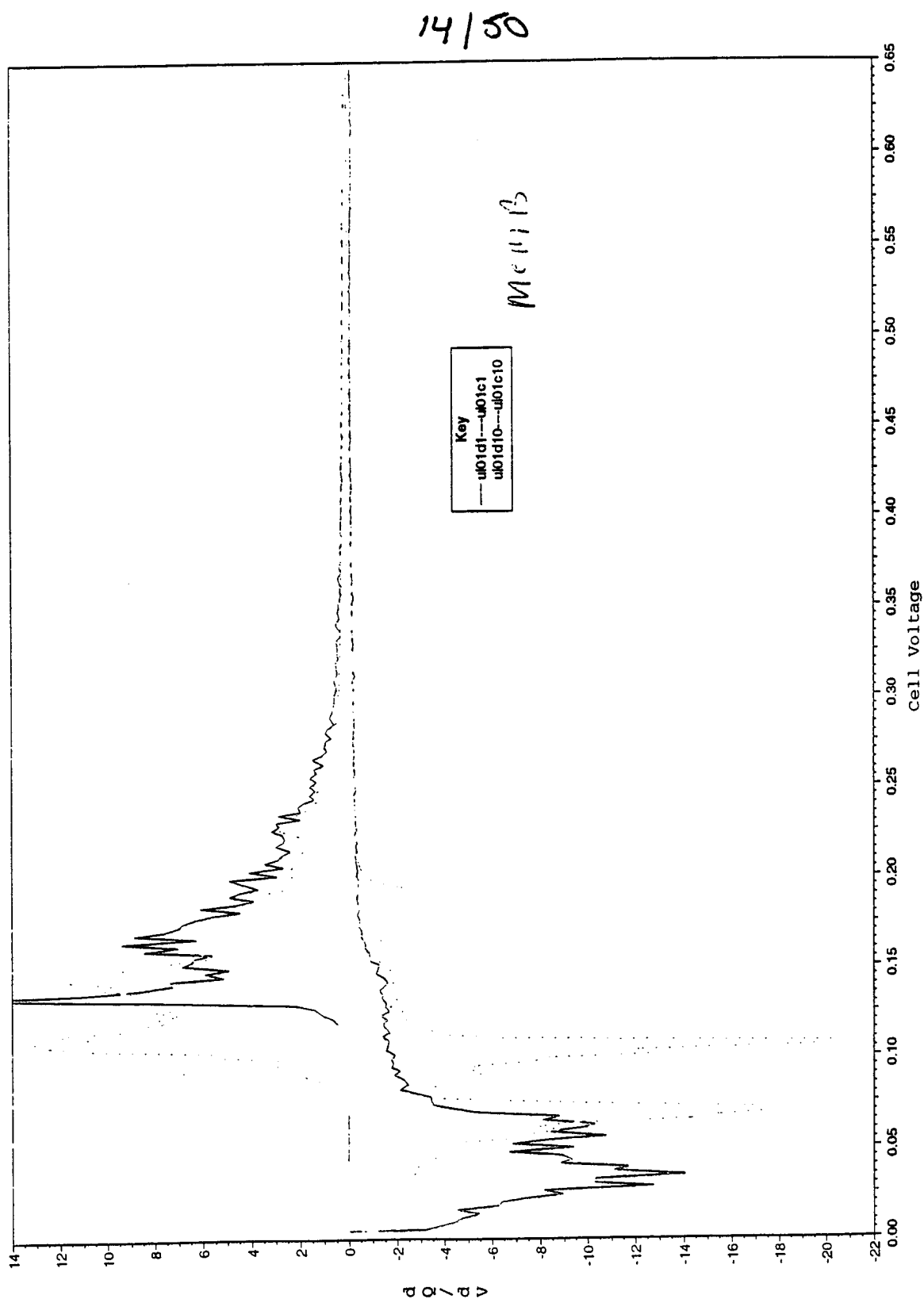


Figure 14

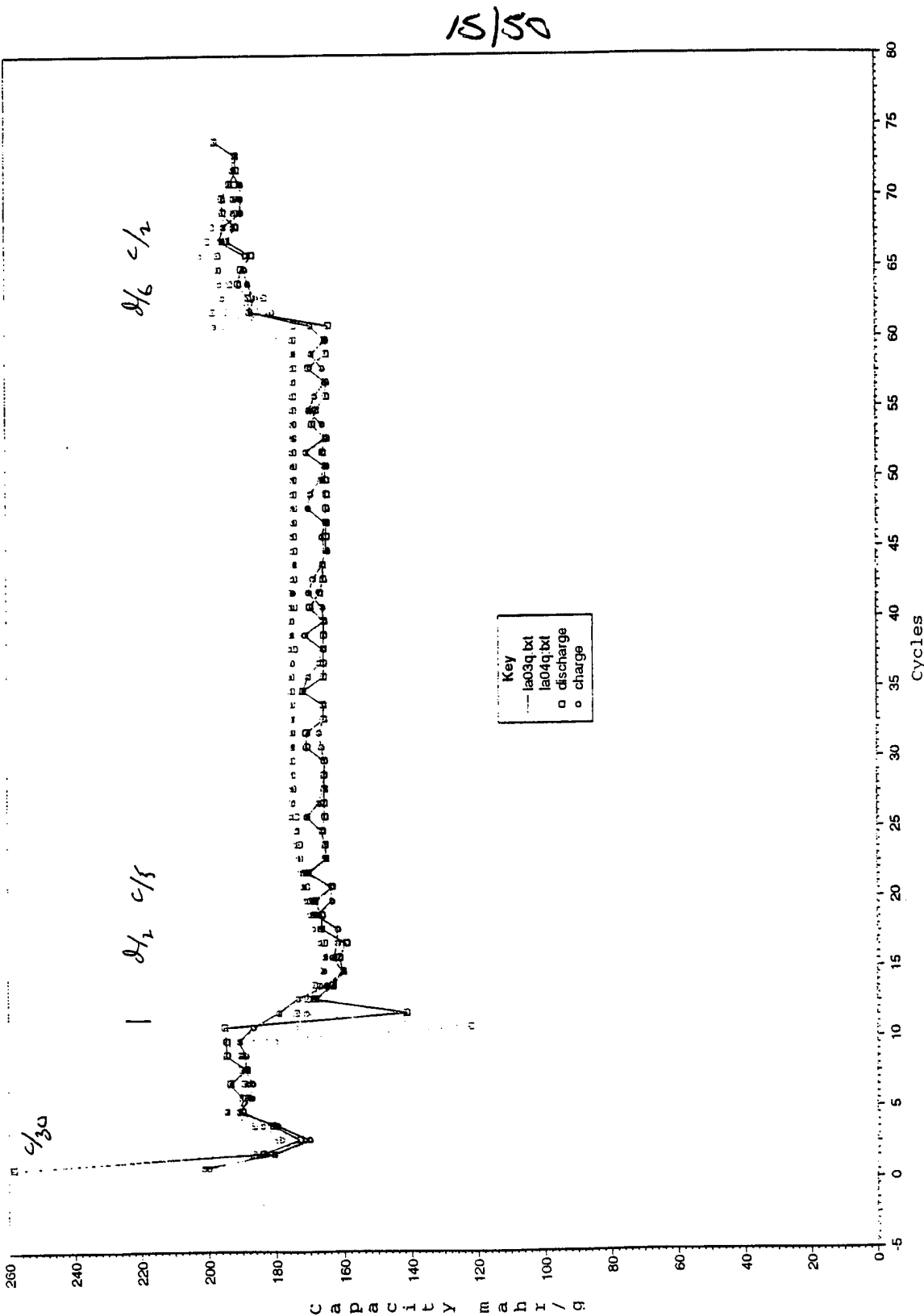


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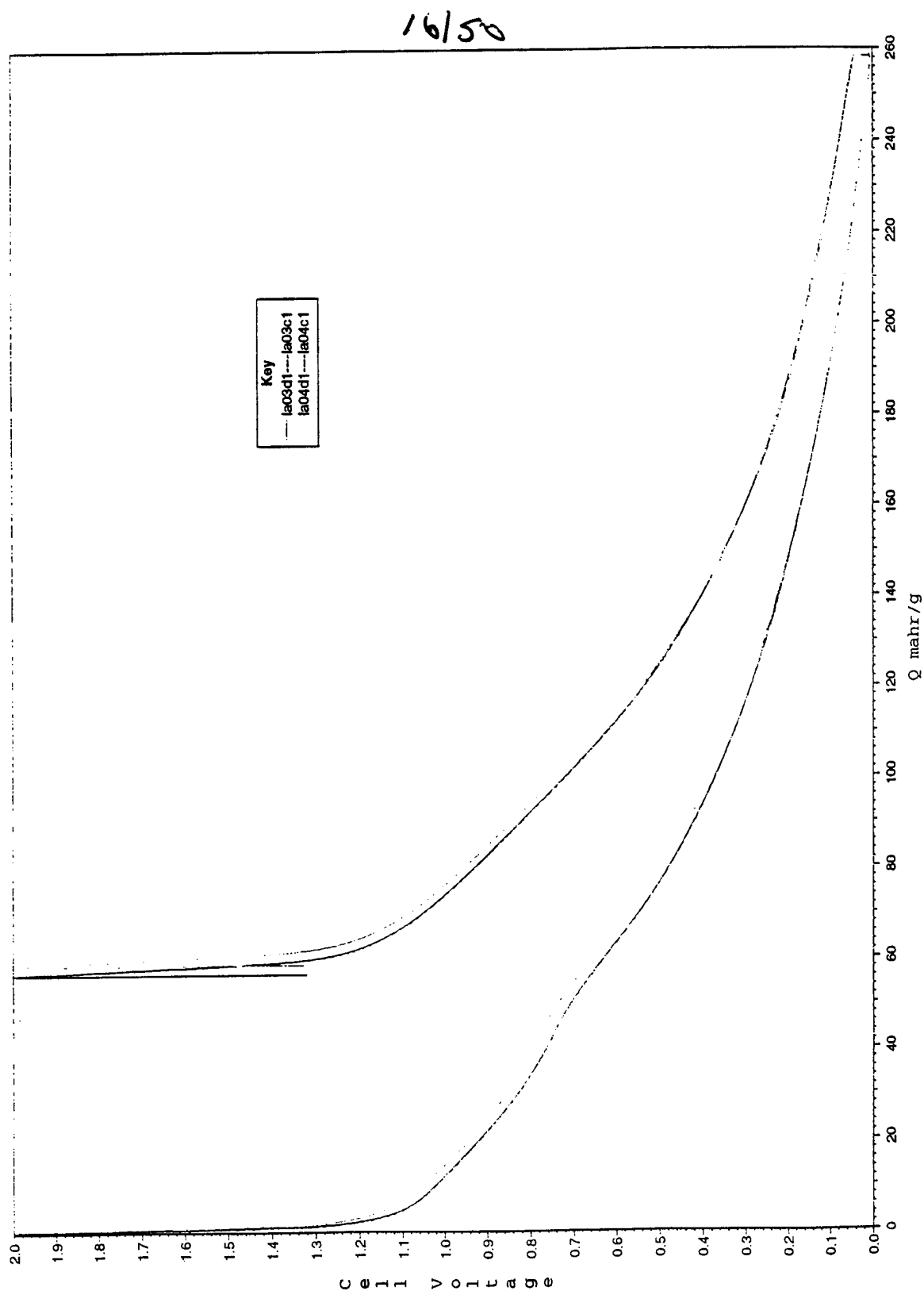


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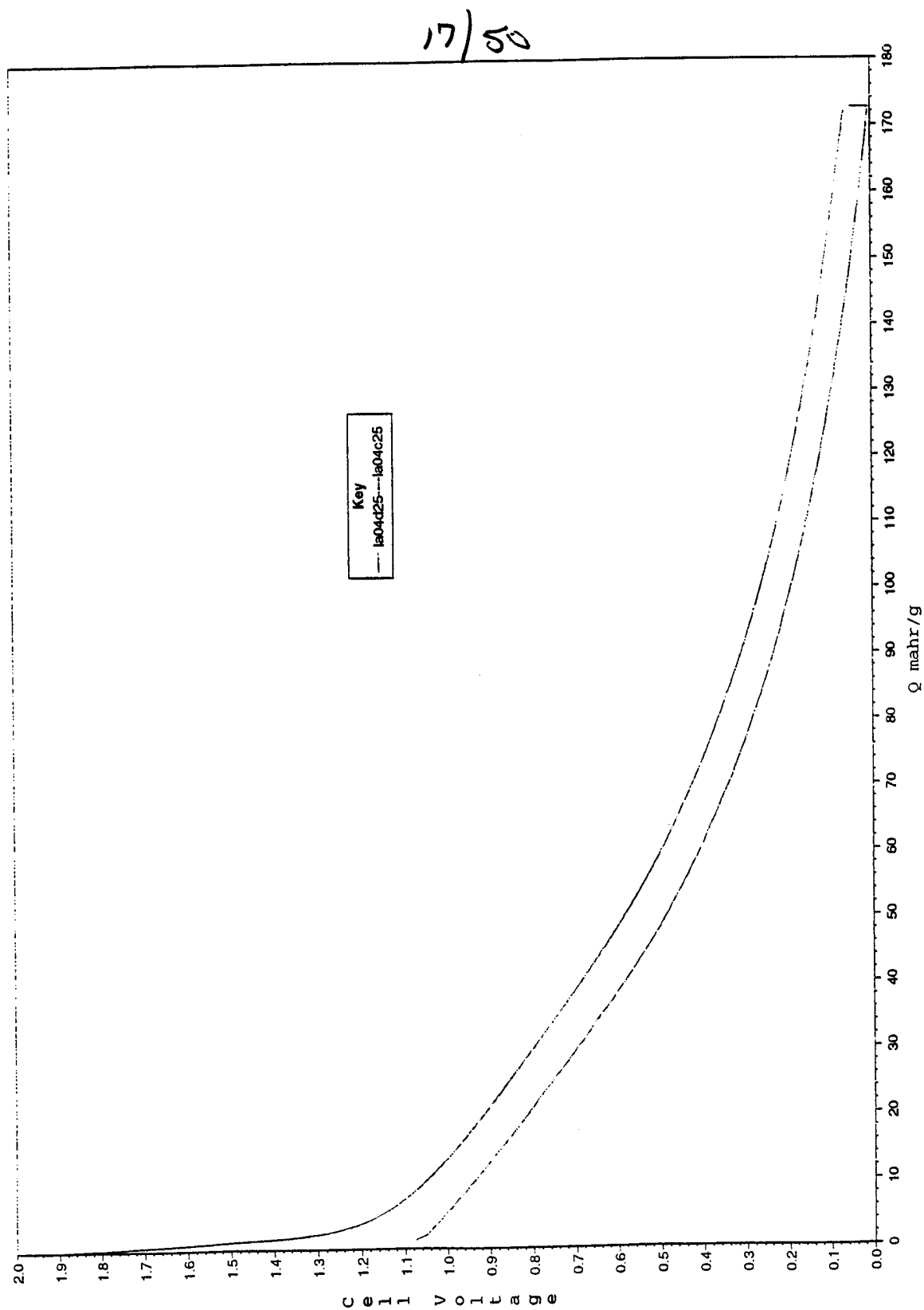


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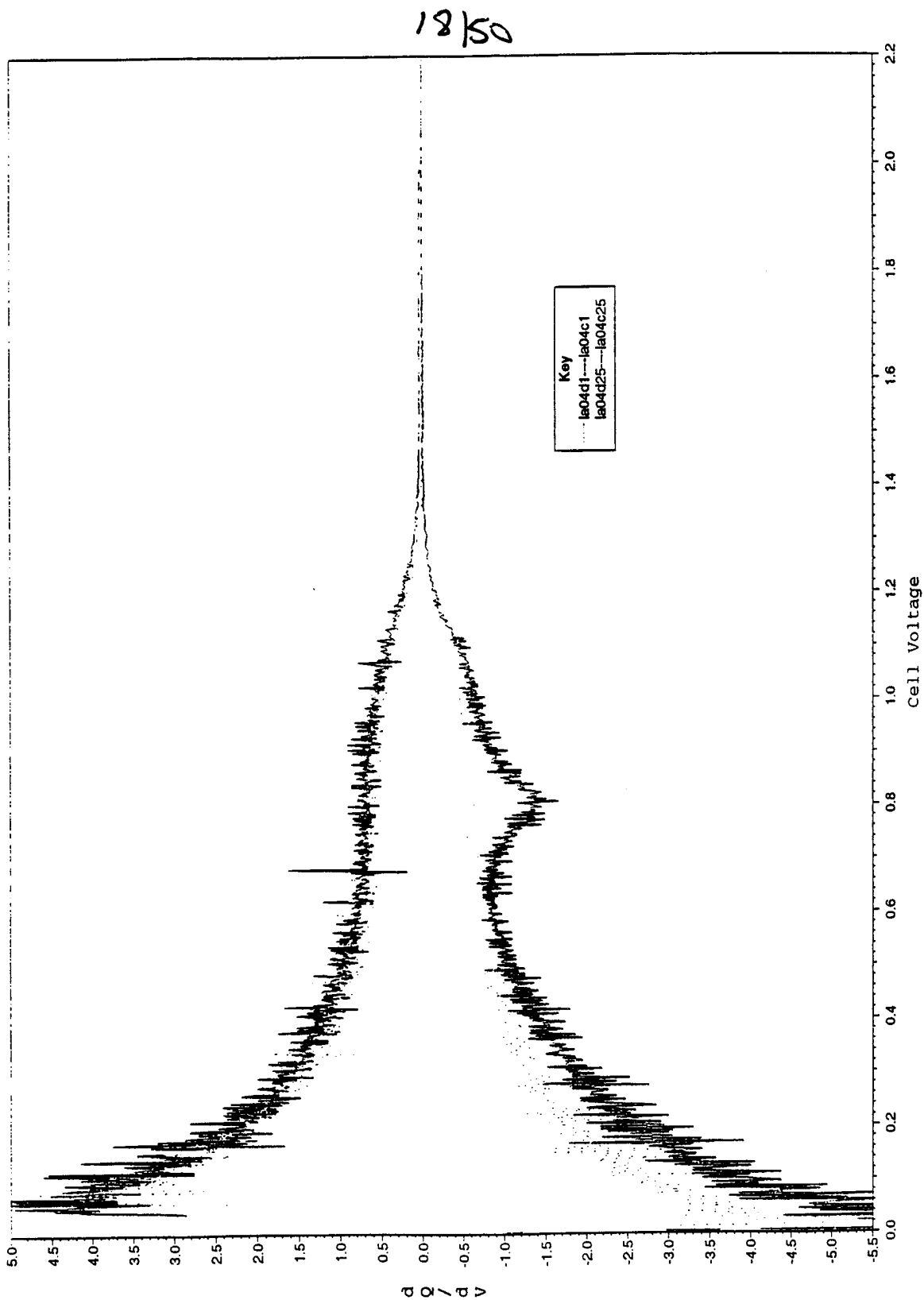


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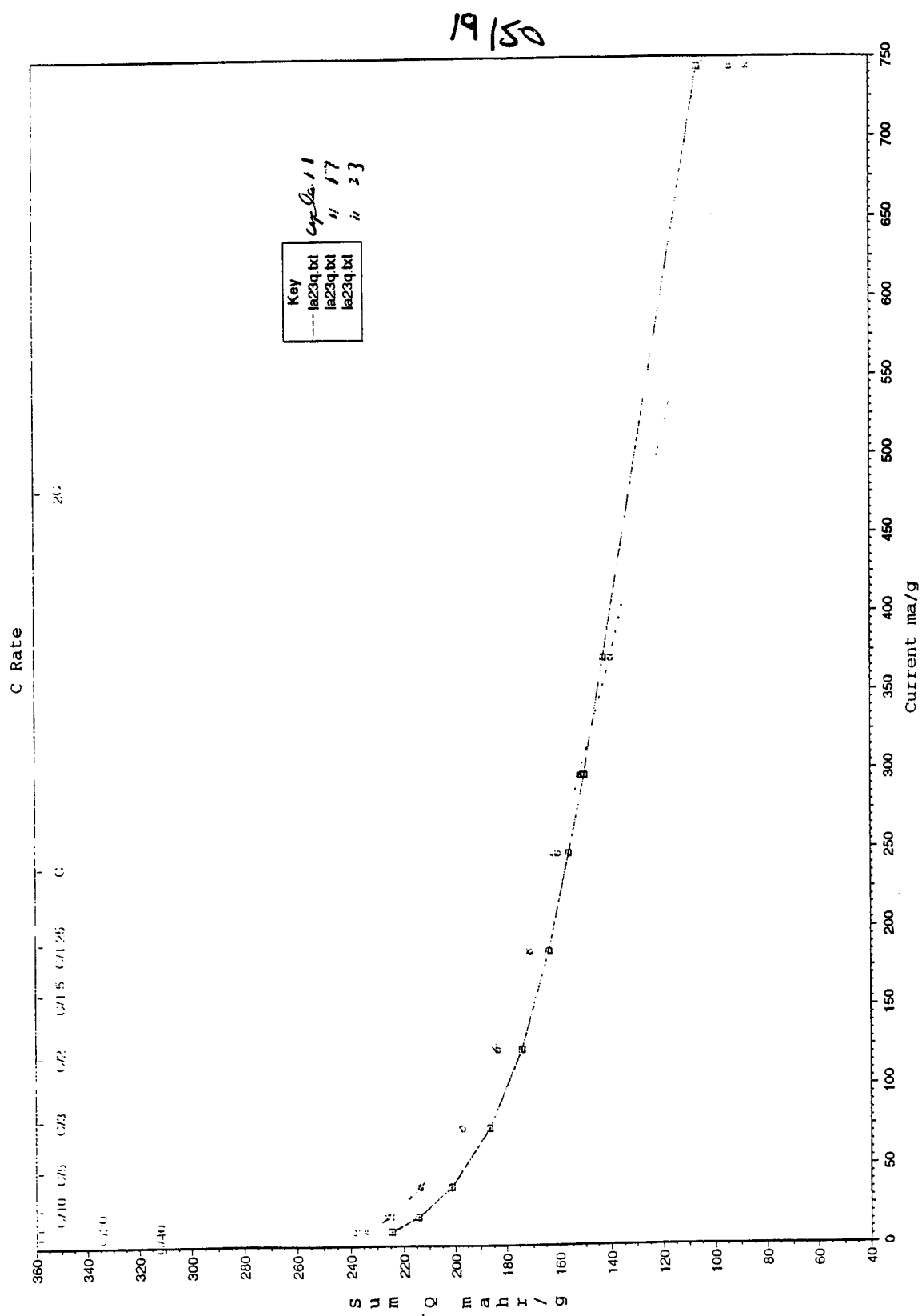


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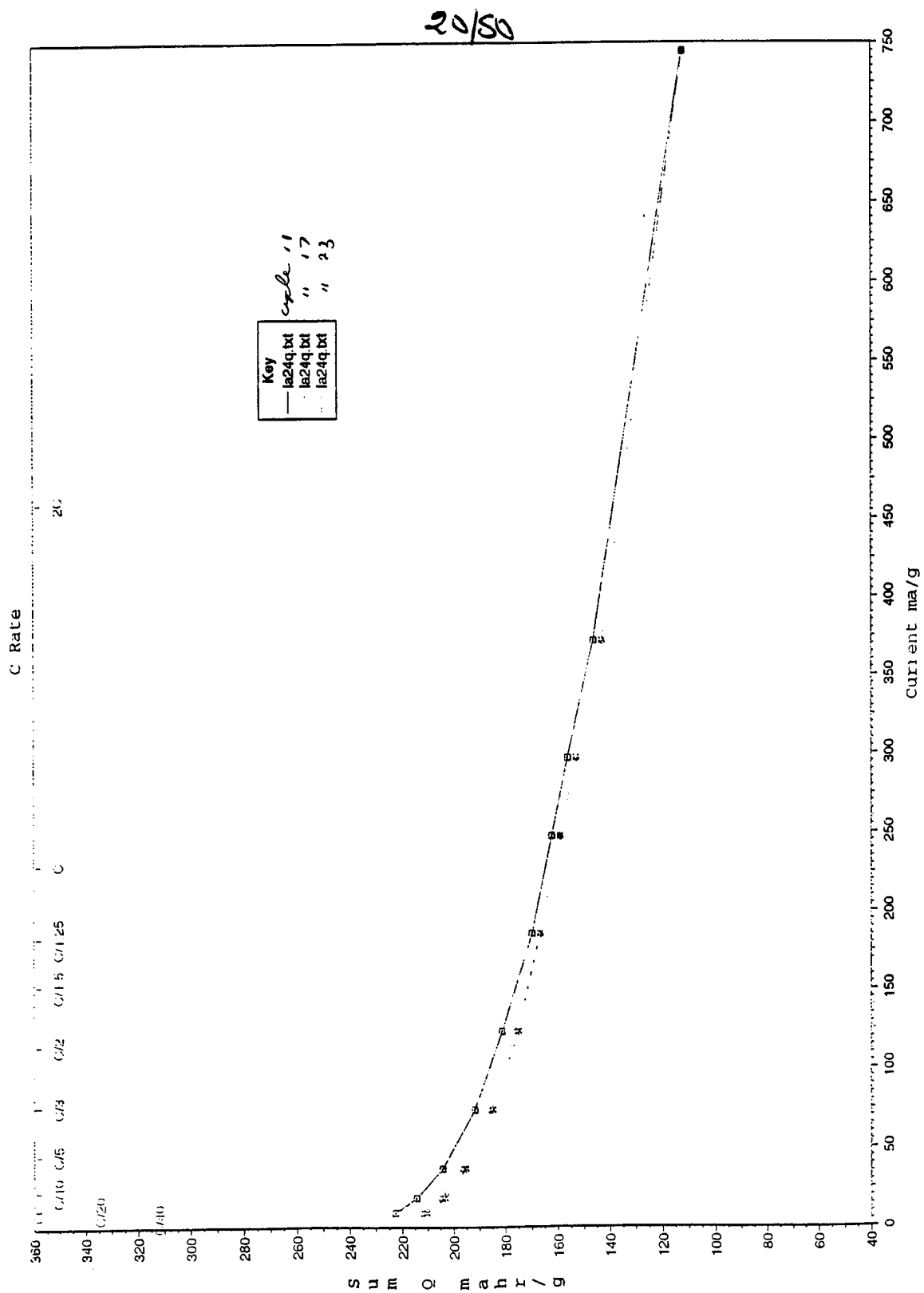


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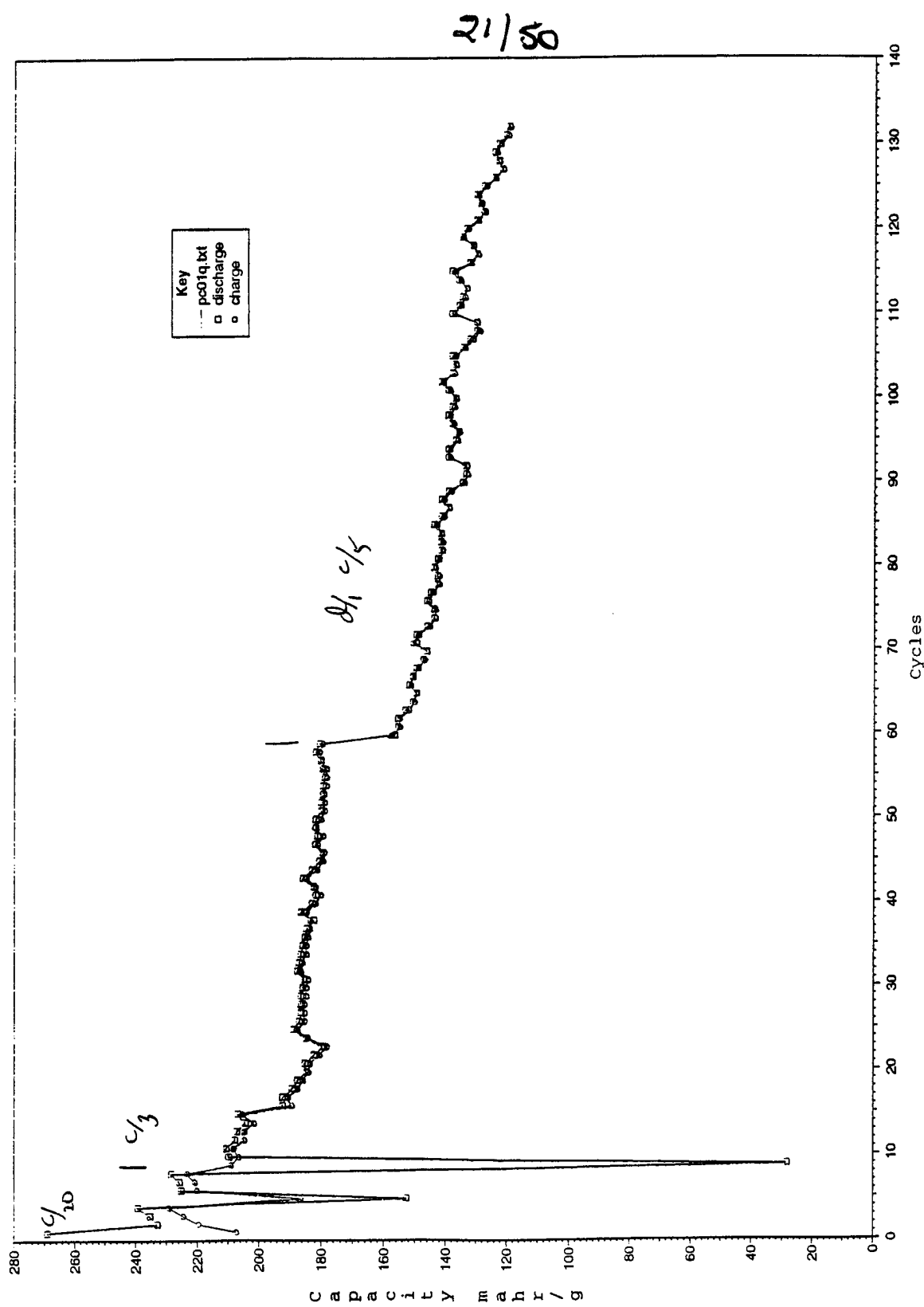


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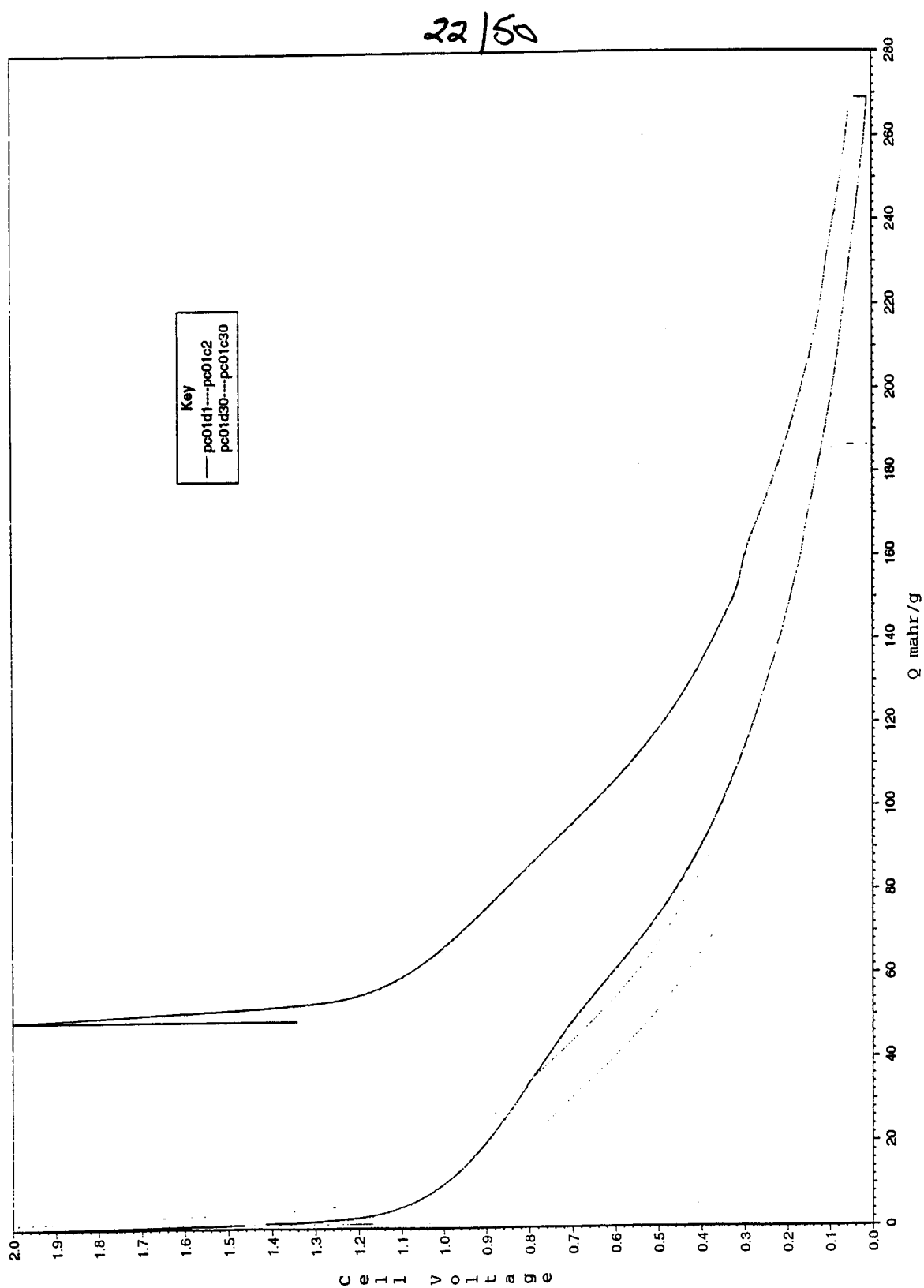


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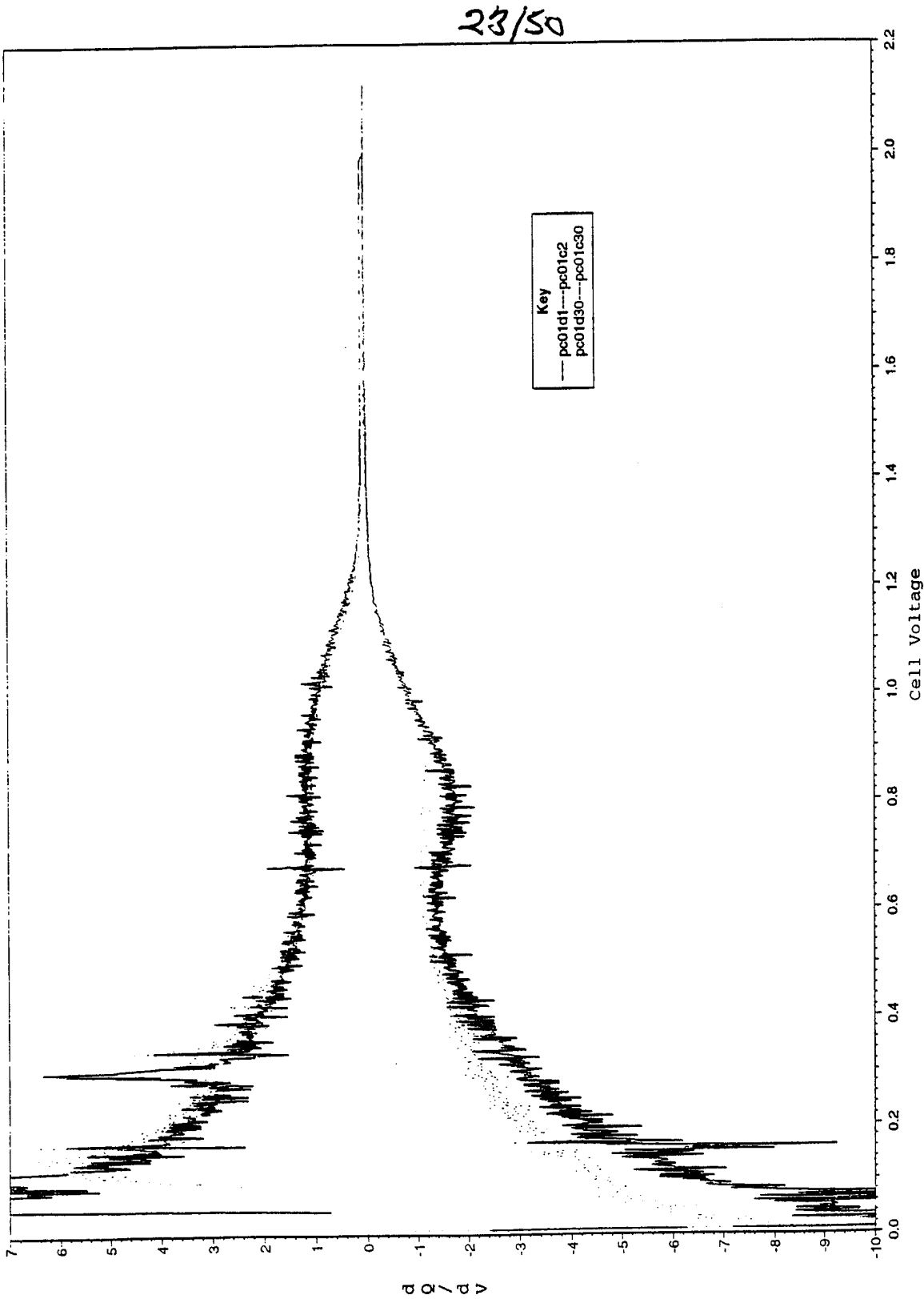


Figure 23

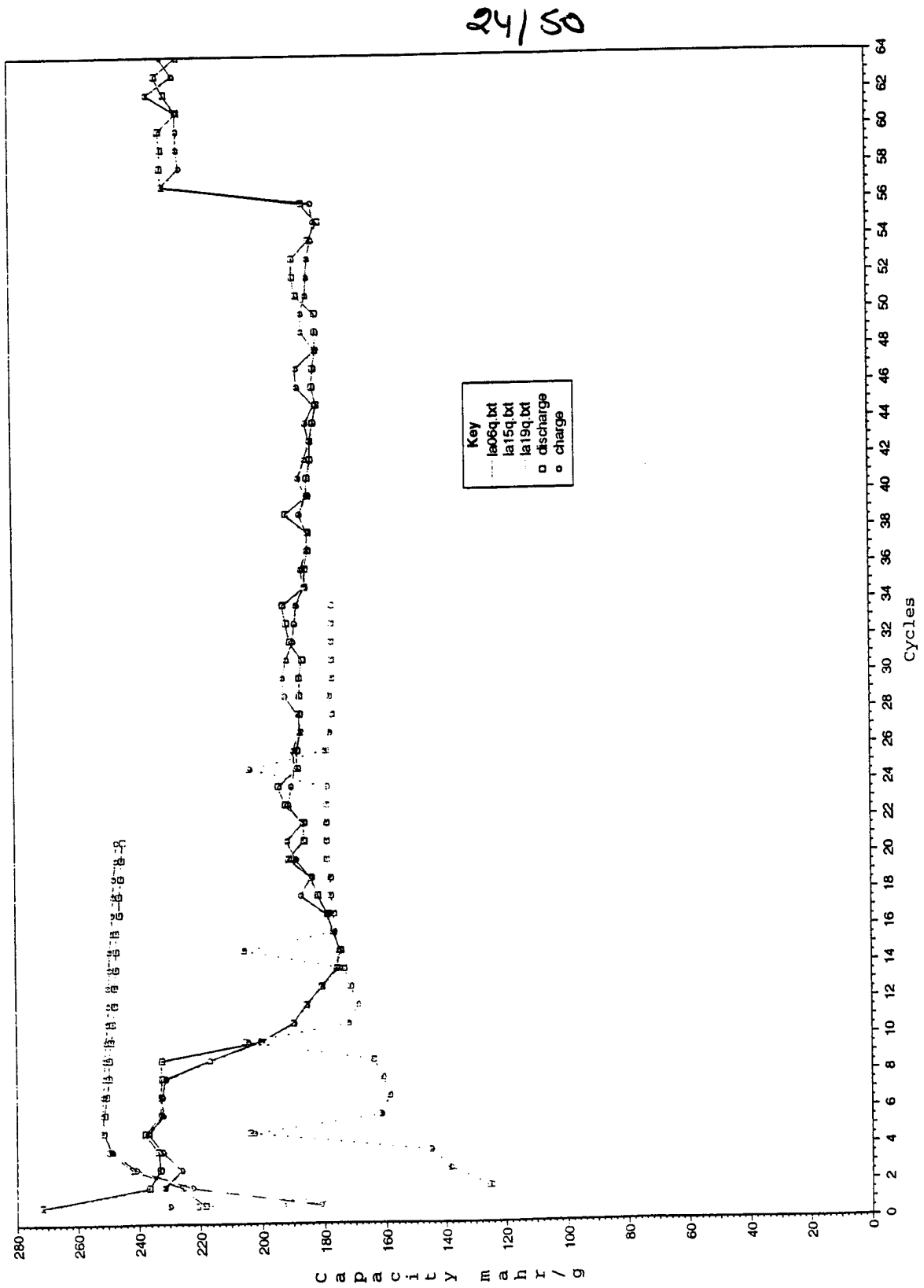


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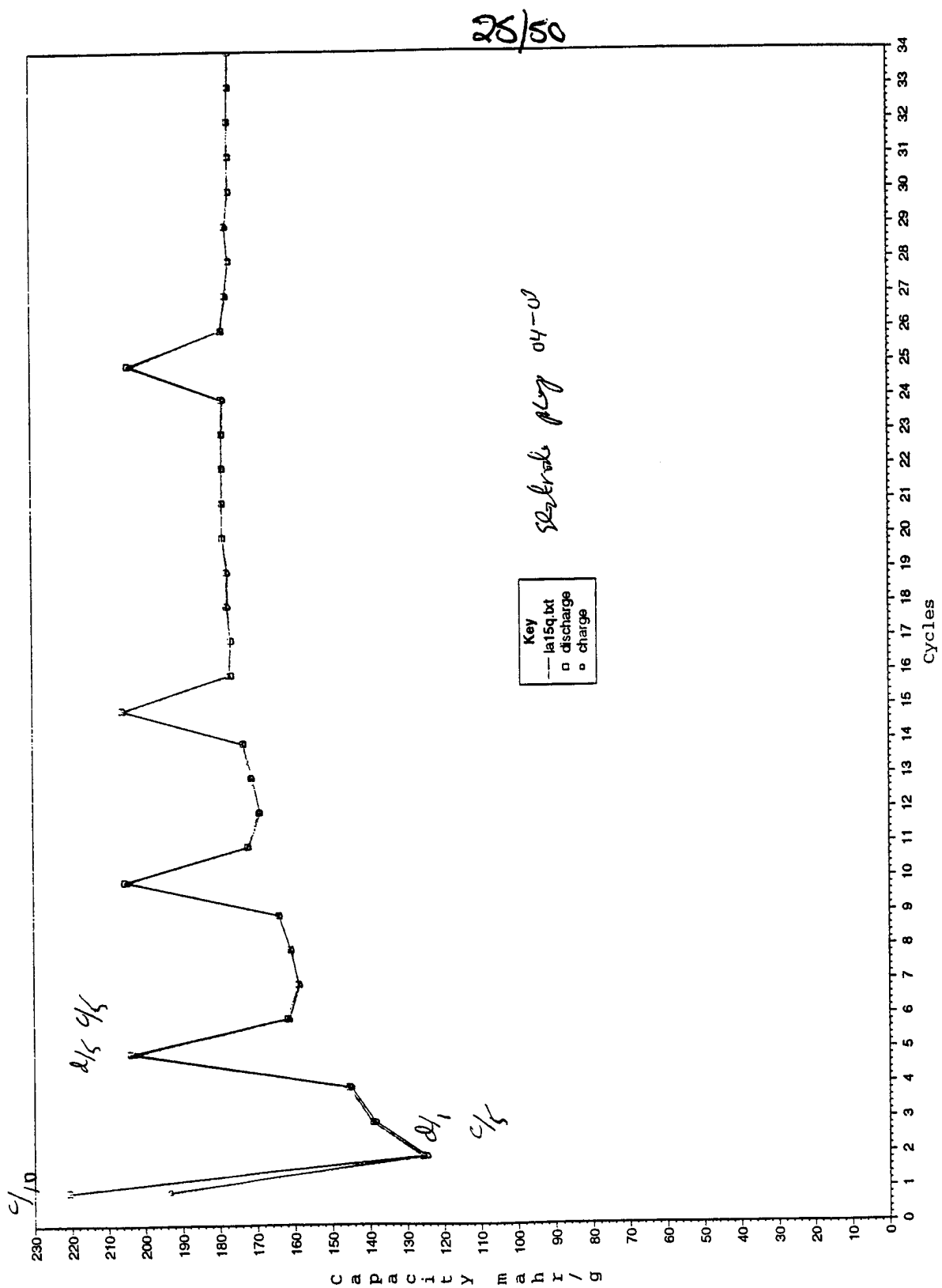


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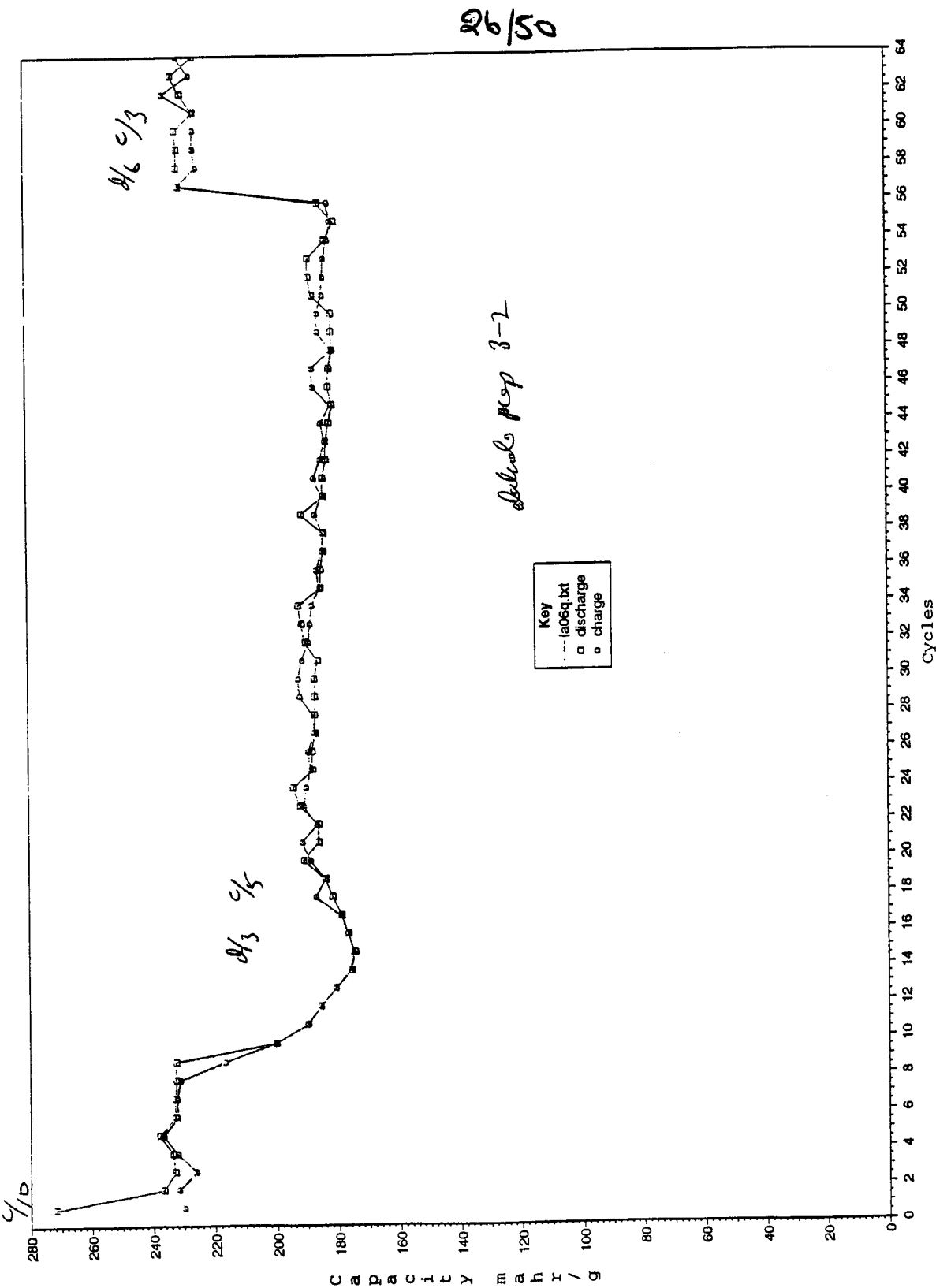


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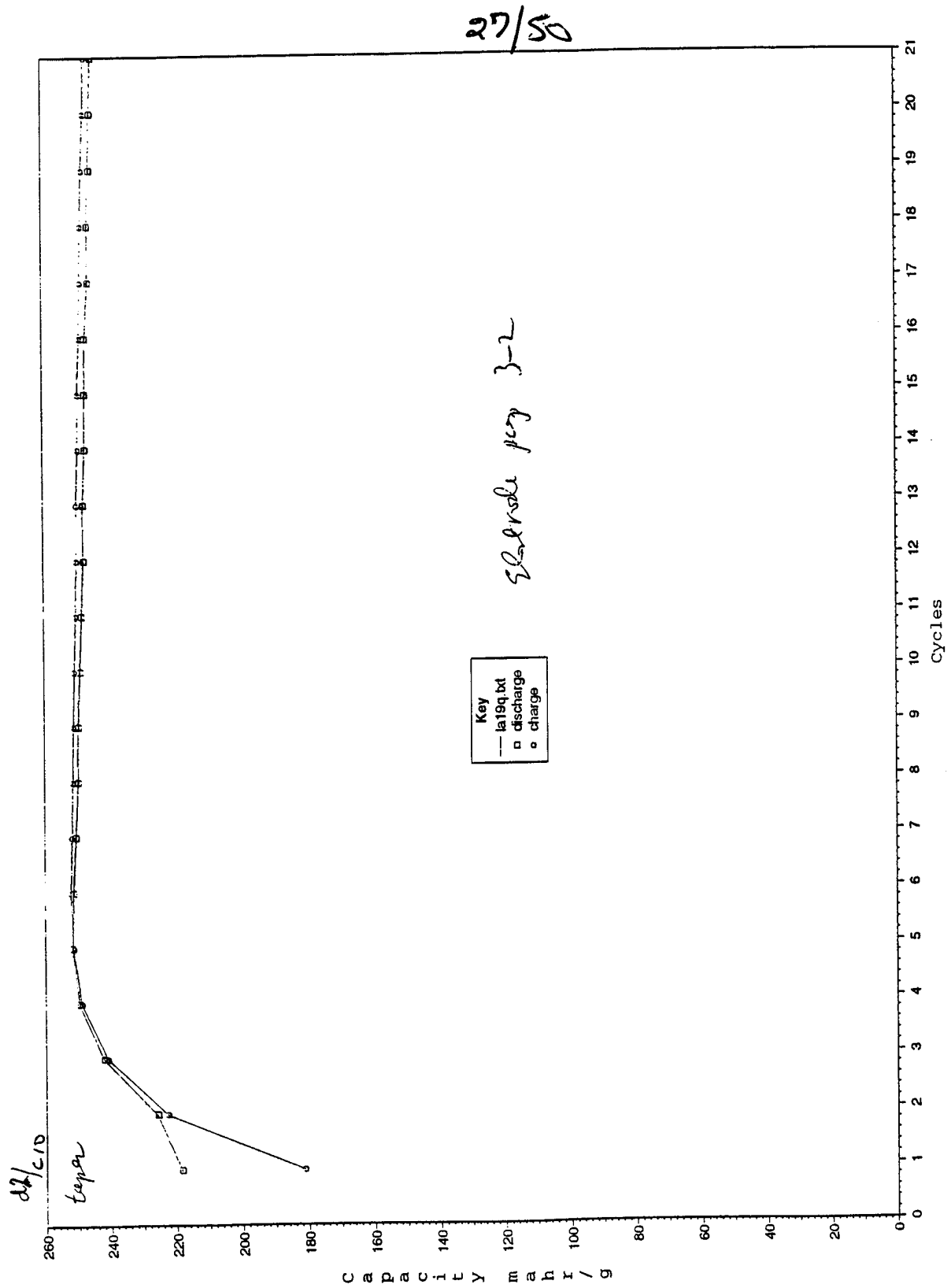


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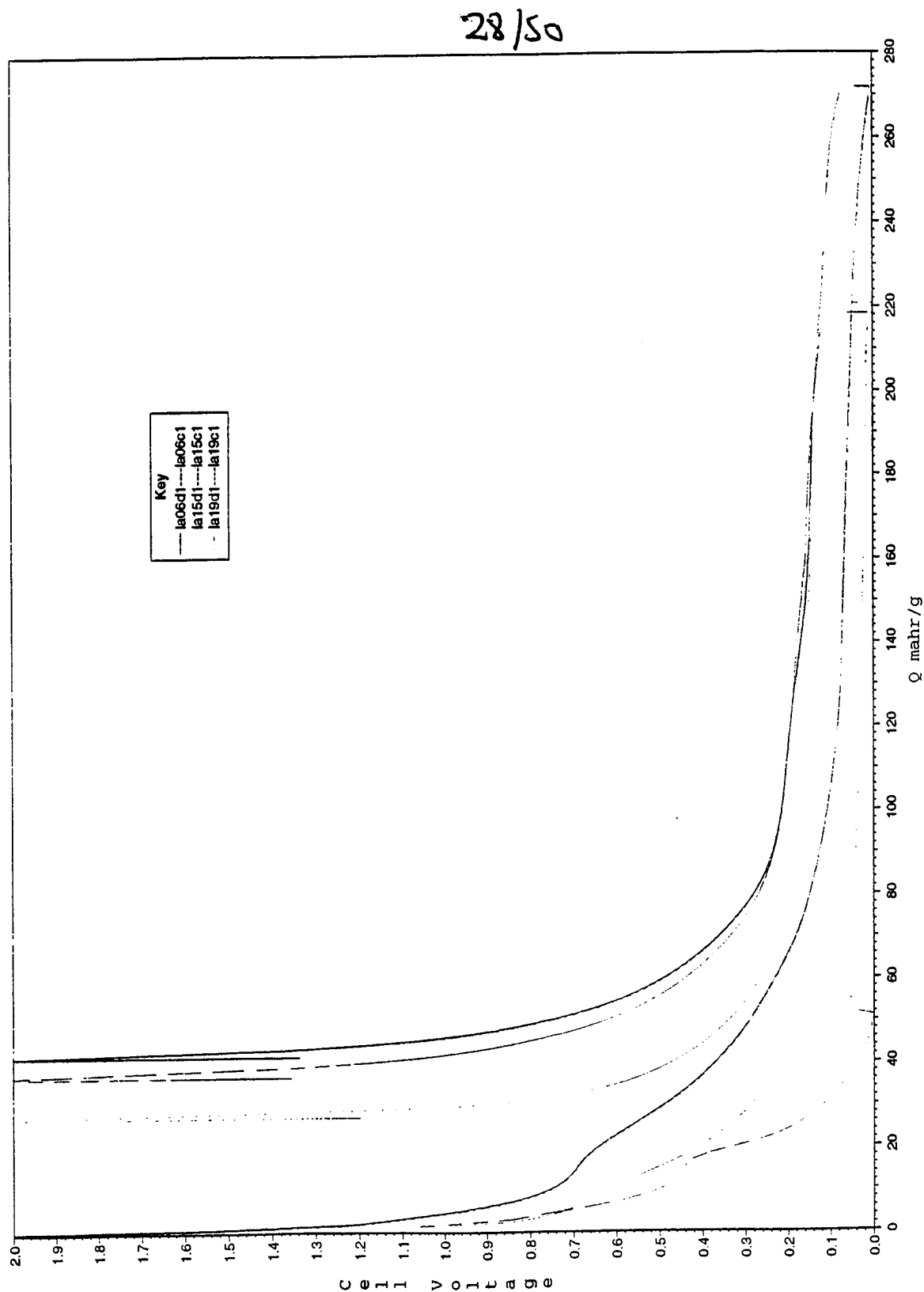


Figure 28

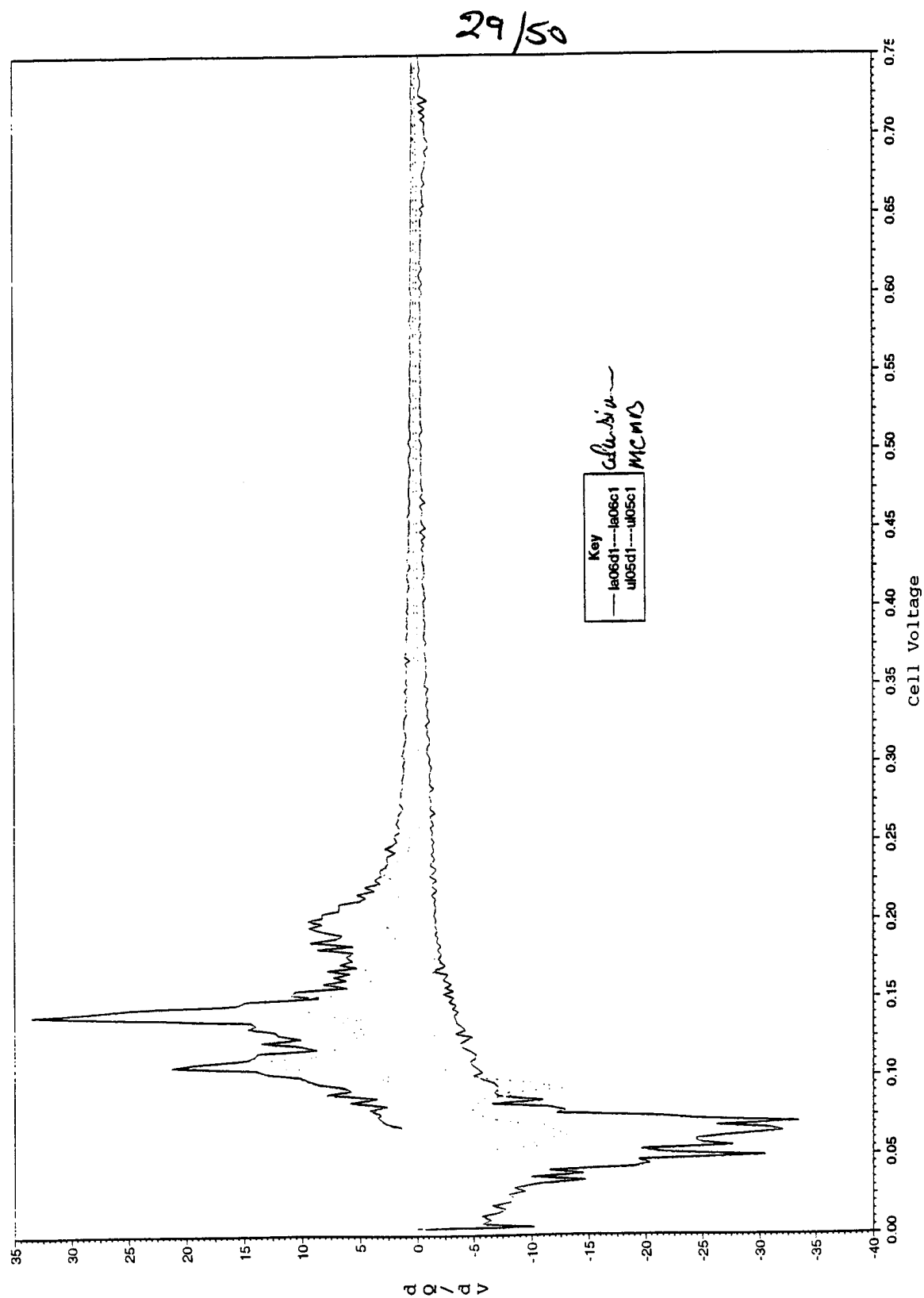


Figure 29

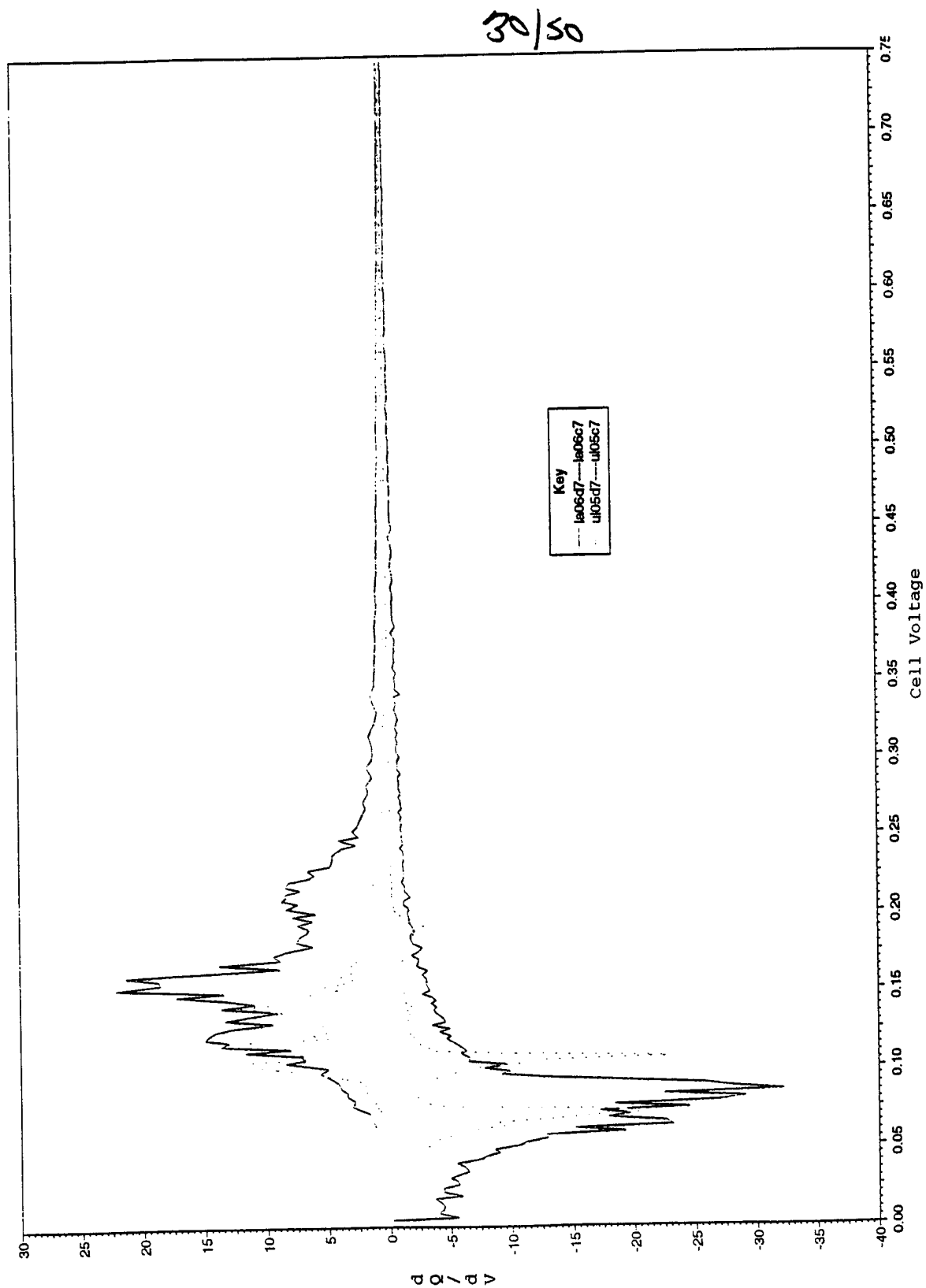


Figure 30

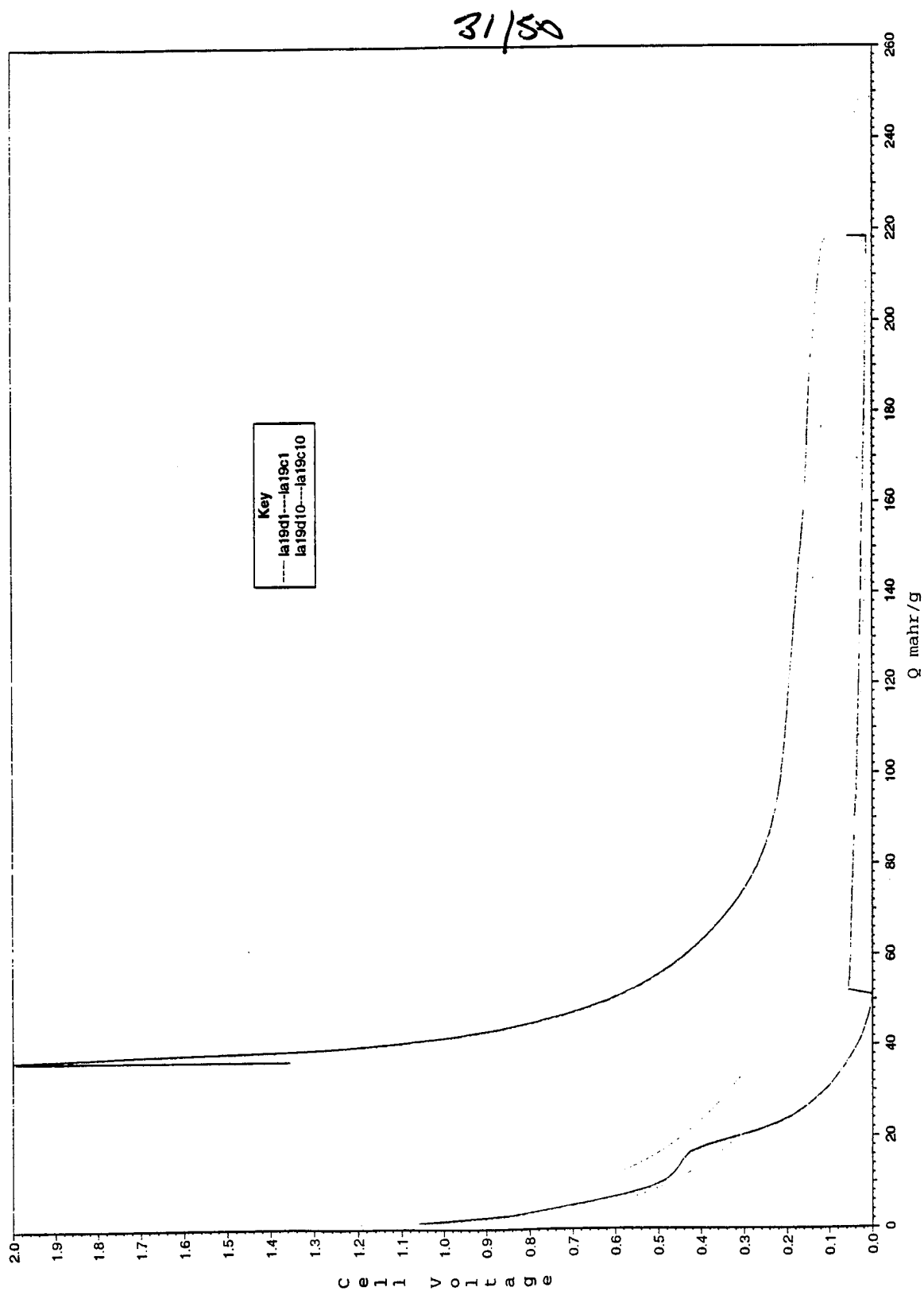


Figure 31

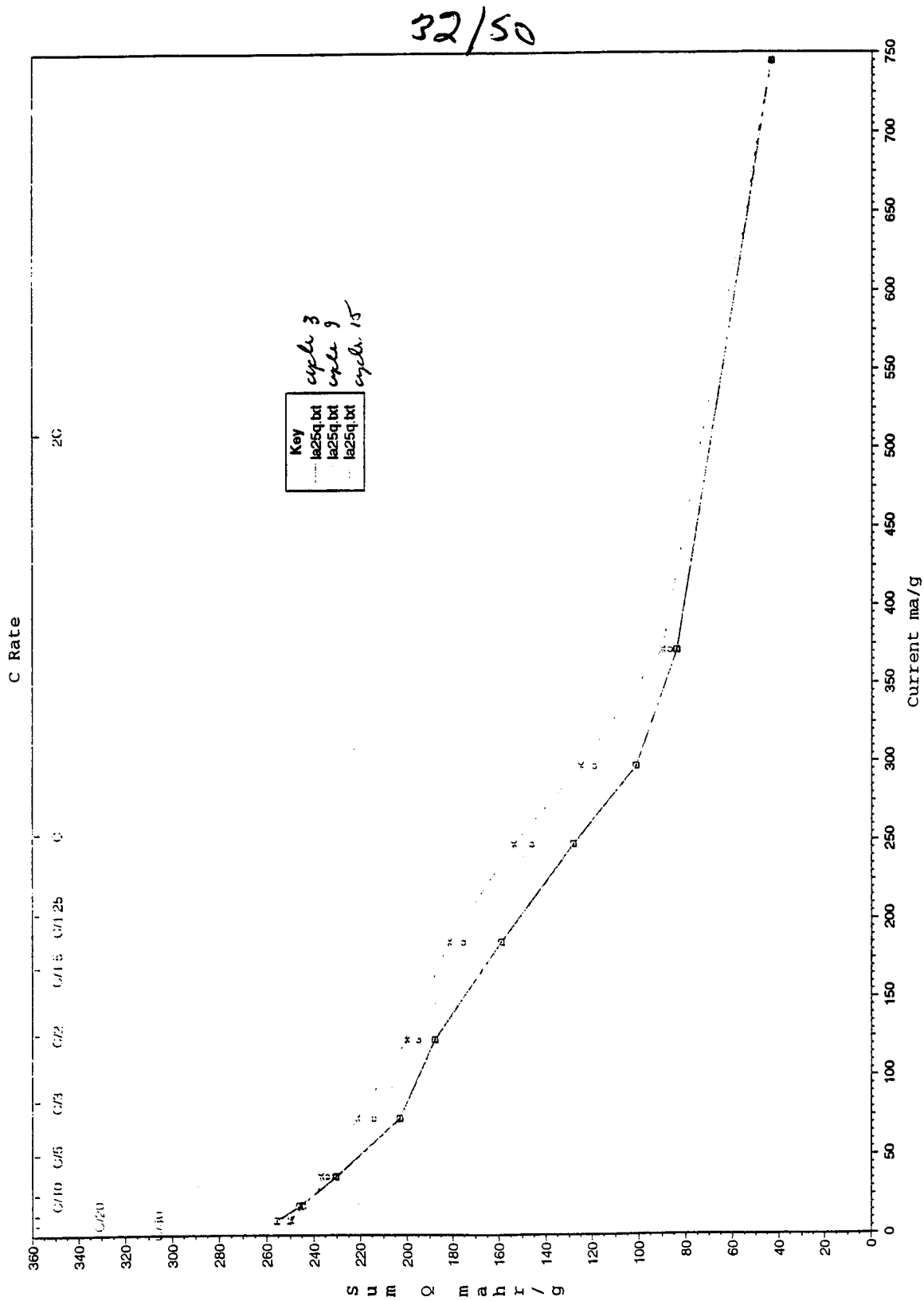


Figure 32

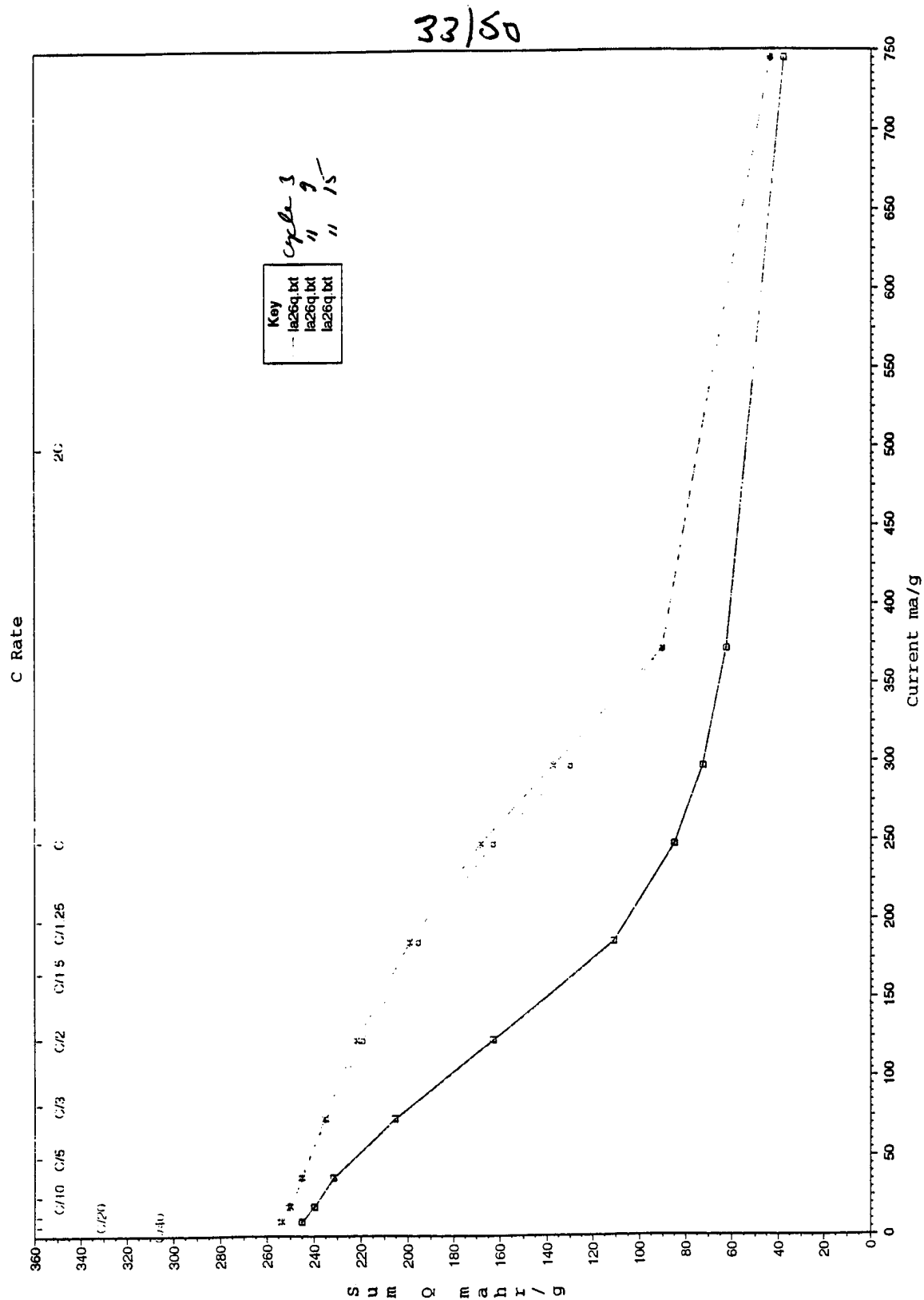


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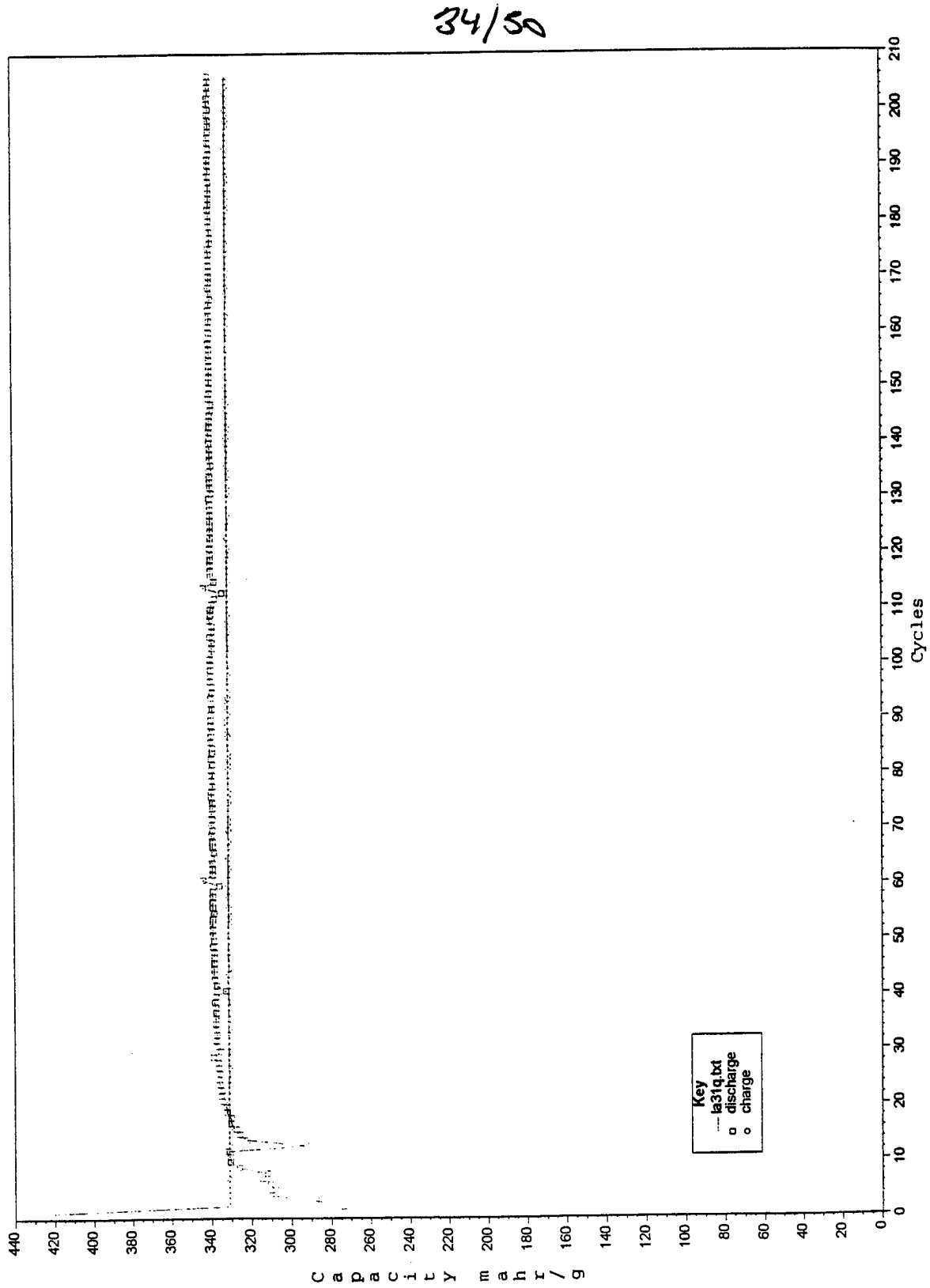


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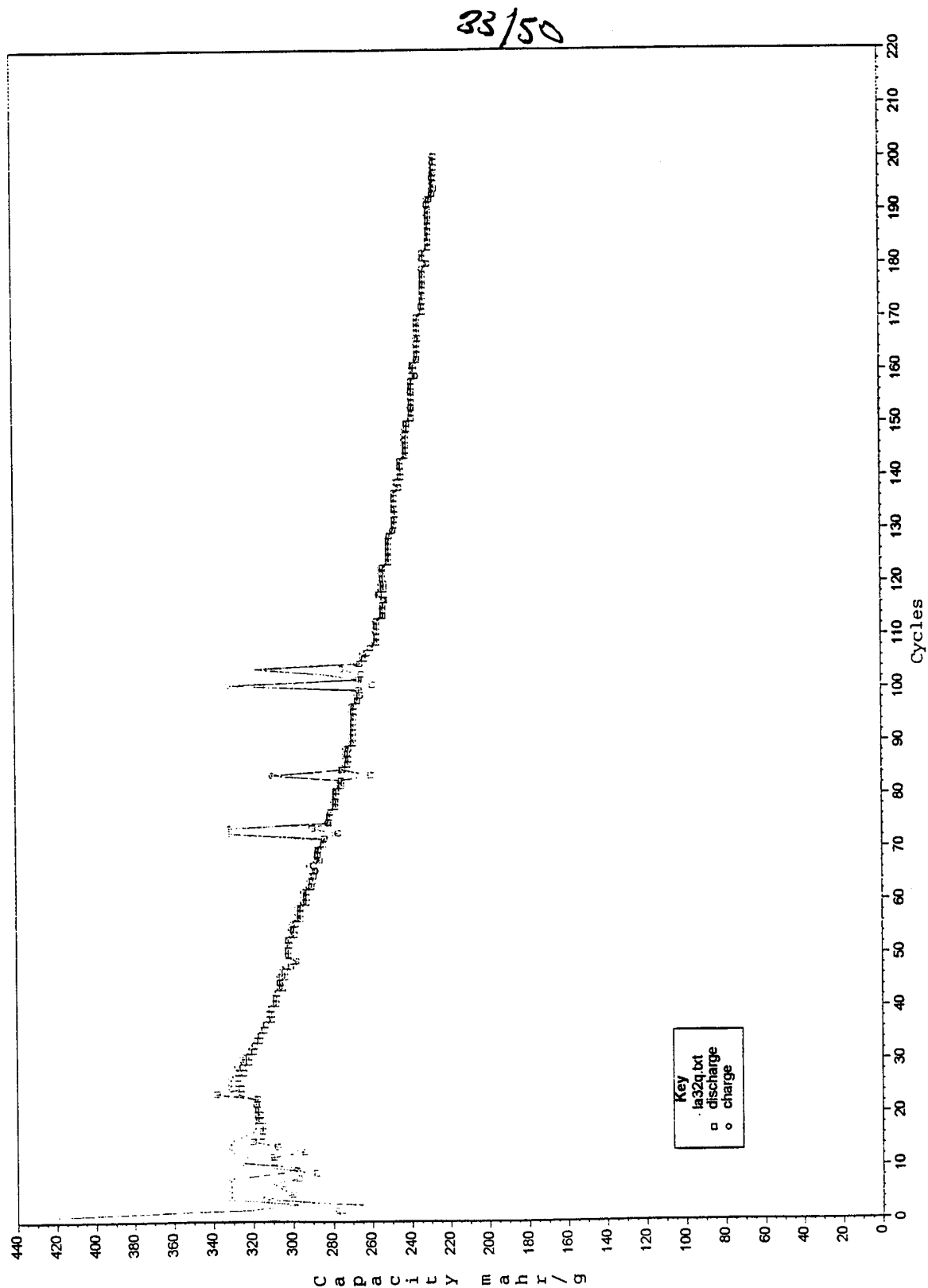


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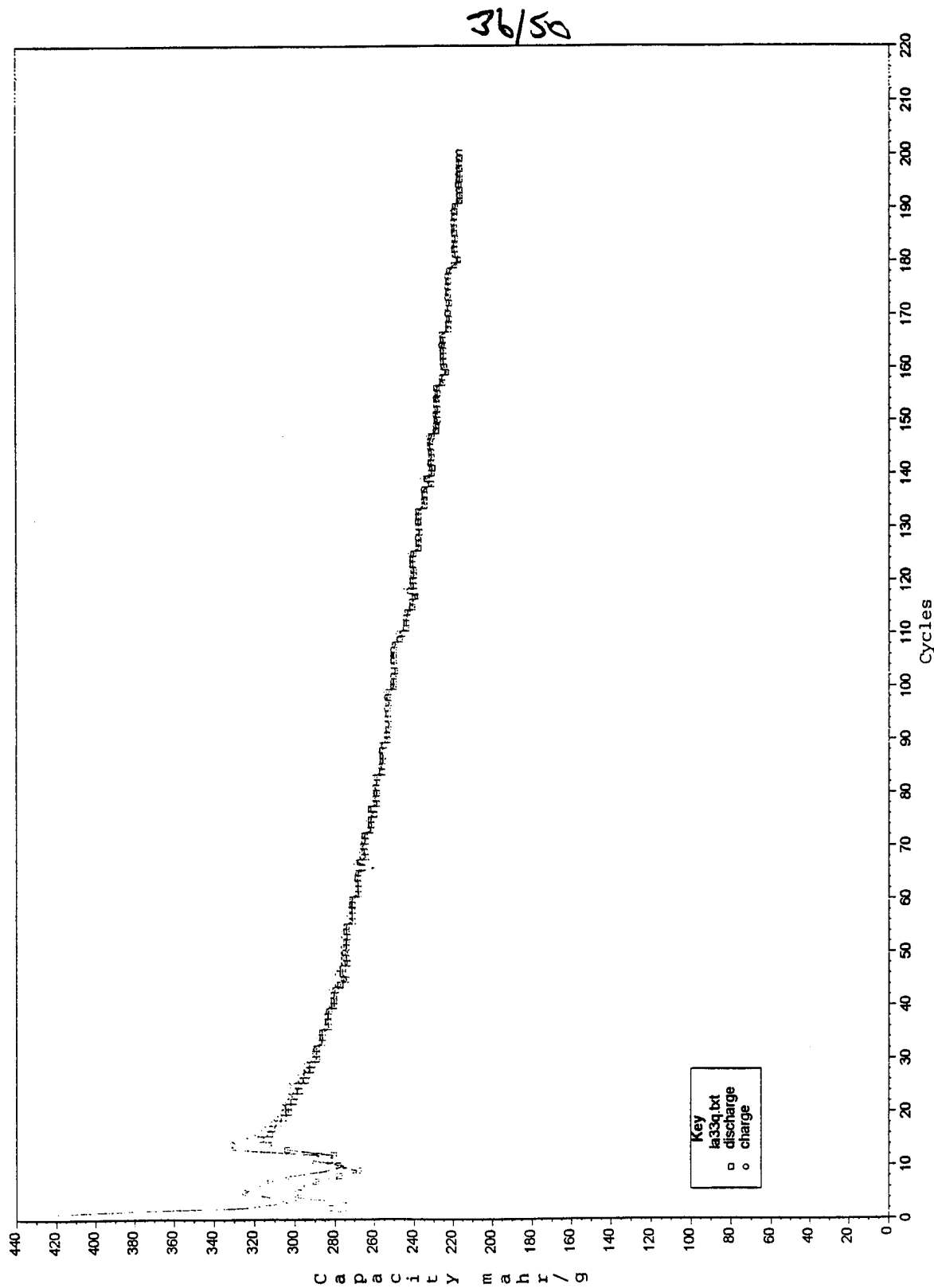


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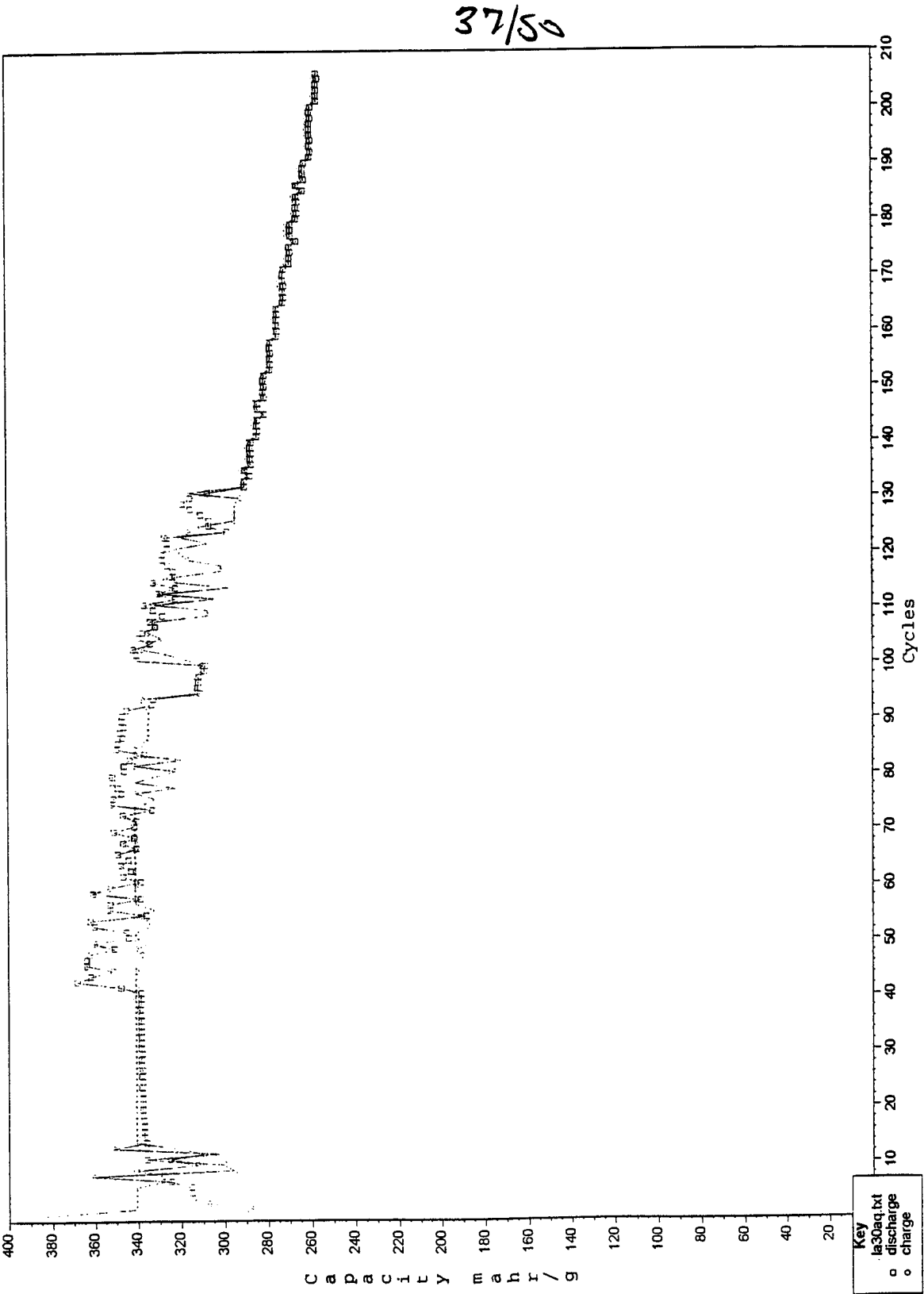


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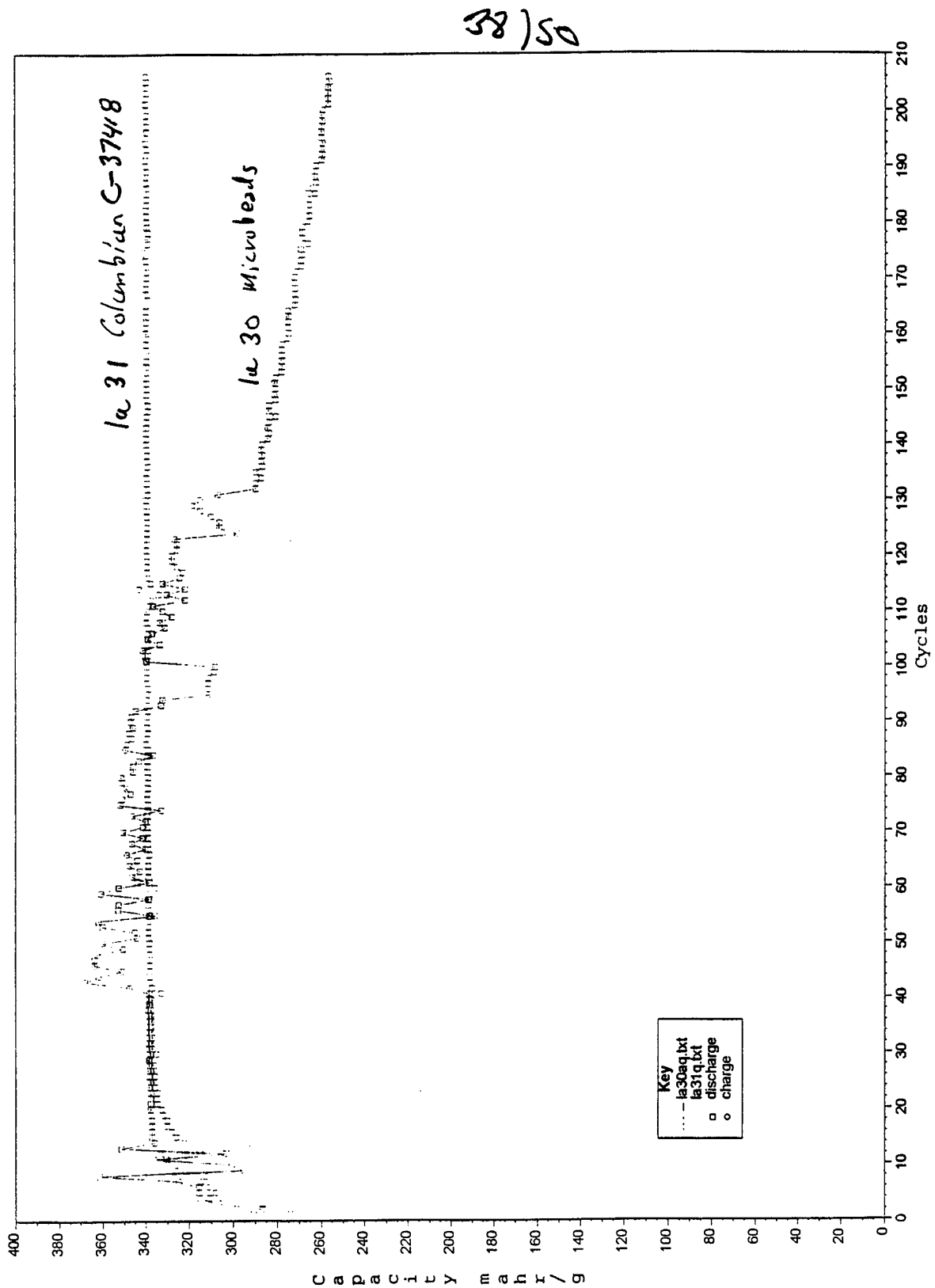


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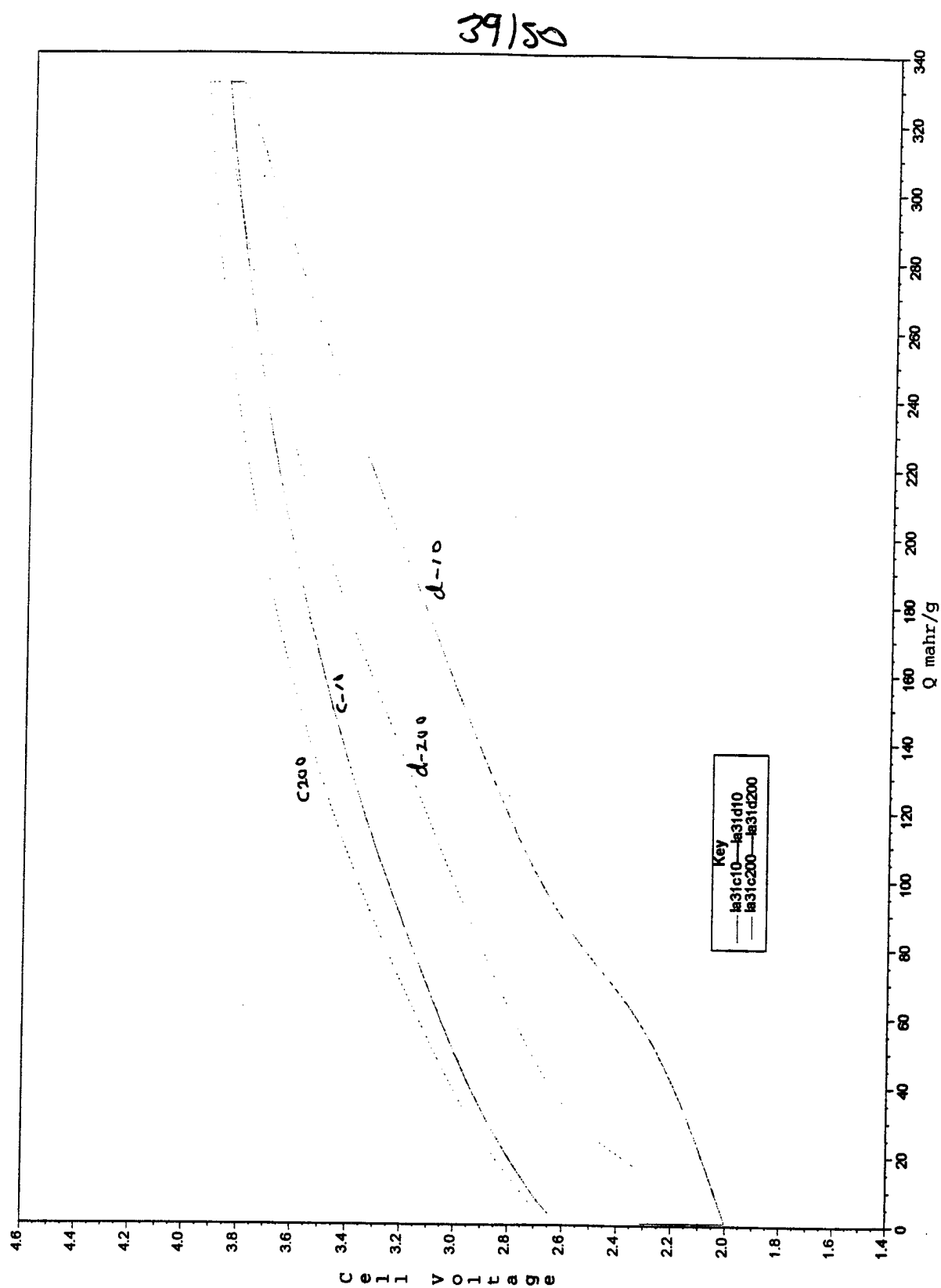


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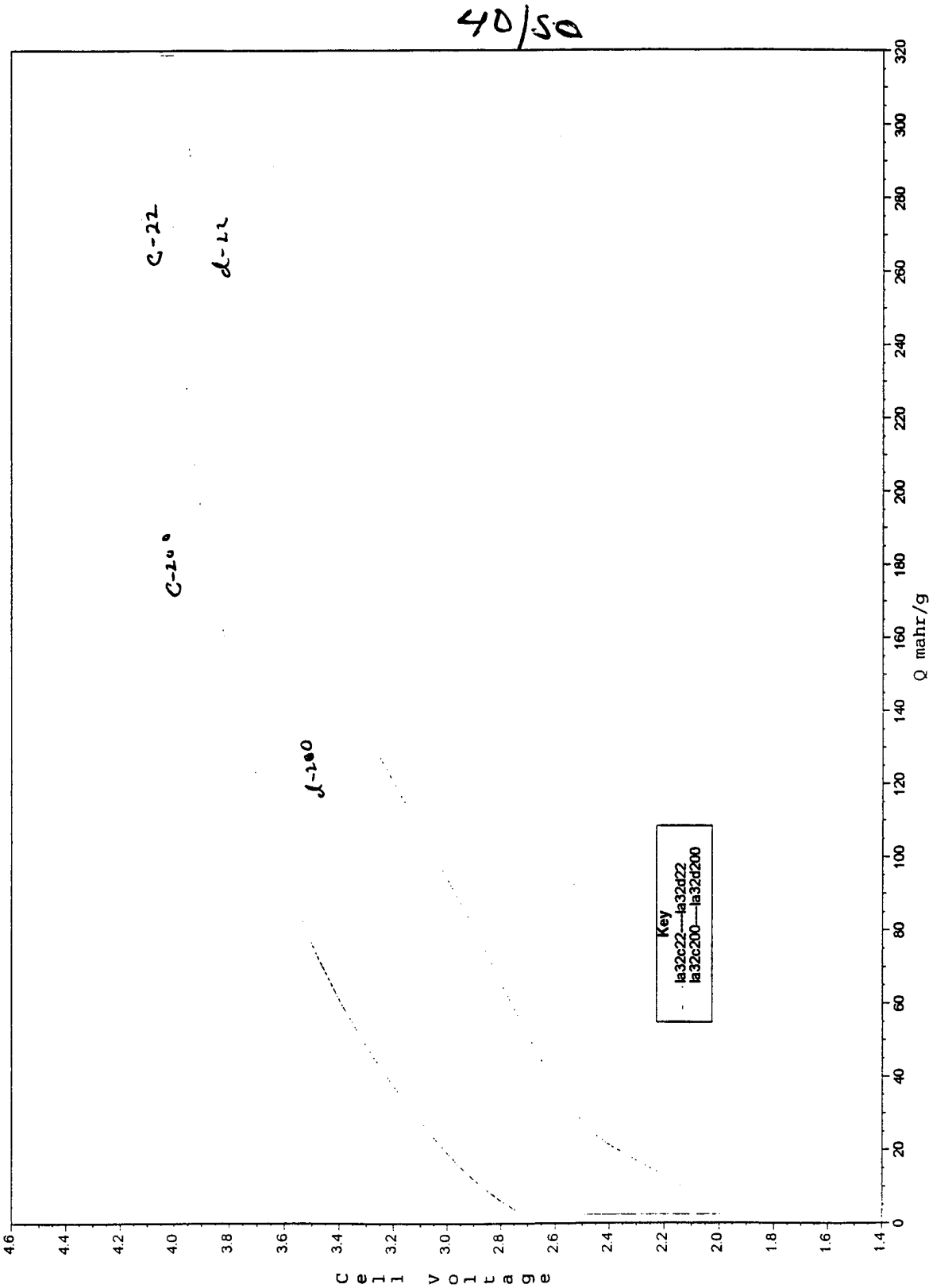


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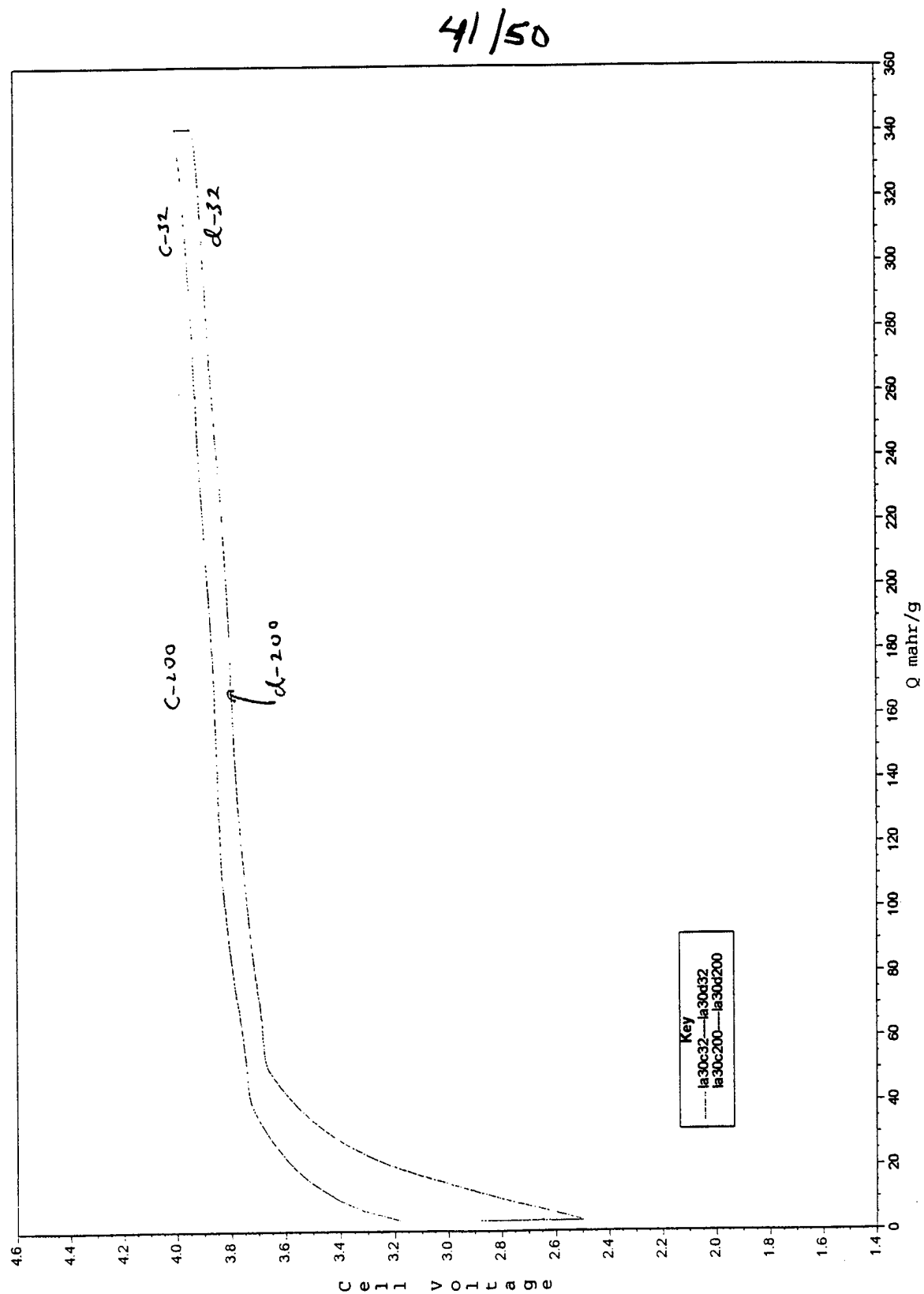


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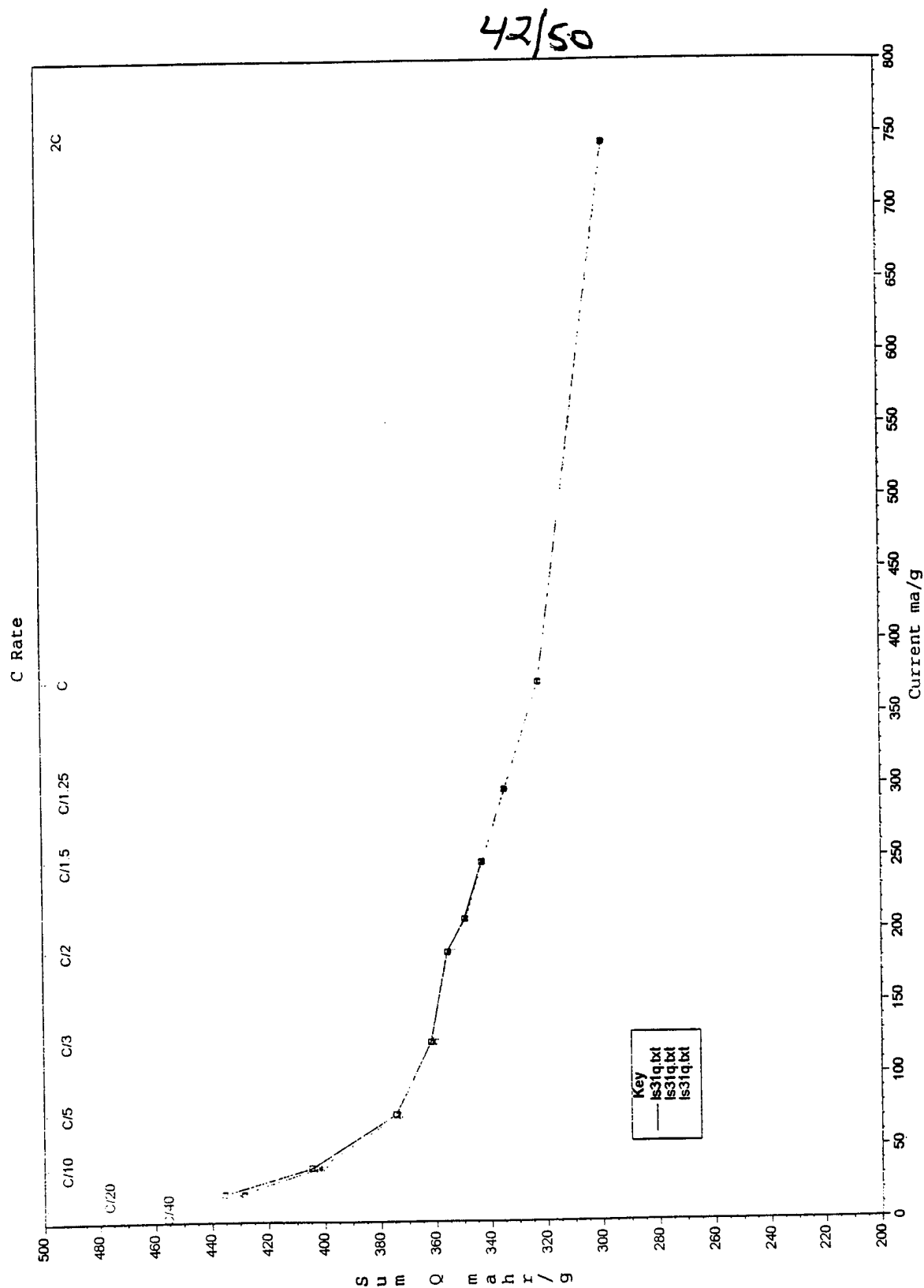


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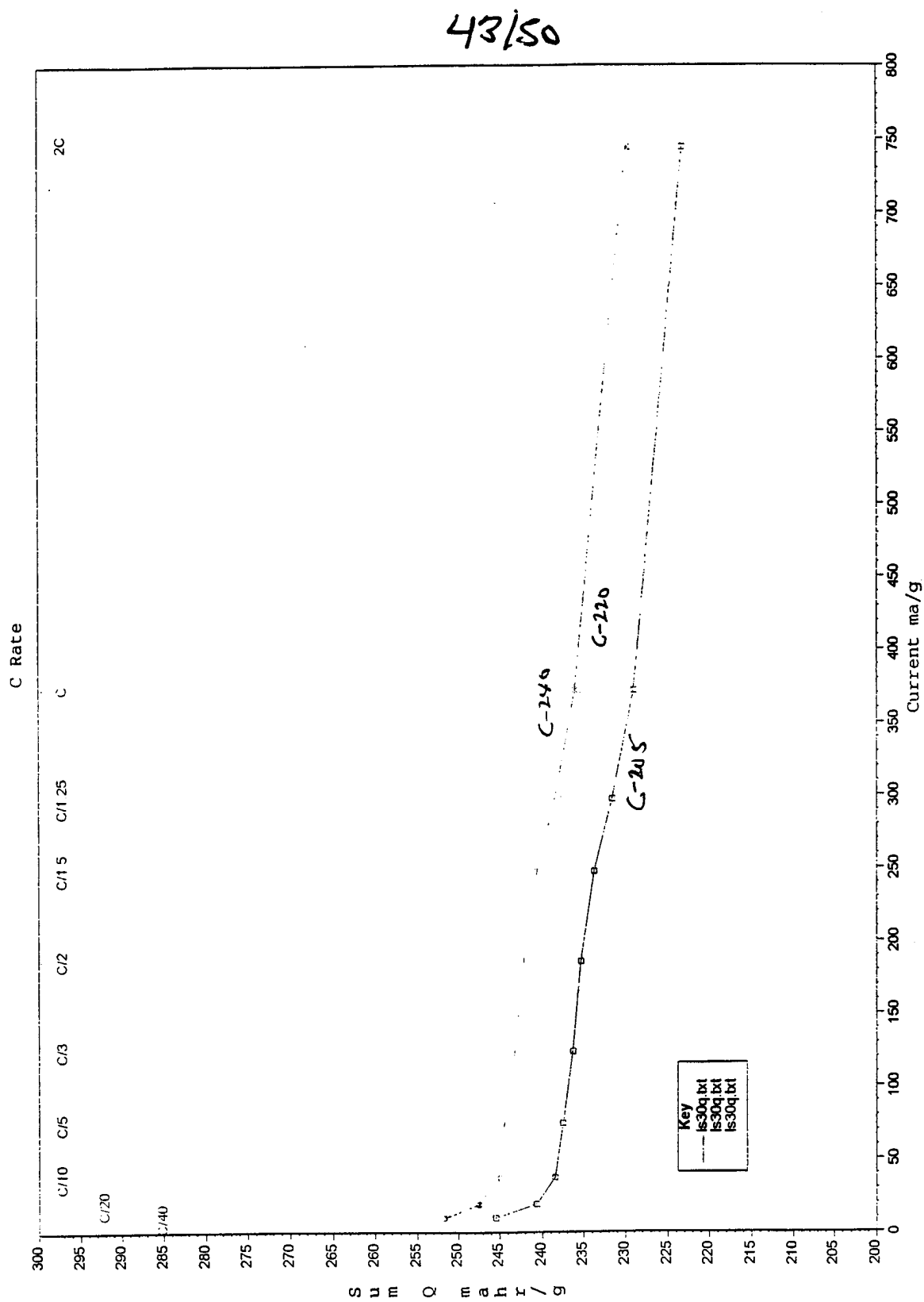


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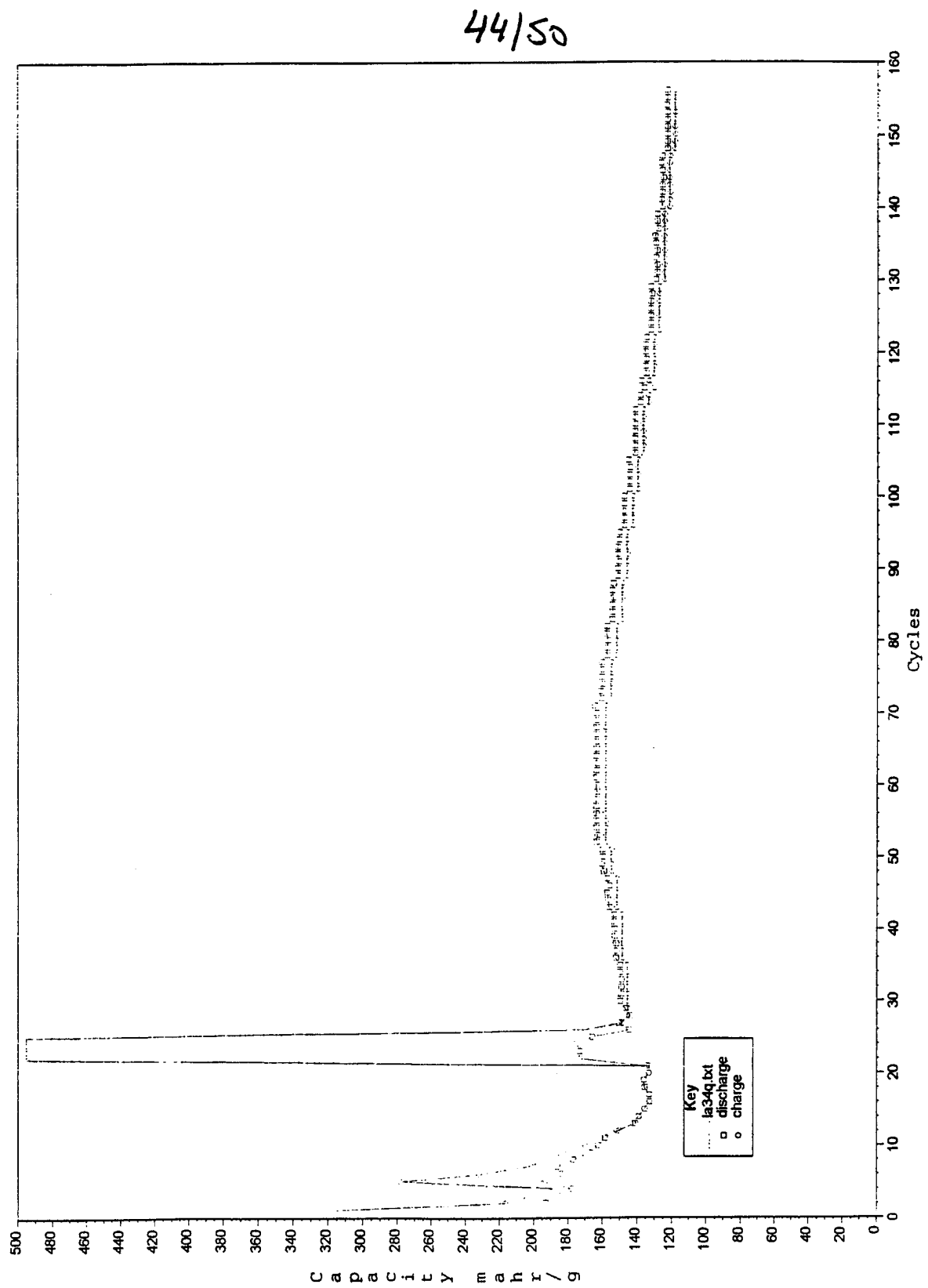


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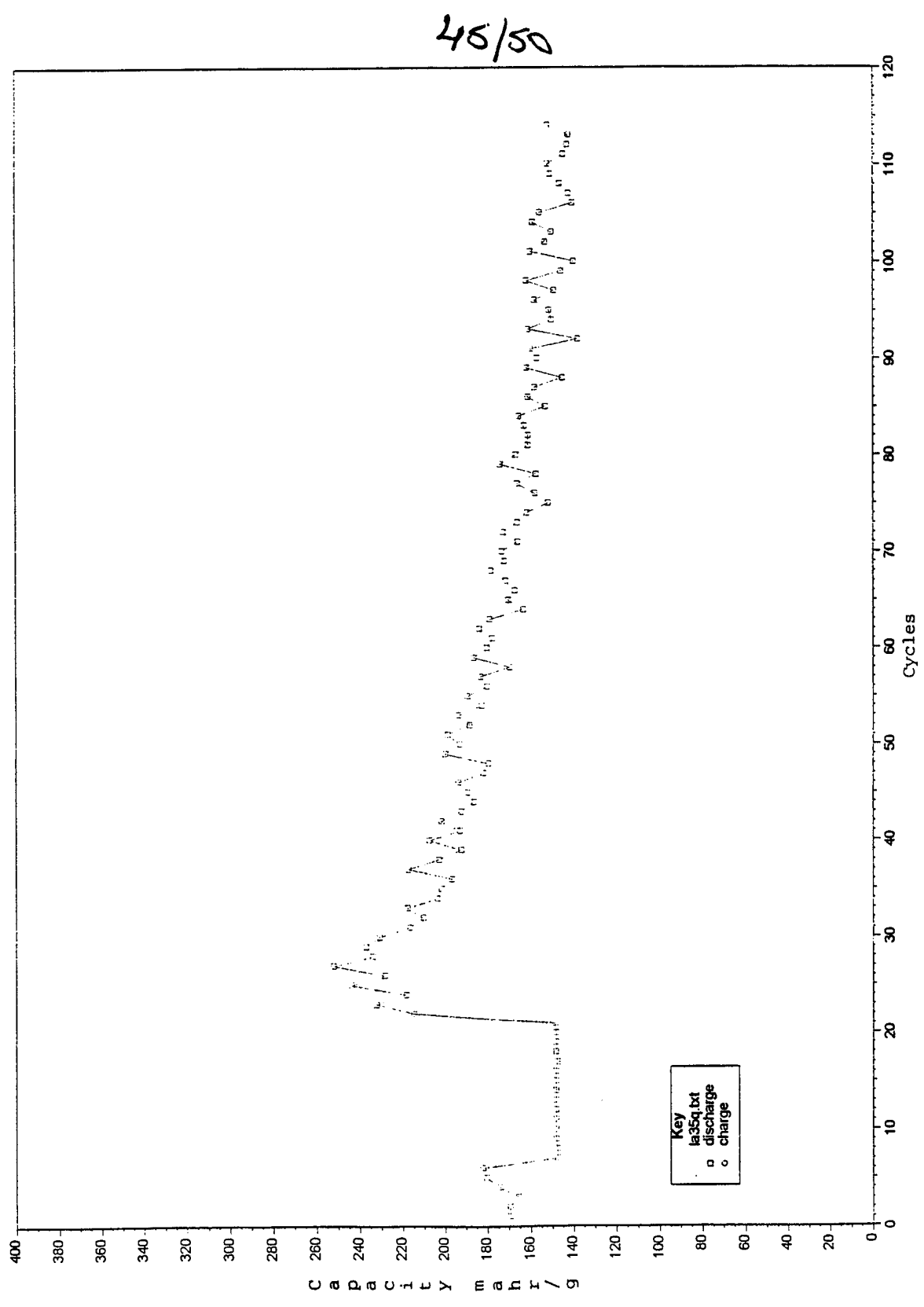


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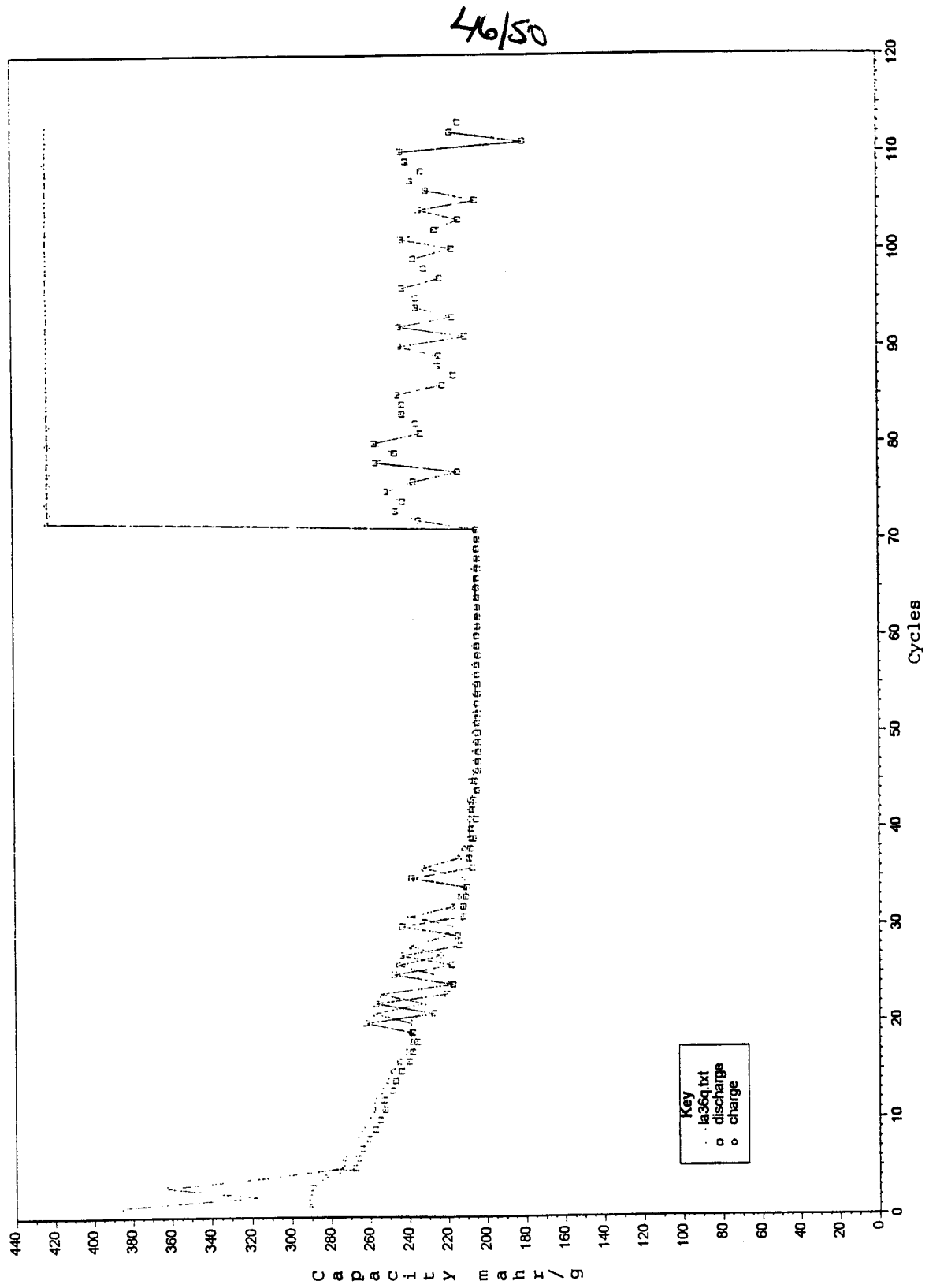


Figure 46

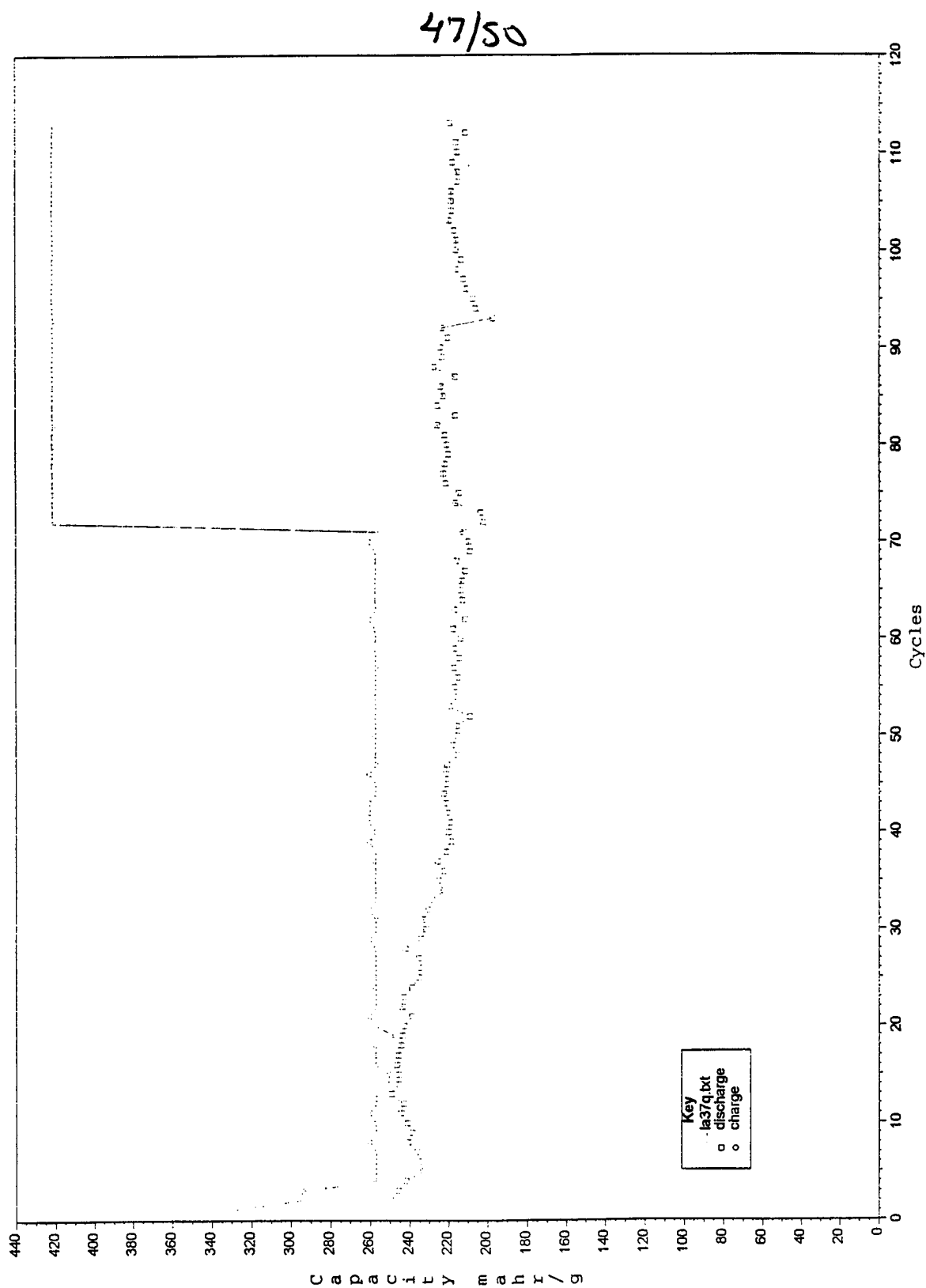


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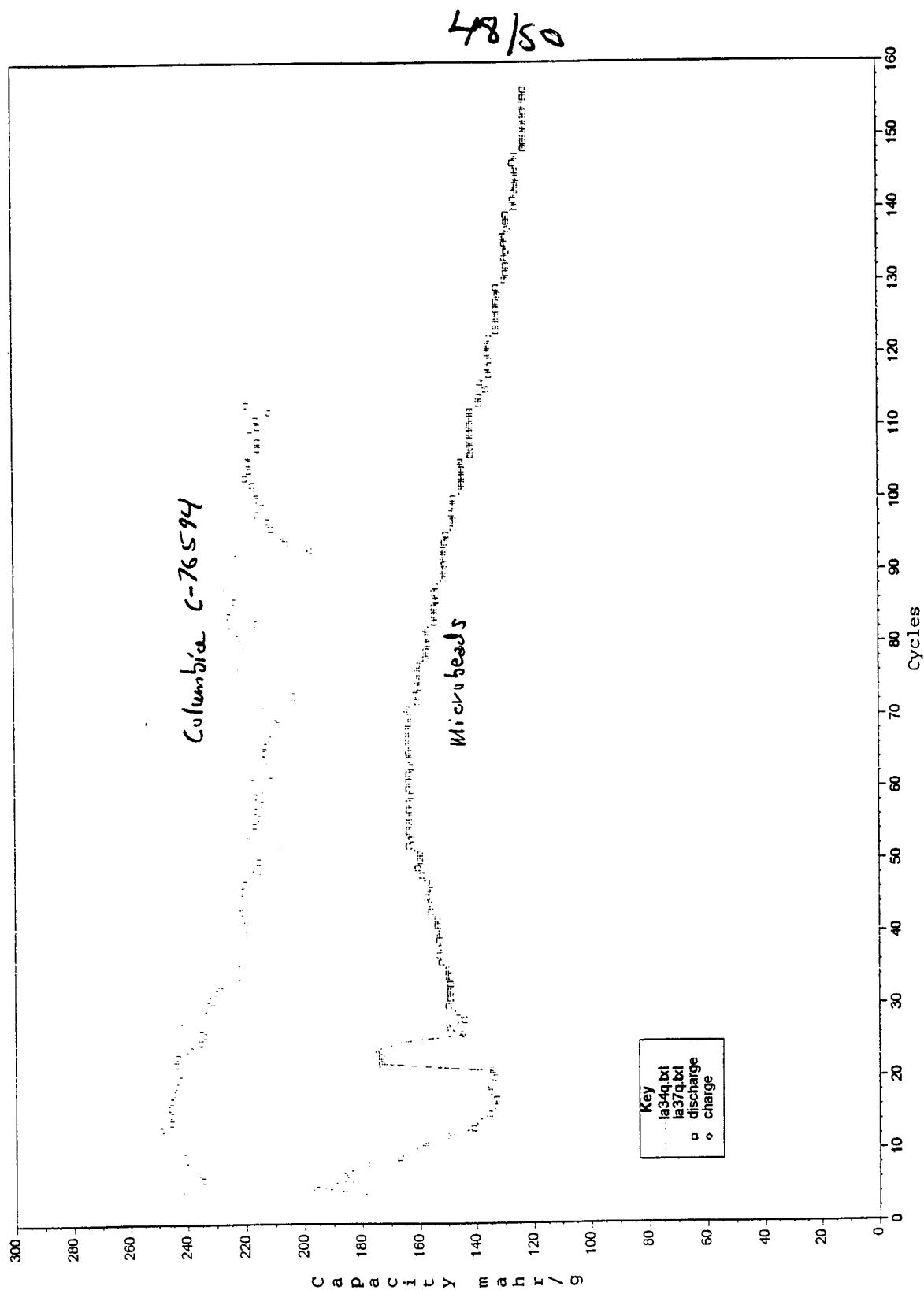


Figure 48

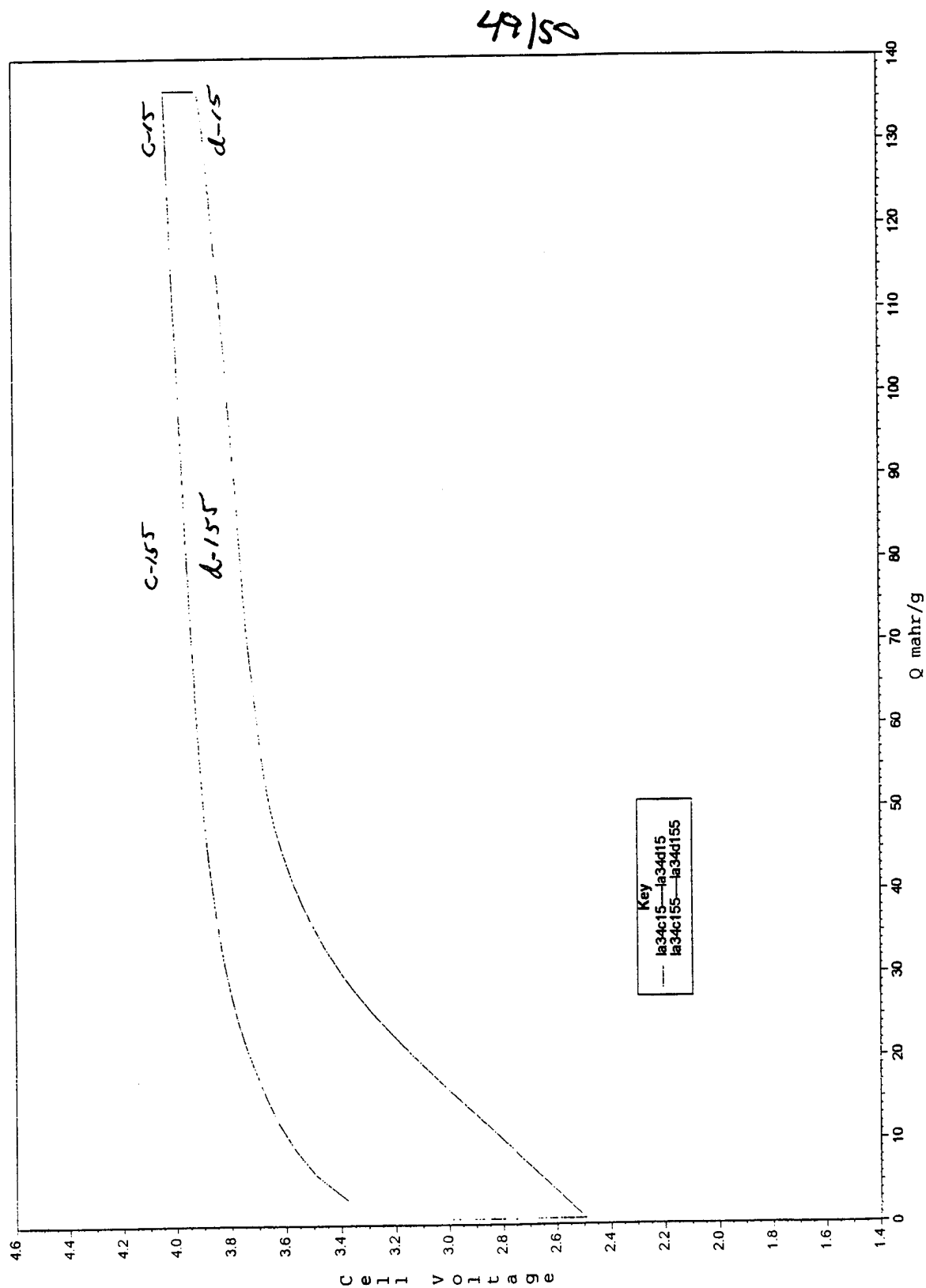


Figure 49

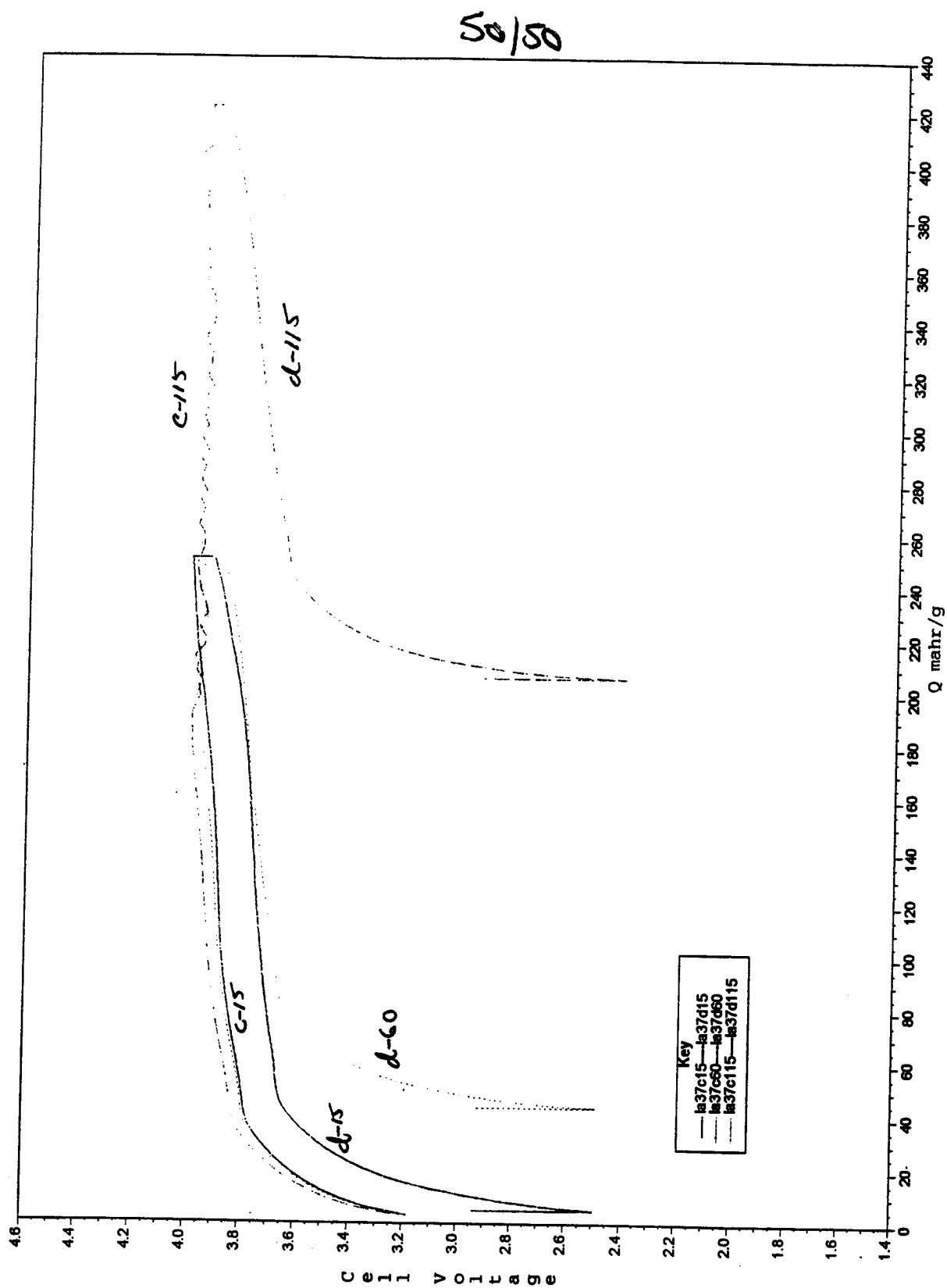


Figure 50