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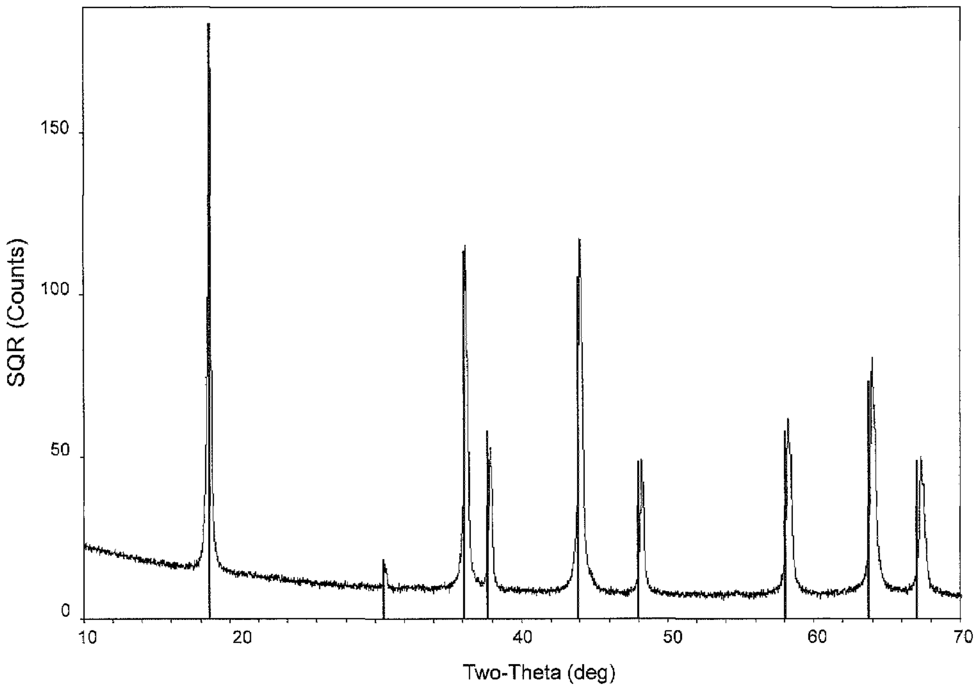
(54) **Titre : COMPOSITIONS DE LITHIUM-OXYDE DE MANGANESE AMELIOREES**
(54) **Title: IMPROVED LITHIUM MANGANESE OXIDE COMPOSITIONS**



(57) **Abrégé/Abstract:**
The present disclosure relates to improved LMO composition suitable for use as cathode material in rechargeable lithium ion batteries. The LMO composition may be doped with an additional metal or undoped. The LMO composition carries a surface treatment of LiF that protects the LMO from acid degradation. Cathodes prepared from the improved LMO have improved fade characteristics.

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(54) **Title**: IMPROVED LITHIUM MANGANESE OXIDE COMPOSITIONS

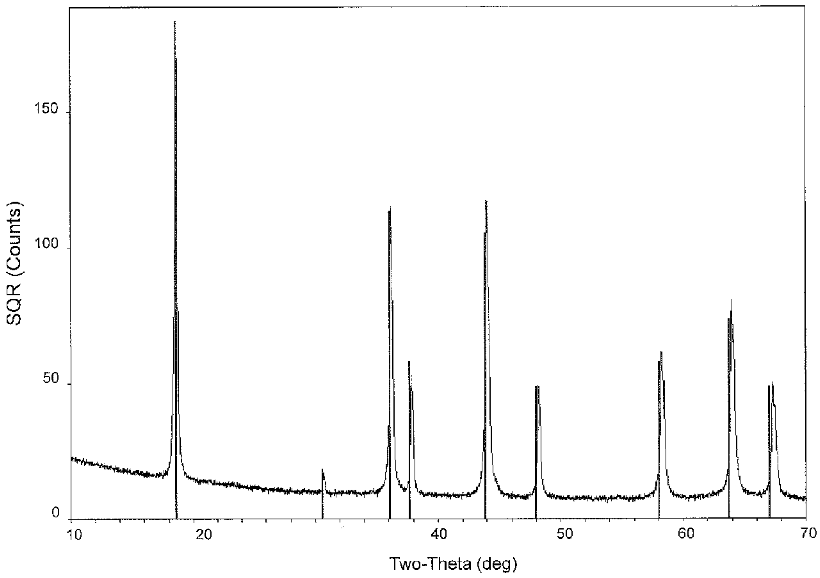

Figure 1a

(57) **Abstract**: The present disclosure relates to improved LMO composition suitable for use as cathode material in rechargeable lithium ion batteries. The LMO composition may be doped with an additional metal or undoped. The LMO composition carries a surface treatment of LiF that protects the LMO from acid degradation. Cathodes prepared from the improved LMO have improved fade characteristics.

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Improved Lithium Manganese Oxide Compositions

BACKGROUND

[0001] Lithium-ion batteries continue to dominate the rechargeable battery market. Found in nearly every type of handheld rechargeable phone, music player and many other devices, secondary batteries relying upon lithium metal oxides as the cathode composition eventually experience fade and loss of capacity. Capacity loss increases over the life of the battery necessitating recharging of the battery more frequently.

[0002] One well-known mechanism responsible for degradation of the cathode material results from the reaction of electrolyte material with water to form hydrofluoric acid. For example, electrolytes such as $LiPF_6$ react with water to form HF according to the following equation:

$$2LiPF_6 + 6H_2O \rightarrow Li_2O + P_2O_5 + 12HF.$$

The resulting HF attacks the metal oxides of the cathode. For example, when using a spinel material such as $LiMn_2O_4$ (also written as $LiMn^{3+}Mn^{4+}O_4$) as the cathode material, the spinel reacts with HF as represented by the following equation:

$$4H^{+} + 2LiMn^{3+}Mn^{4+}O_4 \rightarrow 3\lambda MnO_2 + Mn^{2+} + 2Li^{+} + 2H_2O.$$

Since this reaction generates water and in turn additional HF, over time the reaction will completely degrade the cathode material. As the reaction progresses, the manganese ion passes through the separator and becomes part of the solid electrolyte interface (SEI layer) at the anode. The addition of the manganese ions to the SEI layer inhibits the flow of ions contributing to the loss of capacity by the cell.

[0003] Other common electrolytes including $LiAsF_6$, and $LiBF_4$, and LiTFSI (lithium bis-trifluoromethanesulfonimide) will also produce HF. Further, alternative cathode materials utilizing first row transition metals such as Co, Mn, Ni, Fe and V (possibly doped with other elements) are equally susceptible to degradation by HF. Accordingly, the ability to shield the cathode material from HF attack without detrimentally reducing battery performance will be commercially advantageous.

SUMMARY

[0004] In one embodiment, the present invention provides a cathode composition. The cathode composition includes a lithium metal oxide suitable for use in lithium ion batteries. The lithium metal oxide carries a lithium fluoride surface treatment sufficient to substantially preclude degradation of the lithium metal oxide by acids.

[0005] In another embodiment, the present invention provides a cathode composition prepared from a lithium metal oxide (LMO) spinel material having the general formula of $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc. Alternatively, the cathode composition is prepared from a layered material $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn. When used as the cathode active material both materials carry a lithium fluoride surface treatment sufficient to substantially preclude degradation of the lithium metal oxide by acids. The resulting cathode active material has improved fade over multiple cycles while maintaining the desired capacity.

[0006] Additionally, the present invention provides a method for preparing cathode material. The method includes the steps of dry blending lithium metal oxide with lithium fluoride (LiF) particles followed by heating the resulting dry blend at a temperature and for a period of time sufficient to activate the LiF as a surface treatment on the lithium metal oxide, i.e. the LiF is carried by the lithium metal oxide in a manner to provide the desired protection.

[0007] Further, the present invention provides a method for preparing a cathode material suitable for use in a lithium ion battery. The method includes the steps of dry blending a cathode active material having the general formula of $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent metals from the group Al, Cr. Ga, In and Sc or $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn with lithium fluoride (LiF) particles followed by heating the resulting dry blend at a temperature and for a period of time sufficient to activate the LiF as a surface treatment on the lithium metal oxide. The dry blending step utilizes a sufficient amount of LiF such that the resulting blend has from about 0.25 to about 2.5% by weight LiF. Typically, the dry blending step occurs at a temperature between about 10°C and 30°C. The resulting dry blend material is heated to a temperature between about 700°C to about 850°C to provide a final composition in the form of a cathode active material carrying a surface treatment of LiF. Using the resulting cathode active material provides a cathode having a capacity of at least and more preferably greater than 100mAh/g (milliAmpHour/gram) after 200 cycles.

[0008] Still further, the present invention provides an alternative method for preparing lithium manganese oxide compounds suitable for use as cathode material. This method includes the steps of:

- selecting a cathode active material having the general formula of $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc or $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn;
- preparing a slurry of with LiF particles in water;
- heating the slurry to a temperature between about 40°C and 60°C;

- blending the selected cathode active material into the slurry;
- stirring the slurry of LiF and cathode active until the slurry is a homogeneous dispersion;
- removing water from the slurry by a drying process;
- heating the resulting solids to a temperature between about 450° and 850° for a period sufficient to activate the LiF;
- providing a final composition in the form of a cathode active carrying a surface treatment of LiF.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1a is an X-Ray Diffraction scan of $LiMn_2O_4$ without a surface treatment of lithium fluoride. Figure 1b is an X-Ray Diffraction scan of $LiMn_2O_4$ carrying a surface treatment of lithium fluoride.

[0010] Figure 2 is a graph of the cycling capacity at 60°C comparing $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$ carrying a surface treatment of LiF heat treated in a rotary calciner at 850°C with a residence time of 4 - 5 hours (Line C) to untreated $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$ (Line A) and to $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$, lacking LiF, but heat treated in a rotary calciner at 850°C with a residence time of 4 - 5 hours (Line B). Each data point represents the discharge of the cathode to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes.

[0011] Figure 3 is a graph of the cycling capacity at 60°C comparing $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ carrying a surface treatment of LiF heat treated twice in a box oven at 850°C (Line F) to untreated $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ (Line D) and to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ carrying LiF but not heat treated (Line E). Each data point represents the discharge of the cathode to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes.

[0012] Figure 4 is a graph of the cycling capacity at 60°C comparing $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ carrying a surface treatment of LiF heat treated in a box oven at 850°C (Line H) to untreated

$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ (Line D) and to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ lacking LiF but heat treated in a box oven at 850°C (Line G). Each data point represents the discharge of the cathode to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes.

[0013] Figure 5 is a graph of the cycling capacity at 60°C comparing untreated $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ (Line D) to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ free of LiF but heat treated in a box oven at 850°C (Line G), to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ free of LiF but heat treated twice in a box oven at 850°C (Line J), to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ carrying a surface treatment of LiF heat treated in a box oven at 850°C (Line H) and to $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ carrying a surface treatment of LiF heat treated twice in a box oven at 850°C (Line F). Each data point represents the discharge of the cathode to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes.

[0014] Figure 6 is a graph demonstrating the ability to reduce the concentration of doping metal (Cr) while retaining the original cathode active material structure and improving cathode material capacity by treating with LiF and heat treating the material. Each data point represents the discharge of the cathode to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes.

DETAILED DESCRIPTION

[0015] The present invention provides a lithium metal oxide composition particularly suited for use as cathode material in a lithium ion battery. The particles of lithium metal oxide (LMO) carry a surface treatment of lithium fluoride. Although the lithium fluoride is not a battery active material, the presence of the LiF on the surface of the LMO particle is believed to shield the metal component from acidic digestion. Since the LiF does not contribute to capacity, the preferred embodiment will use only that amount necessary to protect the LMO from acidic digestion without detrimentally impacting capacity.

[0016] Generally, the surface treatment of LiF will not completely encapsulate the LMO particle. Rather, without intending to be limited by theory, we believe the LiF isolates a sufficient portion of the exposed manganese sites on the surface of LMO from the electrolyte thereby limiting the oxidation reaction known to degrade the LMO without interfering with the electrolytic reaction. Expressed on a percent by weight basis, the LiF component of the final LMO particle is between about 0.25% to about 2.0% by weight of the LMO/LiF particle inclusive of LMO material containing a doping metal.

[0017] As known to those skilled in the art, the addition of doping metals to LMO stabilizes the cathode active structure during charge/discharge cycles by replacing a portion of the manganese ions within the cathode active material structure. Thus, the addition of the doping metal does not generally change the LMO particle size. Further, the doping metal does not normally contribute to the capacity of the cathode material under typical lithium ion battery operational conditions. Commonly, LMO can have from about 0.1% to about 15% doping metal by weight. More typically, LMO will have from about 0.5% to about 5% doping metal by weight. Therefore, reducing the concentration of doping metal will enhance battery capacity and reduce manufacturing costs.

[0018] LMO suitable for use as the base particle includes, but is not necessarily limited to, spinel material having the general formula of:

$$Li_{1+x}M_yMn_{2-x-y}O_4$$

where $0<x\leq 0.25$, $0<y\leq 0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc or a layered LMO having the general formula of:

$$Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$$

where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn.

[0019] For the following discussion all particles sizes refer to median particle size as determined by laser granulometry. In general, prior to blending with LiF, the LMO with or without doping metal, will have particle sizes of about 10 microns or less. More commonly, prior to blending with LiF the LMO, with or without doping metal, will have particle sizes ranging from 3 to about 10 microns. The LMO particle with a surface treatment of LiF has a cubic crystalline structure. Thus, neither the surface treatment of LiF nor the method of adding a surface treatment of LiF to the cathode active material alters the crystalline structure of the LMO. Further, the surface treatment of LiF does not form a "layered" LMO as that term is used by those skilled in the art. As reflected in FIG. 1b, the LMO carrying a surface treatment has x-ray diffraction peaks identified by letters P, S and T at 38.6°, 44.84° and 65.46° 2Θ respectively, (Cu Kα radiation) whereas x-ray diffraction scan of FIG. 1a of the untreated LMO does not have the corresponding peaks.

[0020] Preferred LMO cathode active material compositions suitable for carrying the LiF surface treatment include: $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$; $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$; $Li_{1.05}Al_{0.12}Mn_{1.83}O_4$; and $LiNi_{0.5}Mn_{1.5}O_4$. As discussed each compound may be doped with a metal selected from the following group: Mg, Al, Cr, Fe, Ni, Co, Ga, In, Sc, In, Cu or Zn. Use of a doping metal helps to stabilize the structure of the cathode active material during discharge/recharge cycles. The doping metal is generally not a battery active material. Therefore, use of doping metal reduces the overall capacity per gram of the cathode material. Incorporation of the LiF surface treatment will reduce the requirements for doping metal thereby improving capacity of the final cathode material. In general, a cathode material having a LiF surface treatment will require about 50% less doping material than a cathode material lacking LiF surface treatment. Commonly, cathode materials with the LiF surface treatment will have from about 0.5 % to about 2.0 % by weight doping material. Typically, the cathode material will have a capacity of 105 mAH/g to 120 mAH/g.

[0021] As discussed in more detail below, the LMO with surface treatment of LiF is particularly suited for use as a cathode material in lithium ion batteries.

[0022] Preparation of the LMO carrying a surface treatment of LiF may use one of two new methods. Both methods advantageously utilize a neutral salt, thereby eliminating handling problems associated with hydrofluoric acid. The preferred method dry blends the components followed by heating to activate the LiF surface treatment. Both methods are discussed in detail below. Methods for preparing the base LMO are well known to those skilled in the art and will not be discussed herein.

[0023] In the dry blend method, a dry powdered LMO having particle sizes between about 3 microns to about 10 microns is blended with lithium fluoride having particle sizes between about 1 micron to about 5 microns. The amount of LiF added to the dry LMO powder may range from about 0.25% to about 2.5% by weight of the LMO powder initially charged to the blending unit. The type of blending unit is not critical to the current method. Suitable blending units include, but are not limited to, ball mills, vibratory mills, and Scott mills as well as any other convenient dry powder blending mill. Blending typically continues for a period sufficient to achieve a homogenous blend. Although some blending may occur during the heating process, preferably the powders are homogenously blended prior to the following heating step. Depending on the blending unit, typical blending times may range from about 15 minutes to about two hours with the total time dependent upon the quantity of materials and blending conditions. One skilled in the art will be able to readily adjust the blending conditions to achieve the desired homogenous blend of dry materials.

[0024] Following blending, the dry powder is heated. If so equipped, heating may occur within the mixing unit; however, typically the dry powder will be transferred to a rotary calciner. Within the rotary calciner, heating occurs with continued mixing of the powder. In general, the mixing occurring during heating precludes agglomeration and helps maintain even distribution of the particles. The dry powder is heated to a temperature sufficient to adhere the LiF to the surface of the LMO. Typically, the heating step takes place at a temperature sufficient to soften the LiF. As noted above, LiF is not a battery active material. Thus, the addition of too much LiF to the LMO will have a detrimental effect on the resulting cathode material. Therefore, properly controlling the heating of the blended powder will produce a LMO with the desired LiF surface treatment. As such, the heating range approximates the melting point of LiF under the operating conditions. Accordingly, heating generally occurs between 840°C and 855°C. More commonly, heating occurs at about 850°C.

[0025] The heating step takes place over a period of about two to five hours. As discussed above, the heating step is controlled to limit the deposition of LiF on the surface of the LMO and preclude loss of lithium from the cathode active material structure during the heating step. Preferably, the heating step is limited to ensure the production of LMO with a surface treatment of LiF having maximum capacity with maximum protection against acid degradation. As such, heating may vary with operational conditions such as humidity, moisture content of the blended powder, as well as the mass of powder. In general, heating the blended powder will preferably take place over a period of about two to about four hours.

[0026] Without being limited by theory, the heating step is believed to fuse the LiF to the LMO. Regardless of the attachment mechanism, the resulting surface treatment of LiF provides a sufficient barrier to protect the LMO from acid degradation (i.e. acid attack) without substantially inhibiting necessary ion transport. The presence of the LiF on the surface of the LMO precludes reaction of HF or F^- with the LMO thereby precluding loss of the manganese component of the LMO. Without intending to be limited by theory, we believe the LiF isolates a sufficient portion of the exposed manganese sites on the surface of LMO from the electrolyte thereby limiting the oxidation reaction known to degrade the LMO without interfering with the electrolytic reaction. Accordingly, a cathode prepared from the resulting LMO with surface treatment of LiF has reduced fade over a plurality of cycles while retaining substantially all the initial capacity of the LMO lacking the LiF surface treatment.

[0027] In an alternative embodiment, the LMO with surface treatment of LiF may be prepared by a solution process. In the solution process, a slurry of LiF is prepared in water and heated to a temperature between about 40°C and 60°C. The final slurry has from about 0.1% to about 1.0% LiF by weight. The method then blends LMO into the slurry. Stirring of the blended slurry continues until the slurry is a homogenous dispersion of LiF and LMO. The solids are separated from the slurry by drying or other convenient method and subsequently heated to a temperature between about 600°C and 850°C. The heating step continues for a period sufficient to provide a surface treatment of LiF on the LMO.

[0028] Both methods for preparing the treated LMO, the method will commonly include the further step of sifting or sieving the final product to isolate particles having the desired size. Final particle sizes may range from 3μm to about 30μm. Typically, final particles ranging from about 3 μm to about 10 μm are desired for formation of cathodes used in lithium ion batteries.

[0029] The present invention also provides an improved cathode material utilizing the LMO with surface treatment of LiF discussed above. Cathode material utilizing the LMO/LiF composition will have improved fade characteristics and an initial capacity comparable to the same LMO lacking the surface treatment of LiF. As reflected by FIGS. 2-5, the LMO/LiF composition actually provides both improved fade characteristics and improved capacity. As reflected in the FIGS. 3-6, cathodes prepared from LMO carrying surface treatment of LiF had significantly better capacity after 250 discharge/charge cycles thereby reflecting improved fade characteristics. Additionally, each sample of LMO/LiF had an initial capacity within 10% of the untreated LMO.

[0030] The LiF treated LMO was used to produce the cathodes incorporated into coin cell batteries for the purposes of determining capacity and fade rate of the cathodes. As reported in FIGS. 2-6 and Table 1 below, the LMO treated with LiF carried 1% by weight LiF. Except as indicated in Examples 6 and 7 below, each indicated heat treatment occurred at 850°C for a period of 120 minutes in a box oven. (Note: although described in connection with a box oven, any conventional heating device suitable for heating the LMO carrying LiF for a period sufficient to activate the LiF will suffice.) Each sample, with or without a surface treatment of LiF, was prepared using the dry blending method described above. The FIGS. reflect the initial capacity of the active cathode material, i.e. the LiF treated LMO, in mAh/g and the capacity of the cathode following repeated charge and discharge cycles. All coin cell batteries were cycled at 1C discharge rate and C/3 charge rate at 60°C with each cell discharged to an indicated 3 volts over 60 minutes followed by recharging to an indicated 4.3 volts over 180 minutes. FIG. 2 depicts capacity testing results for cathodes prepared from untreated LMO (line A), LMO lacking LiF but heat treated once at 850°C as described below in Example 6 (line B) and LMO carrying the LiF treatment and heat treated at 850°C as described below in Example 7 (line C). In FIG. 3, line D reflects the capacity for a cathode prepared from LMO free of LiF. Line E reflects the capacity of a cathode prepared using LiF treated LMO but not heat treated. Line F reflects the capacity of a cathode prepared from LiF/LMO heat treated twice at 850°C. In FIG. 4, line D corresponds to line D of FIG. 3. Line G reflects the capacity of a cathode prepared from LMO free of LiF with a single heat treatment at 850°C. Line H reflects the capacity of cathode prepared from a LiF treated LMO heat treated once at 850°C. In FIG. 5, line D corresponds to Line D in FIGS. 3 and 4 and line F corresponds to line F in FIG. 3. Lines G and H correspond to lines G and H in FIG. 4. Line J reflects the capacity of a cathode prepared from LMO free of LiF but heat treated twice at 850°C. As reflected in FIG. 5, Line J has greater initial capacity than Lines F and H; however, Line J has a greater fade rate than Lines F and H. Although not wishing to be bound by theory, we believe that the double heat treatment of the LMO reduced the number of defects in the LMO leading to increased capacity. With reference to FIG. 6, Line K represents an LMO doped with 1.4 weight % Cr, but lacking LiF thereby providing a final LMO with the formula of ($Li_{1.05}Cr_{0.05}Mn_{1.9}O_4$). The line K material had an initial capacity of 118.2 mAh/g and a capacity of 78.0 mAh/g after 300 cycles. Line L represents an LMO doped with twice as much Cr (2.9 weight %), but lacking LiF thereby providing a final LMO with the formula of ($Li_{1.05}Cr_{0.1}Mn_{1.84}O_4$). The line L LMO had an initial capacity of 115.9 mAh/g and a capacity of 83.2 mAh/g after 300 cycles. Line M represents LMO with only 1.4 weight% Cr; however, the Line M LMO was treated with LiF and heat treated at 850°C. The Line M LMO is represented by ($Li_{1.05}Cr_{0.05}Mn_{1.9}O_4$). The Line M material had an initial capacity of 118.2 mAh/g and a capacity of 99.5 mAh/g after 300 cycles. As reflected in FIG. 6, the LiF treatment is even more effective at stabilizing the capacity of the LMO than additional dopant in the structure. Table 1 provides the individual cycle values in mAh/g for each sample depicted in FIGS. 2-5.

Material	Formula not including LiF treatments	Heat Treatments 120 minutes at 850°C	Initial Capacity (mAh/g)	Maximum capacity (mAh/g)	Fade rate after 300 cycles (%/cycle) at 60°C
A	$Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$	0	114.1	114.1	-0.052
B	$Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$	1	116.4	117.1	-0.058 (cycle 246)
C	$Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$	1	112.9	115.4	-0.033
D	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	0	108	110.5	-0.055
E	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	0	106.2	109.5	-0.057
F	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	2	106.1	109.7	-0.016
G	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	1	111.4	114.0	-0.031
H	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	1	110.7	111.9	-0.021
J	$Li_{1.06}Al_{0.18}Mn_{1.76}O_4$	2	113.9	115.1	-0.033
K	$Li_{1.05}Cr_{0.05}Mn_{1.9}O_4$	0	118.2	119.9	-0.109
L	$Li_{1.05}Cr_{0.1}Mn_{1.84}O_4$	0	115.9	118.9	-0.093
M	$Li_{1.05}Cr_{0.05}Mn_{1.9}O_4$	1	118.2	118.9	-0.056

Table 1 – Lines C, E, F, H and M include LiF Surface Treatments

[0031] With reference to FIG. 2 and Table 1, the LMO treated with LiF and heat treated at 850°C as described in Example 7 (linc C) had an initial capacity of 112.9 mAh/g. After cycling 246 times, the line C sample had a final capacity value of 104.9 mAh/g. In contrast, the untreated LMO (line A) had an initial capacity 114.1 mAh/g. Following cycling 246 times, the line A sample had a capacity value of 95.6 mAh/g. LMO free of LiF but heat treated once at 850°C as described in Example 6 (line B) had an initial capacity of 116.4 mAh/g and a capacity of 99.4 mAh/g following 246 cycles.

[0032] With reference to FIGS. 3-6, LMO treated with LiF and heat treated once at 850°C (line H) had an initial capacity of 110.7 mAh/g and a capacity of 104.5 mAh/g after 250 cycles. The sample represented by line H had a capacity of 103.9 mAh/g after 300 cycles. LMO treated with LiF and heat treated twice at 850°C (line F) had an initial capacity of 106.1 mAh/g and a capacity of 102.0 mAh/g after 300 cycles. Line D, reflecting untreated LMO, indicates an initial capacity of 108.0 mAh/g and a capacity of 93.1 mAh/g after 250 cycles. Line E, reflecting LMO treated with LiF but not heat treated, indicates an initial capacity of 106.2 mAh/g, a capacity of 91.7 mAh/g following 250 cycles and a capacity of 89.8 mAh/g following 300 cycles. Line G, reflecting LMO lacking LiF but heat treated once at 850°C, indicates an initial capacity of 111.4 mAh/g, a capacity of 103.9 mAh/g following 250 cycles and a capacity of 102.6 mAh/g following 300 cycles. Line J, reflecting LMO lacking LiF but heat treated twice at 850°C, indicates an initial capacity of 113.9 mAh/g, a capacity of 104.3 mAh/g following 250 cycles and a capacity of 102.9 mAh/g following 300 cycles. Each Line in Figures 2-6 represents capacity values for the cathode material used in the coin cell batteries prepared as described in the following examples. The coin cell batteries were cycled at 1C discharge rate and C/3 charge rate at 60°C.

[0033] Example 1. A spinel material with a nominal composition of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ was prepared as follows. 216.0g of Mn_2O_3, 59.62g of Li_2CO_3 and 14.036g of Al_2O_3 were mixed together and the mixture was then ball milled for 2 hours (enough to thoroughly mix the materials but not decrease particle size). This mixture was then heated in a ceramic dish in a box furnace at 850°C for 10 hours. (This ten-hour heat treatment forms the initial LMO material. Application of the LiF surface treatment generally includes an additional heat treatment step.) Following the ten-hour heat treatment to prepare LMO, the temperature was decreased from 850°C to room temperature at a rate of 2°C/min. The resulting conventional LMO product was then passed through a -325 mesh screen.

[0034] Example 2. A lithium coin cell battery was made with a cathode disk containing 30 percent by weight of carbon black as a conductivity aid, 5 percent by weight of polyvinylidene fluoride (PVDF) as a binder and 65 percent by weight of the cathode active material from Example 1, a Li foil anode and an electrolyte comprised of 1M LiPF6 dissolved in a mixture of equal parts by weight of ethylene carbonate and dimethylcarbonate. The coin cell battery was cycled at 1C discharge rate and C/3 charge rate at 60°C. Line D in Figure 3 represent the capacity values of the cathode material prepared from the conventional non-heat treated LMO material prepared in Example 1 and incorporated into the cathode of a coin cell battery prepared in Example 2.

[0035] Example 3. To demonstrate the effect of an additional heat treatment on conventional LMO, about 50g of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ from Example 1 was heated in a ceramic dish in a box furnace at 850°C for 2 hours. The temperature was decreased from 850°C to room temperature at a rate of 2°C/min. This material was passed through a -325 mesh screen and then tested in a lithium coin cell battery as prepared in Example 2. Line G in Figure 4 represents the capacity values for a cathode material prepared from the heat treated conventional LMO.

[0036] Example 4. To demonstrate the effect of LiF treatment in conjunction with two heat treatment steps, 201.4 g of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$ from Example 1 was mixed with 2.0 g of LiF (1% by weight) and ball milled for 2 hours. 20g of this mixture was heated at 850°C for 2 hours in a ceramic crucible placed in a box furnace. Once cooled, the powder was hand mixed with a mortar and pestle to ensure homogeneity and reheated again at 850°C for an additional 2 hours. The temperature of the box furnace was decreased to room temperature at a rate of 2°C/min. This material was passed through a -325 mesh screen and then tested in a lithium coin cell battery as prepared in Example 2. Line F in Figure 3 represents the capacity values of cathode material prepared from the LiF treated LMO. FIG. 3 clearly demonstrates the improvement provided to the coin cell by using a cathode incorporating LMO having a surface treatment of LiF and prepared using two heat treatments over the heat treated conventional LMO and the non-heat treated conventional LMO.

[0037] Example 5. A conventional LMO was prepared using a spinel material with a nominal composition of $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$ was prepared as follows. 37.784kg of Mn_2O_3, 2.017kg Cr_2O_3 and 10.185kg of Li_2CO_3 were placed in a vibratory mill and mixed with ceramic media for 45 minutes. This step was repeated until about 700kg of spinel premix was obtained. The premix was then reacted in a rotary calciner with temperature settings of 850°C in all heating zones. An oxygen rich atmosphere was flowing through the calciner during the first pass through. Subsequent passes were achieved with normal air flow through the calciner. The material was repeatedly passed through the calciner until a total residence time of 10 hours at 850°C was attained. The material was then passed through the calciner one more time, with the temperature decreasing through the heating zones. This allowed for a slow cool rate of about 1.5°C/min down to 600°C. The cooled product was passed through a -325 mesh screen and then tested in a lithium coin cell battery as prepared in Example 2. Line A in Figure 2 represents the capacity values for cathode material prepared from the non-heat treated, LiF free LMO.

[0038] Example 6. To demonstrate the effect of a heat treatment on the LMO of Example 5, approximately 25kg of $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$ prepared in Example 5 was passed through a rotary calciner at 850°C at a rate sufficient to achieve a 4-5 hour residence time. The material was then passed through a rotary calciner a second time with the temperatures in the heating zones decreasing to achieve about a slow cool rate of about 1.5°C/min down to 600°C. The cooled product was passed through a -325 mesh screen and then tested in a lithium coin cell battery as prepared in Example 2. Line B in Figure 2 represents the capacity values for a cathode material prepared from the heat treated conventional LMO.

[0039] Example 7. To demonstrate the effect of LiF treatment and a single heat treatment step, 4.4kg of $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$ prepared in Example 5 was combined with 44g of LiF. This mixture was placed in a vibratory mill and mixed with ceramic media for 45 minutes. This step was repeated until about 70kg of LiF treated spinel premix was obtained. This material was passed through a rotary calciner at 850°C at a rate sufficient to achieve a 4-5 hour residence time. The material was then passed through a rotary calciner a second time with the temperatures in the heating zones decreasing to achieve about a slow cool rate of about 1.5°C/min down to 600°C. The cooled product was passed through a -325 mesh screen and then tested in a lithium coin cell battery as prepared in Example 2. Line C in Figure 2 represents the capacity values for a cathode material prepared from the heat treated, LiF treated LMO. FIG. 2 clearly demonstrates the improvement provided to the coin cell by using a cathode incorporating the LMO carrying a surface treatment of LiF prepared using a single heat treatment step over the heat treated conventional LMO and the non-heat treated conventional LMO.

[0040] Coin cell batteries using cathodes incorporating LMO corresponding to Materials E, H, J, K, L and M from Table 1 were also prepared according to the above procedures with the heat treatments and LiF surface treatments as identified in Table 1. Cathode material capacity values for each coin cell battery are reported as the corresponding lines E, H, J, K, L and M in FIGS. 3-6. Thus, FIGS. 2-6 demonstrate that the utilization of a cathode prepared from LMO having a surface treatment of LiF provides an improved secondary battery.

[0041] Other embodiments of the present invention will be apparent to one skilled in the art. As such, the foregoing description merely enables and describes the general uses and methods of the present invention. Accordingly, the following claims define the true scope of the present invention.

What is claimed is:

1. A method for preparing lithium manganese oxide compounds having a surface treatment of LiF comprising:

selecting a cathode active starting material from the group consisting of: $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc; and $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn;

dry blending LiF particles with the selected starting material, wherein the resulting dry blend comprises from 0.25 to 2.5% by weight LiF;

heating the resulting dry blend at a temperature between 700°C and 850°C for two hours to six hours to activate the LiF and to provide a final composition in the form of a cathode active material carrying a surface treatment of LiF on the cathode active material, wherein when expressed on a percent by weight basis the LiF of the final composition is between 0.25% and 2.5% by weight of the final composition.

2. A method for preparing a cathode:

selecting a cathode active starting material from the group consisting of: $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc; and $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn;

dry blending LiF particles with the selected starting material, wherein the resulting dry blend comprises from 0.25 to 2.5% by weight LiF;

heating the resulting dry blend at a temperature between 700°C and 850°C for two hours to six hours to activate the LiF thereby yielding a final composition with a surface treatment of LiF, wherein when expressed on a percent by weight basis the LiF of the final composition is between 0.25% and 2.5% by weight of the final composition; and,

preparing said cathode using the final composition with surface treatment of LiF said cathode characterized by having a capacity greater than 100mAh/g after 200 cycles when cycled at 60°C to a complete discharge to an indicated 3 volts over 60 minutes and recharged to an indicated 4.3 volts over 180 minutes.

3. The method of claim 1 or 2, wherein the starting material is selected from the group consisting of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$, $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$, $Li_{1.05}Al_{0.12}Mn_{1.83}O_4$, $Li_{1.17}Cu_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Mg_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Ca_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Zn_{0.05}Mn_{0.58}Ni_{0.2}O_2$.

4. The method of claim 1 or 2, wherein the step of dry blending occurs at a temperature between 10°C to 30°C.

5. The method of claim 1 or 2, wherein the step of dry blending continues until the LiF is homogenously distributed.

6. The method of claim 5, wherein the step of dry blending continues for 20 to 60 minutes and wherein following the step of dry blending the selected starting material and LiF has the same particle size as prior to the step of dry blending.

7. The method of claim 1 or 2, wherein the step of heating the dry blend occurs under atmospheric conditions.

8. The method of claim 1 or 2, wherein the resulting final composition has a particle size between 4μm and 28μm.

9. A method for preparing lithium manganese oxide compounds comprising:

selecting a cathode active starting material from the group consisting of: $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq 0.25$, $0<y\leq 0.5$ and M is one or more trivalent metals from the group Al, Cr, Ga, In and Sc; and $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq 0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn;

preparing a slurry of LiF particles in water;

heating the slurry to a temperature between 40°C and 60°C;

blending the selected starting material into the slurry;

stirring the slurry of LiF and starting material until the slurry is a homogeneous dispersion of LiF and starting material;

drying the slurry to isolate the solids;

heating the resulting solids at a temperature between 450° and 850° for two hours to six hours to activate the LiF and to provide a final composition in the form of a cathode active material carrying a surface treatment of LiF on the cathode active material, wherein, when expressed on a percent by weight basis, the LiF of the final composition comprises from 0.25 to 2.5% by weight LiF of the final composition.

10. The method of claim 9, wherein the starting material is selected from the group consisting of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$, $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$, $Li_{1.05}Al_{0.12}Mn_{1.83}O_4$, $Li_{1.17}Cu_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Ca_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Zn_{0.05}Mn_{0.58}Ni_{0.2}O_2$, and $Li_{1.17}Mg_{0.05}Mn_{0.58}Ni_{0.2}O_2$.

11. The method of claim 9, wherein the resulting cathode active material has a particle size between 4μm and 28μm.

12. A method for preparing a cathode comprising:

providing the cathode active material prepared according to the method of claim 9, and

forming said cathode active material into said cathode, said cathode characterized by a capacity greater than 100mAh/g after 200 cycles when cycled at 60°C to a complete discharge to an indicated 3 volts over 60 minutes and recharged to an indicated 4.3 volts over 180 minutes.

13. The method of claim 9, further comprising the step of drying the solids removed from said slurry, said drying step taking place at a temperature between 50°C and 140°C.

14. A cathode comprising:

a cathode composition comprising a cathode active material having the general formula of $Li_{1+x}M_yMn_{2-x-y}O_4$ where $0<x\leq0.25$, $0<y\leq0.5$ and M is one or more trivalent

metals from the group Al, Cr, Ga, In and Sc or $Li[Li_{(1-2x)/3}M_yMn_{(2-x)/3}Ni_{x-y}]O_2$ where $0<x<0.5$, $0<y\leq0.25$, $x>y$ and M is one or more metals chosen from Ca, Cu, Mg and Zn, and;

a surface treatment of LiF carried on said cathode active material wherein said cathode active material has x-ray diffraction peaks at 38.6°, 44.84°, and 65.46° 2Θ respectively, wherein from 0.25 to 2.5 percent by weight of said cathode composition is LiF.

15. The cathode of claim 14, wherein said cathode active material is selected from the group consisting of $Li_{1.06}Al_{0.18}Mn_{1.76}O_4$, $Li_{1.06}Cr_{0.1}Mn_{1.84}O_4$, $Li_{1.05}Al_{0.12}Mn_{1.83}O_4$, $Li_{1.17}Cu_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Mg_{0.05}Mn_{0.58}Ni_{0.2}O_2$, $Li_{1.17}Ca_{0.05}Mn_{0.58}Ni_{0.2}O_2$, and $Li_{1.17}Zn_{0.05}Mn_{0.58}Ni_{0.2}O_2$.

16. The cathode of claim 14, wherein said cathode composition is free of Mn_2O_3.

17. The cathode of claim 14, wherein the cathode active material has a median particle size between 4μm and 30μm.

18. The cathode of claim 14, wherein said cathode has a capacity greater than 100mAh/g after 200 cycles.

19. The cathode of claim 14, further comprising a doping metal.

20. The cathode of claim 19, wherein said doping metal is from 0.1% to 15% by weight of said cathode composition and said doping metal is selected from the group consisting of: Mg, Al, Cr, Fe, Ni, Co, Ga, In, Sc, In, Cu and Zn.

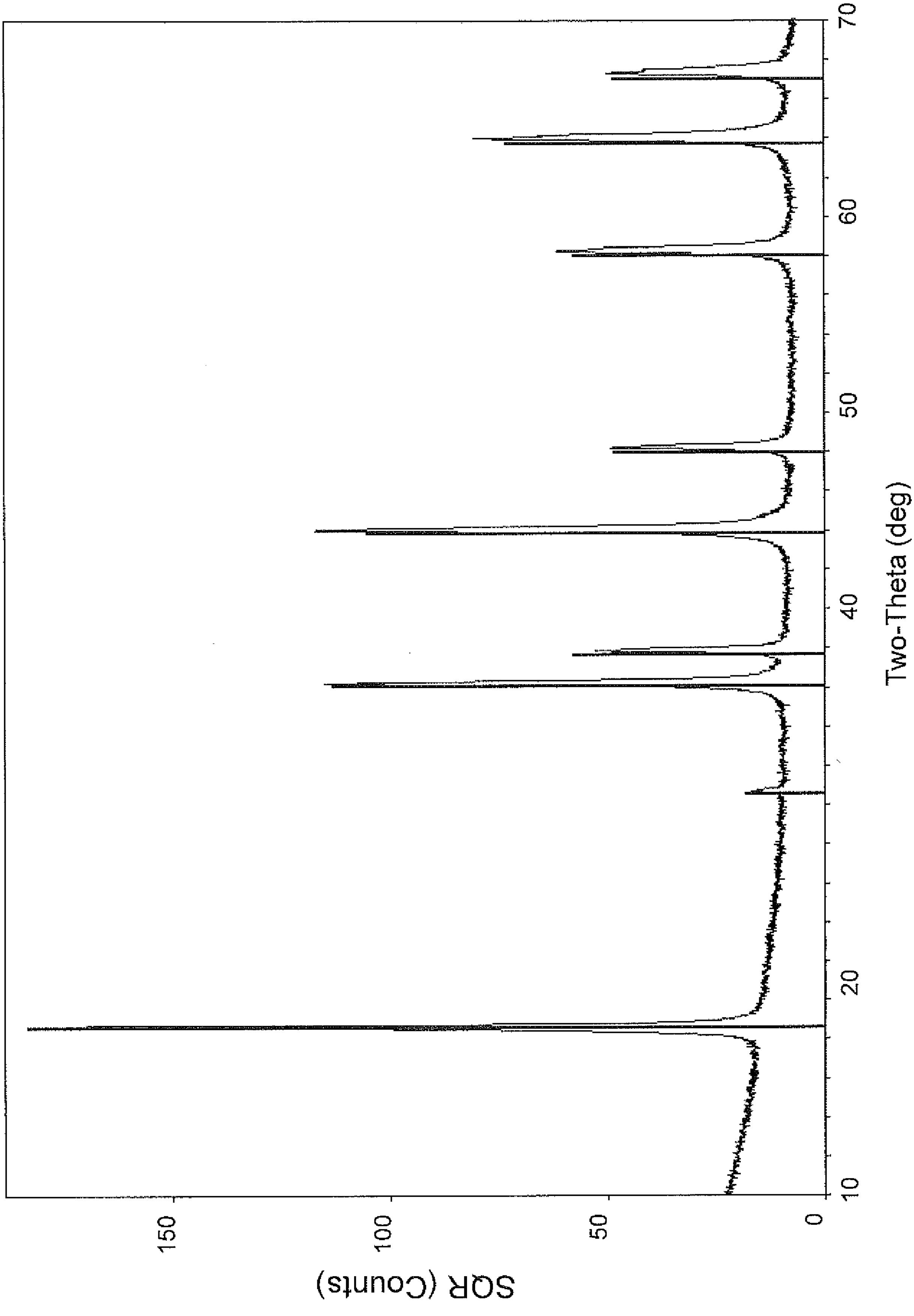


Figure 1a

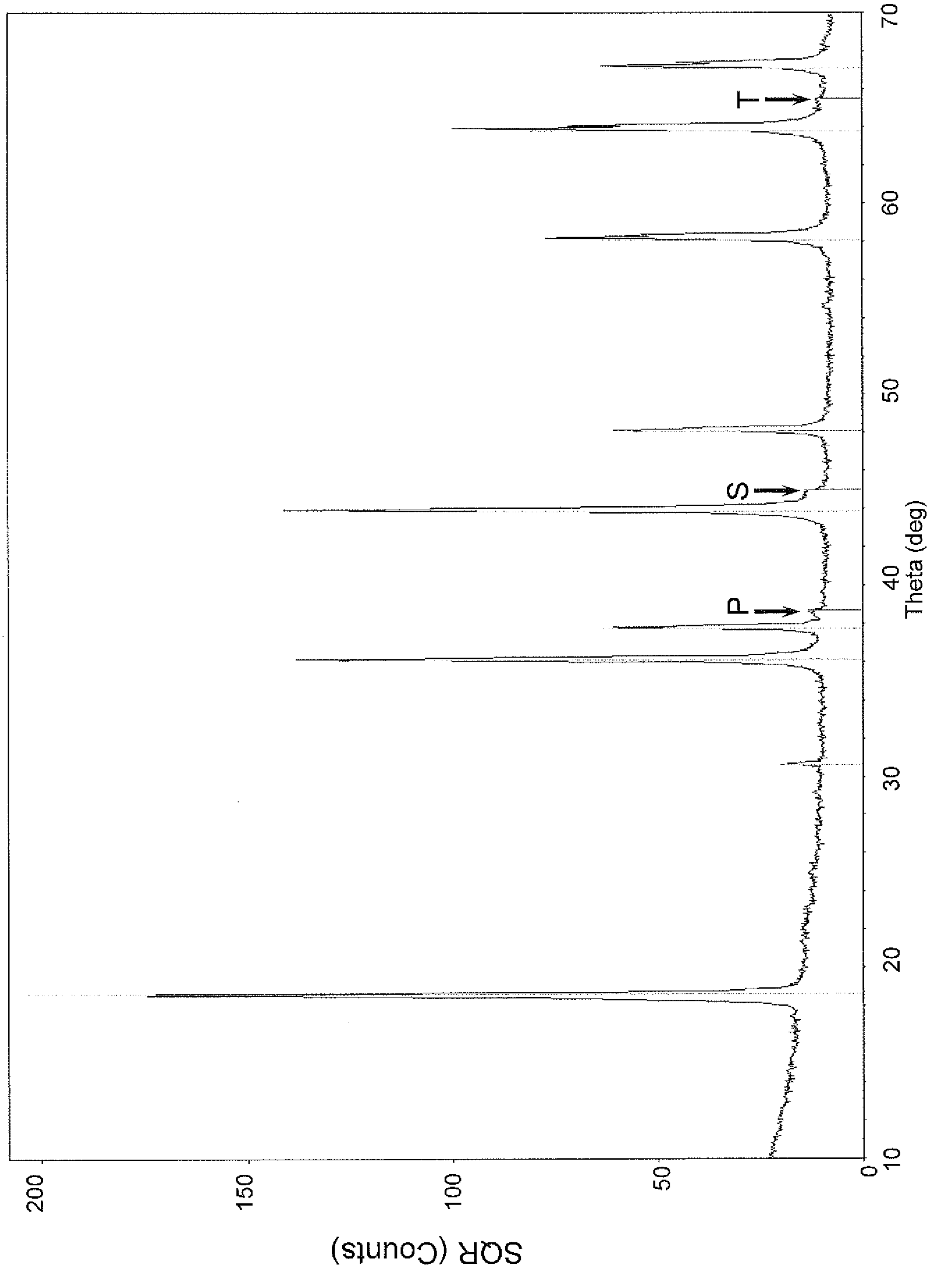
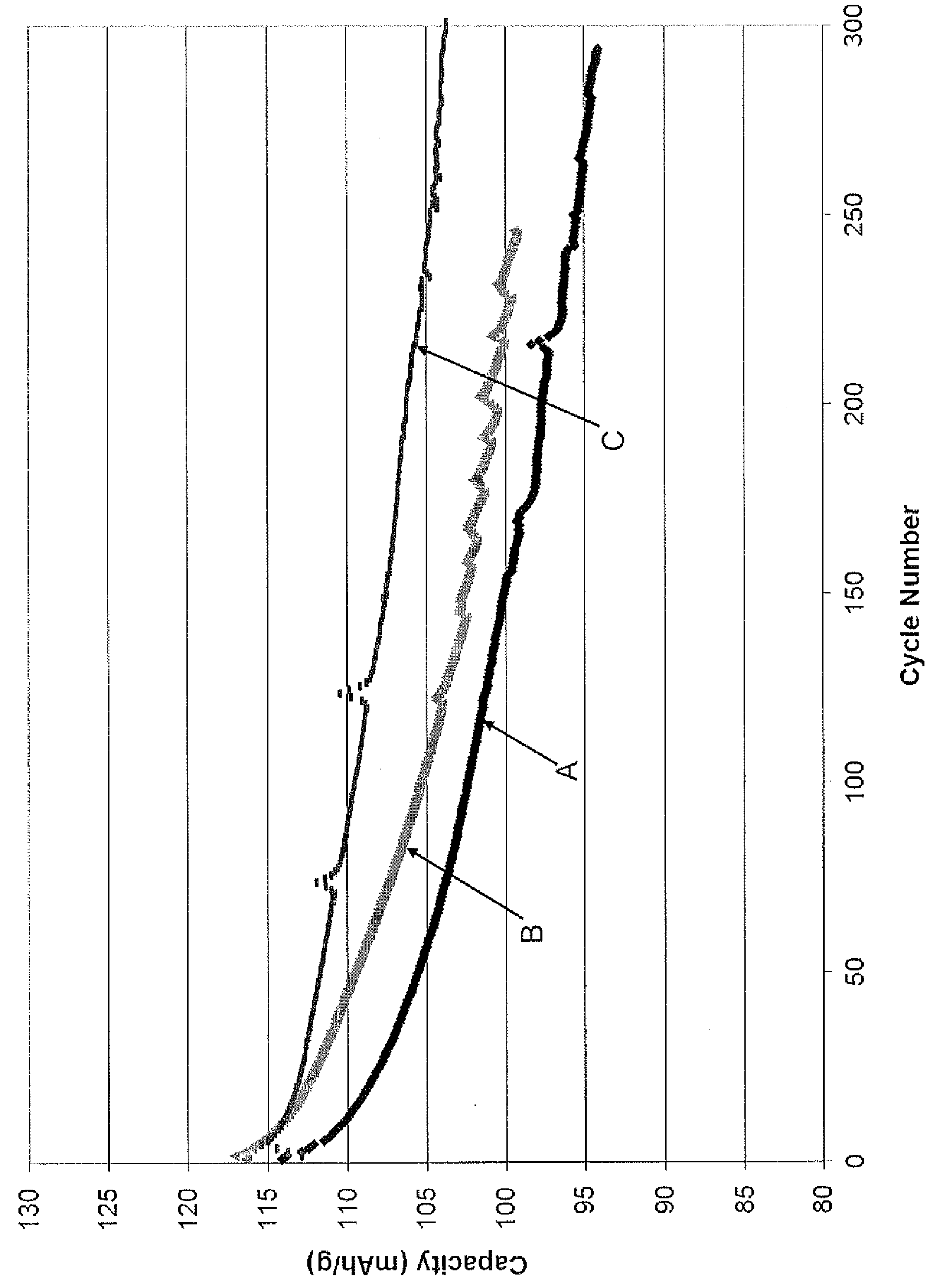


Figure 1b


Capacity (mAh/g)
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125
120
115
110
105
100
95
90
85
80
Cycle Number
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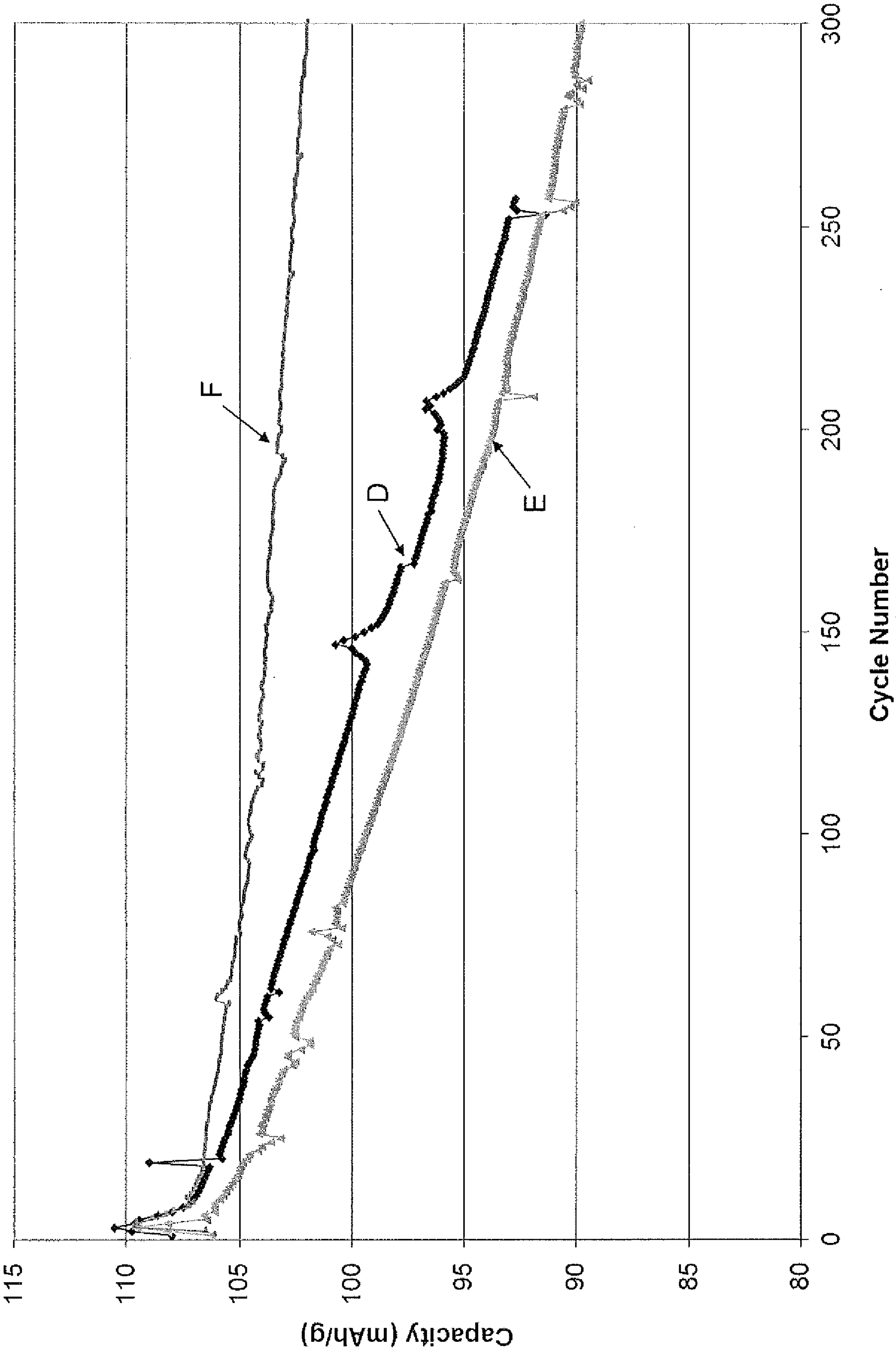
50
100
150
200
250
300
A
B
C

Figure 2


Capacity (mAh/g)
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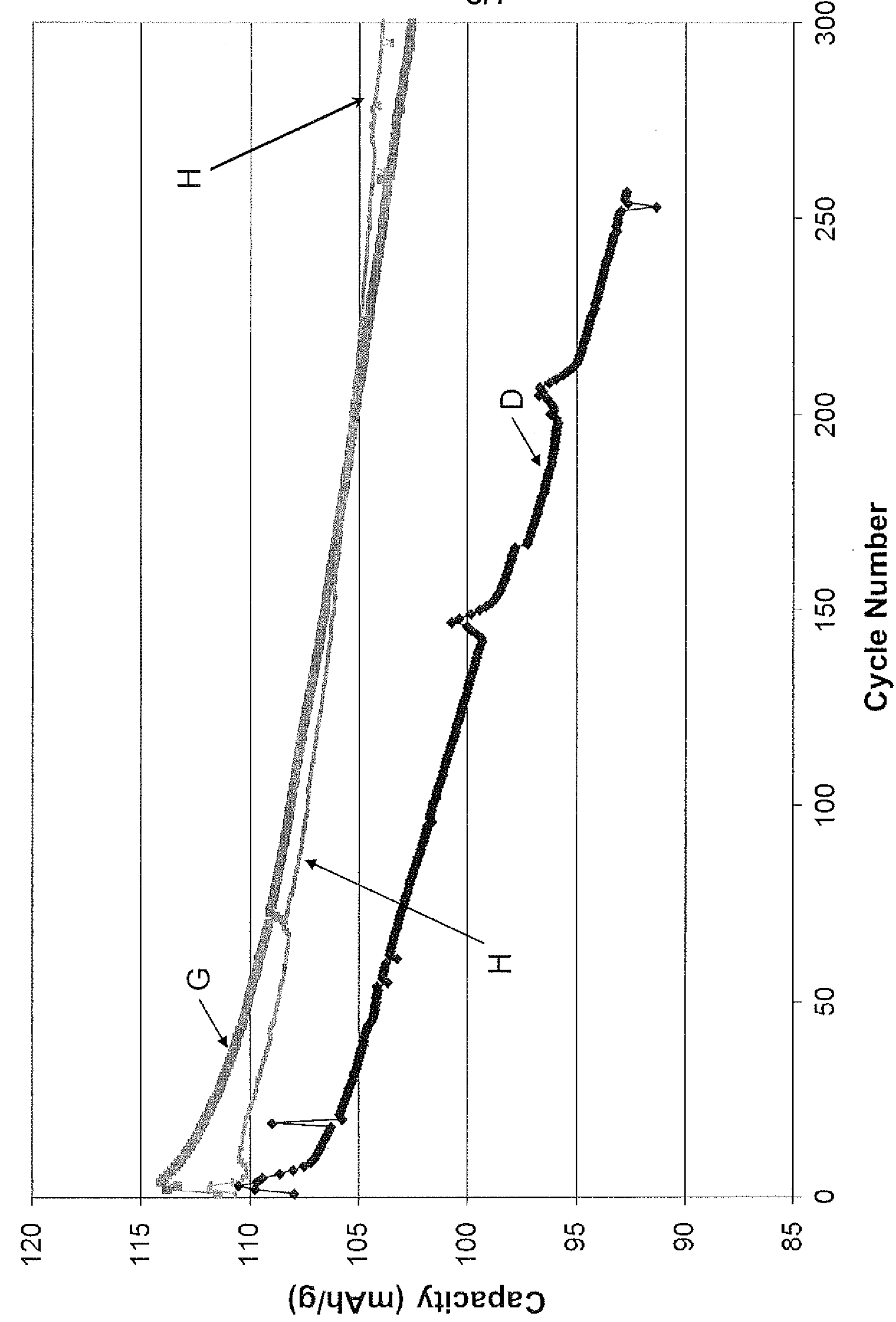
110
105
100
95
90
85
80
Cycle Number
0
50
100
150
200
250
300
F
D
E

Figure 3


Capacity (mAh/g)
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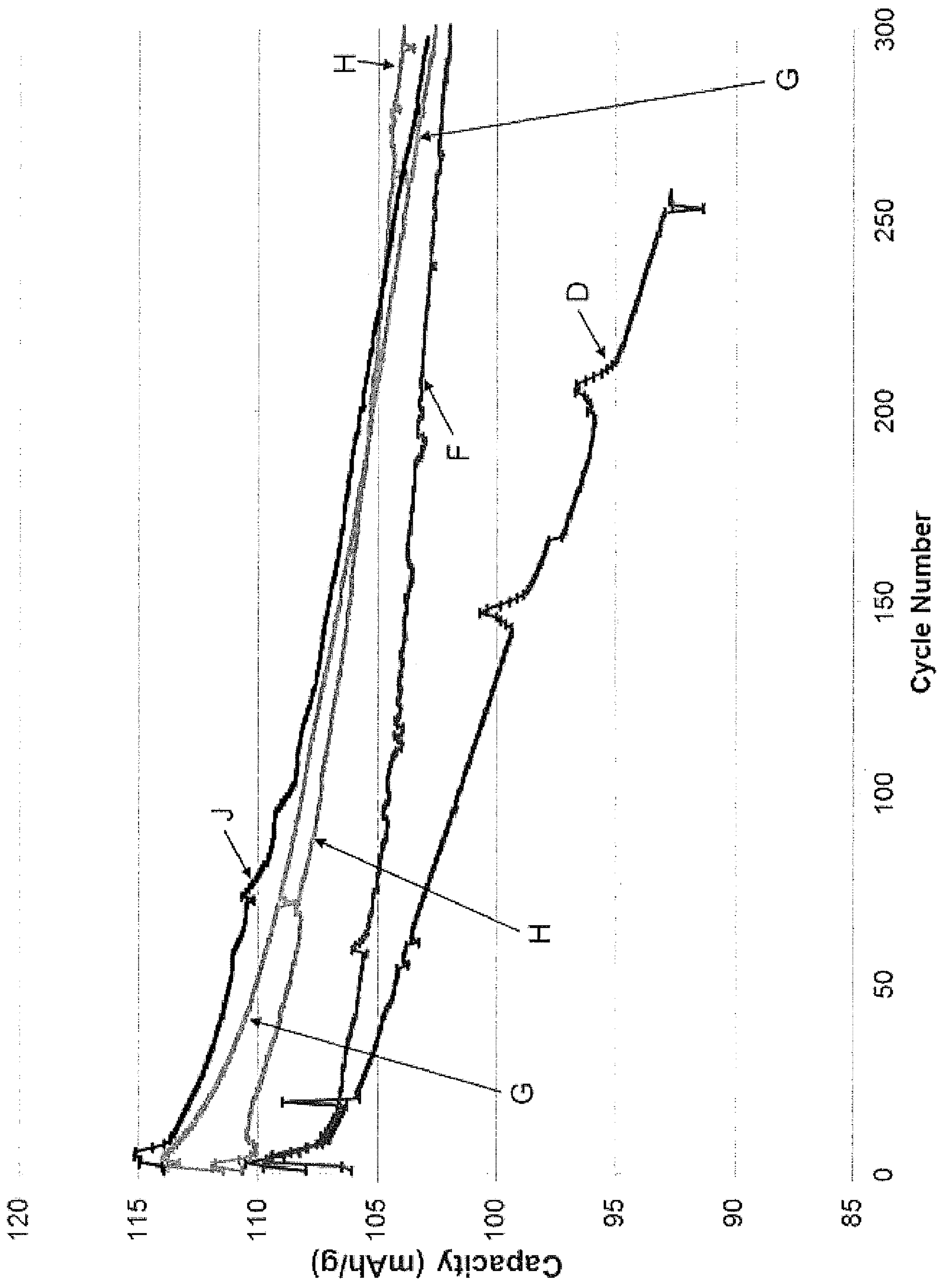
110
105
100
95
90
85
0
50
100
150
200
250
300
Cycle Number
G
H
H
D

Figure 4


Capacity (mAh/g)
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115
110
105
100
95
90
85
Cycle Number
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50
100
150
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250
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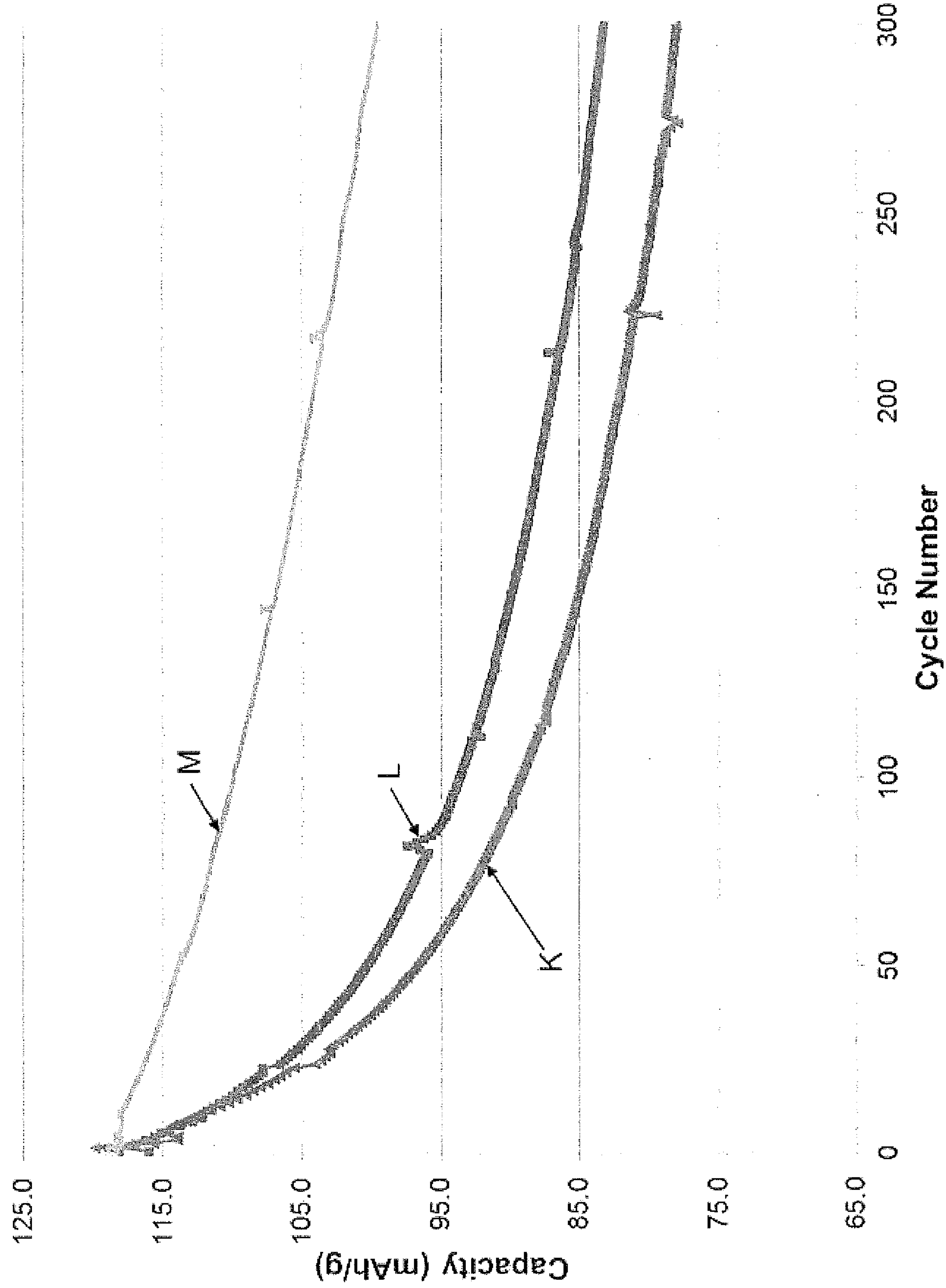
J
G
H
F
D
G
H

Figure 5


M
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K
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115.0
105.0
95.0
85.0
75.0
65.0
Capacity (mAh/g)
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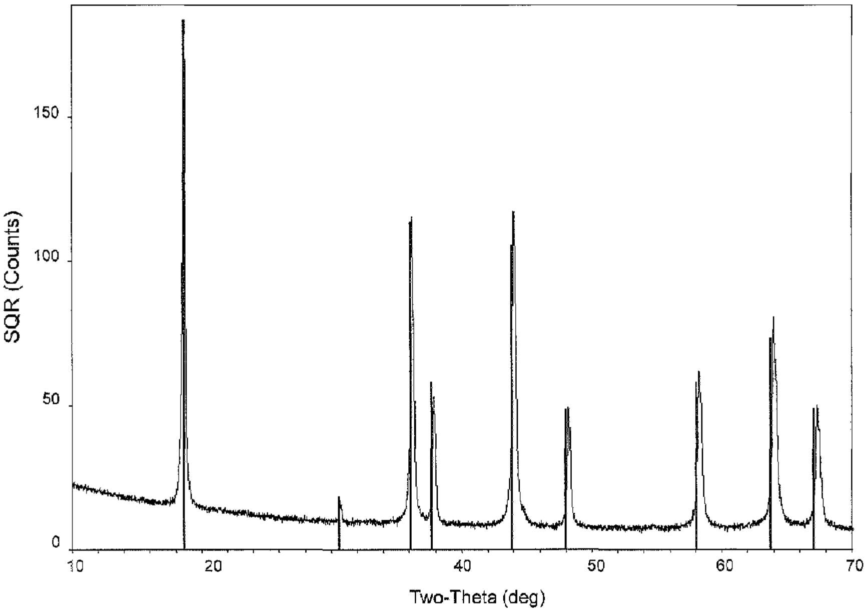
50
100
150
200
250
300
Cycle Number

Figure 6


SQR (Counts)
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100
50
0
10
20
40
50
60
70
Two-Theta (deg)