Bi-2212 based anode materials for Li-ion batteries

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Keywords
2212, based, anode, materials, for, ion, batteries

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Bi-2212 Based Anode Materials for Li-ion Batteries

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Abstract: A number of studies have previously examined the insertion of lithium into superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) materials. A maximum lithium uptake of two moles of lithium per mole of Bi-2212 was reported amongst these studies which corresponds to a capacity of 60 mAh/g. Two Bi-2212 materials are examined here an undoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ and doped Bi$_2$Sr$_2$Ca$_{0.3}$Y$_{0.7}$Cu$_2$O$_8$ material. Both materials exhibited a capacity of over 60 mAh/g in both the as produced state and when subjected to further processing in the form of ball milling in the presence of carbon. The highest initial discharge capacity of 441 mAh/g was demonstrated by the unmilled undoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ material, though more capacity was maintained by the milled materials. In all cases however the cycle life of the materials was poor.

Keywords: Bi-2212, Lithium Battery, Anode

1. INTRODUCTION

High temperature superconductivity with two transitions at 110K and 80K was observed in the Bi-Sr-Ca-Cu-O system [1,2]. Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) has two immediately adjacent Cu-O planes, these planes are perpendicular to the c axis and hence parallel to the a-b plans [3]. A number of studies have investigated the electrochemical insertion of lithium into Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ superconductors [4-8] using compressed powder pellets with no conductivity additive. A number of stoichiometries of the Bi-2212 phase were examined in these investigations and a range of electrochemical properties reported. The amount of lithium inserted into the structure varied between the investigations up to a reported maximum of two moles per mole of Bi-2212 [5]. One investigation suggested Bi-2212 as a potential electrode material for reversible lithium cells [7]. The lithium diffusion coefficients for the two investigations where it was determined ranged from 10$^{-7}$ cm$^2$ s$^{-1}$ [7] to 10$^{-13}$ cm$^2$ s$^{-1}$ [4]. Two different reaction mechanisms were also proposed the first was the insertion of lithium between the bismuth – oxygen planes [6, 8] and the second was the substitution of lithium with copper [8]. Strobel et. al. [8] in fact proposed that the insertion reaction (1) was reversible up to a lithium content of 0.15 mole whilst the substitution reaction (2) occurred at higher lithium content. The presence of copper oxide was not however detected from the higher lithium contents.

Taking the maximum reported lithium content of two moles into account the theoretical capacity of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ would only be 60 mAh/g due to the large molecular weight of the Bi-2212 phase. Assuming the same maximum lithium content is realised for Bi$_2$Sr$_2$Ca$_{0.3}$Y$_{0.7}$Cu$_2$O$_8$ the theoretical capacity is just lower at 58 mAh/g.

\begin{align}
\text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_{8+\delta} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \\
\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} + x\text{Li}^+ + xe^- \rightarrow \text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{2-x}\text{Li}_x)\text{O}_{8+\delta} + x\text{CuO}
\end{align}

2. EXPERIMENTAL

Two Bi-2212 (Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$) samples were examined with nominal compositions corresponding to x = 0 and 0.7. These were produced from nitrate precursor materials through a spray drying process followed by calcining and sintering operations. All calcining and sintering operations were carried out in an air atmosphere. The nitrate precursors (Table 1) were weighed out in the required proportions and dissolved in distilled water with the aid of stirring, nitric acid additions, and a hot water bath. The solution was then retained in the hot water bath whilst it was spray dried using a Yumato Pulvis GB22 unit.

The powder material from the spray drying process was then decomposed in a calcining operation of six hours duration at 550°C in a Eurotherm controlled Ceramic Engineering muffle
furnace. The calcined material was then ground by hand in a mortar and pestle before being placed into 25 mm diameter dies for pellet formation. The pellets were formed by compressing the powders in the metal dies using a hydraulic press with the pressure set on 4000 psi and delivered at this level for 8 seconds.

The pellets were then sintered in a 1300°C Laboratory muffle furnace featuring a Eurotherm 903P controller with a thermal program consisting of a five hour ramp to 850°C, a five hour dwell at 850°C followed by a five hour ramp down to 120°C. The pellets were then reground and pressed in preparation for a second sintering operation. The second sintering operation was carried out at 860°C for the undoped sample (x = 0) and 890°C for the doped sample (x = 0.7) with a thermal program consisting of a two hour ramp to temperature followed by twenty-four hours at temperature and furnace cooling to room temperature. To allow ball milling to be carried out the pellets were once again broken down into powder through hand grinding in an agate mortar and pestle.

Both the doped and undoped materials were then ball milled using a Pulverisette-5 planetary ball mill at a speed of 160 rpm in a steel-milling vessel. The milling vessel had an internal diameter of 85 mm and volume of approximately 140 cm³. The milling media were 5 mm diameter stainless steel balls utilised with a ball to powder ratio of approximately 20:1 for both the undoped (77.631 g balls: 3.874 g powder) and doped (62.934 g balls: 3.144 g powder) materials. The powder charge did not consist of the Bi-2212 material alone as it consisted of Bi-2212 powder along with an addition of Vulcan XC-72 (10.0 and 9.6 weight percent respectively for the undoped and doped samples). Vulcan XC-72 is a form of carbon black which was introduced to improve the conductivity of the material.

Ethanol was also added as a process control additive to the level of the top of the balls. Powder was removed at a number of intervals in small quantities up to a total milling time of 190 hours. Powder was removed at total milling times of 50, 120 and the final milling time of 190 hours. Where milling continued after powder was removed ethanol was added to the milling jar if required to bring it back up to its initial level. The various powders and other results derived from their use will be referred to using a prefix of UBM or DBM followed by the milling time of the powder in hours with the unmilled material referred to as UBM0 or DMB0. The U is indicative of undoped samples (Bi₂Sr₂Ca₁Cu₂O₈₊δ) whilst the D is indicative of the doped samples (Bi₂Sr₂Ca₀.₃Y₀.₇Cu₂O₈₊δ).

Each material was examined using X-ray diffraction (XRD) carried out on a Phillips PW1730 diffractometer with Cu Kα radiation using an accelerating voltage of 40 kV and current of 20 mA. Brunauer –Emmet – Teller (BET) was utilised to determine the specific surface area of final ball milled material of the doped and undoped materials. Degassing and BET measurements were carried out on a Quantachrome Nova 1000 tester with analysis of the results performed with Nova enhanced data reduction software. Samples were vacuum degassed for three hours at 200°C prior to BET measurement of adsorption and desorption isotherms over the P/P₀ range of 0.27 to 0.36.

Electrodes were produced using a slurry made up of the Bi-2212 powders, a 5 wt. % polyvinylidene fluoride (PVDF) binder in dimethyl phthalate (DMP) solution and Vulcan XC-72 as a conductive additive. Using the slurry electrodes were produced by pasting onto copper foil of approximately 1 cm diameter. Pasted electrodes were subsequently dried overnight at 120°C before being pressed and placed into a glove box (Mbraun, Unilab, Germany) prior to assembly in custom Teflon based test cells [9]. The fabrication of electrodes resulted in loadings of approximately 1 mg for all the samples. The final composition of the electrodes corresponded to 75 wt. % powder, 20 wt. % conductivity additive and 5 wt. % PVDF. Cell assembly was completed in the glovebox using 1 M LiPF₆ in a 1:1 mixture by volume of ethylene carbonate (EC) and dimethyl carbonate (DMC) electrolyte (Merck LP30,
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Germany) and lithium foil for the counter electrode in custom Teflon based test cells [9]. Whilst the Bi-2212 materials are being evaluated as anode materials for lithium ion batteries in the test cells they are cathodes versus metallic lithium anodes. During discharge of such cells lithium ions will be inserted whilst during charge they will be removed from the Bi-2212 cathodes.

3. RESULTS AND DISCUSSION

3.1. Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_{8+\delta}$

XRD of the material following the first sintering operation indicated that the Bi-2212 phase had started to form though a number of other phases were also present (Figure 1). Following the second sintering operation Bi-2212 was the main phase (JCPDS card 41-317) though other phases were present in small quantities. On ball milling of the Bi-2212 material significant broadening of the peaks is not evident however the intensity of the peaks are reduced and diminish into the background (Figure 2).

In order to examine the effect of milling on the particle size of the Bi-2212 powders SEM was used to examine the particle size (Figure 3). Only the UBM0 material had a particle size of greater than 1 μm with a particle size of 2 μm. BET analysis reported the specific surface area of the UBM190 material as 30 m$^2$/g. Whilst the specific surface area of the unmilled material was not determined through measurement it can be estimated by considering the surface area on a theoretical basis. Taking the 2 μm particle size of the unmilled material observed using SEM and considering this as the diameter of spherical particles the specific surface area would be under 0.5 m$^2$/g. If instead the particles are considered as cylinders with a 1 μm radius and height of 0.1 μm the specific surface area would be under 3.4 m$^2$/g. Both of these figures are substantially lower than the 30 m$^2$/g determined from measurement of the UBM190 material.

The electrochemical properties determined from constant current charge/discharging (50 μA, 0.70 – 3.00 V) of Bi-2212 electrodes varied with milling time. The first discharge capacity (Figure 4) was highest for the unmilled material (441 mAh/g) whilst the milled materials had the same capacity of 280 mAh/g though the discharge profiles did vary.

The first charge capacity (Figure 5) was also highest for the unmilled material (77 mAh/g) with the capacities of the milled mate-
rials between 64 and 71 mAh/g though the charge profiles varied. Following the second cycle however the charge capacities (Figure 7) were highest for the UBM120 material but were under 42 mAh/g within 10 cycles. The discharge capacities (Figure 6) on the other hand were highest for the UBM190 following the first discharge and were under 42 mAh/g within 10 cycles.

Extraction of lithium from the Bi-2212 structure is difficult as the charge capacities are much lower than the discharge capacities in the initial cycles. Although ball milling reduced the initial discharge capacity the capacity remained higher after the first cycle in the milled materials. The situation was similar with the charge capacity though the capacity of UBM0 was higher than that of UBM50 for the first four cycles. Differential capacity plots of the first charge and discharge of UBM190 (Figure 8) showed a distinct peak at 1.75 V corresponding to lithium insertion during discharge and a single broad peak at 2.7 V corresponding to lithium extraction during the charge.

3.2. Bi$_2$Sr$_2$Ca$_{0.3}$Y$_{0.7}$Cu$_2$O$_{8+δ}$

XRD of the material following the first sintering operation indicated that the Bi-2212 phase was already well formed though other minor phases were also present (Figure 9). Following the second sintering operation the Bi-2212 phase (JCPDS card 41-317) was also dominant with lower amounts of other phases. On ball milling the peaks did broaden though still remained evident above the background (Figure 10).

In order to examine the effect of milling on the particle size of the Bi-2212 powders SEM was used and the DBM0 material had a particle size of 1 μm whilst the milled materials all had a particle size under 1 μm. BET analysis reported the specific surface area of the DBM190 material as 63 m$^2$/g. As was the case for the undoped material the specific surface area of the unmilled material was not measured. It has however been estimated as under 0.9 m$^2$/g considering the 1 μm particles as spheres and under 6.8 m$^2$/g when considered as cylinders (0.5 μm radius and 0.05 μm height). Figures that are well under the 63 m$^2$/g of the DBM190 material.
The electrochemical properties determined from constant current charge/discharging (50 μA, 0.70 – 3.00 V) of Bi-2212 electrodes varied with milling time. The first discharge capacity (Figure 12) was highest for the milled materials which all had a capacity of 300 – 310 mAh/g with varied discharge profiles whilst the unmilled material had a capacity of 267 mAh/g.

The first charge capacity (Figure 13) was also highest for the milled materials (80 – 87 mAh/g) though the charge profiles did vary whilst the capacities of the unmilled material was 53 mAh/g. Following the second cycle however the charge capacities (Figure 15) were highest for the DBM120 material but were under 62 mAh/g within 10 cycles. The discharge capacities (Figure 14) were also highest for BM120 following the first discharge and were under 73 mAh/g within 10 cycles.

Extraction of lithium from the Bi-2212 structure is difficult as the charge capacities are much lower than the discharge capacities in the initial cycles. Ball milling has increased the first charge and discharge capacity as well as that on further cycling over that of the unmilled material.

Differential capacity plots of the first charge and discharge of
DBM190 (Figure 16) showed two distinct peaks at 0.85 and 1.65 V corresponding to lithium insertion at different positions of the layered Bi$_2$Sr$_2$Ca$_0.3$Y$_0.7$Cu$_2$O$_8$ during discharge, and a two broad peaks at 1.0 and 2.5 V corresponding to lithium extraction from different positions of the layered Bi$_2$Sr$_2$Ca$_0.3$Y$_0.7$Cu$_2$O$_8$ during the charge. The different behaviour in differential capacities of Bi$_2$Sr$_2$CaCu$_2$O$_8$ and Bi$_2$Sr$_2$Ca$_0.3$Y$_0.7$Cu$_2$O$_8$ may relate with the doping element yttrium [10], which occupied some positions and make lithium intercalation at Cu-O plane or at positions between Cu-O planes.

The doped and undoped Bi-2212 materials produced through spray drying and modified by ball milling with carbon demonstrated that the microstructure has an important influence on the electrochemical properties of the material. In both cases the discharge capacities were much higher than expected based on the previously reported maximum lithium uptake of two moles of Li per mole of Bi-2212.

Differential capacity plots of the BM190 materials indicated only one reaction on the first charge and discharge for the undoped (Bi$_2$Sr$_2$CaCu$_2$O$_8$) material and two for the doped material (Bi$_2$Sr$_2$Ca$_0.3$Y$_0.7$Cu$_2$O$_8$). The discharge capacities observed for all the materials were much higher than previously reported leaving uncertainty over the reaction mechanism responsible for the capacity. The use of compressed pellets in previous investigations compared to the pasted electrodes utilised here may provide some explanation for the differences observed. The resistances of the pellet electrodes would be expected to be much higher in comparison than the pasted electrodes.

4. CONCLUSIONS

Both the doped (Bi$_2$Sr$_2$Ca$_0.3$Y$_0.7$Cu$_2$O$_8$) and undoped (Bi$_2$Sr$_2$CaCu$_2$O$_8$) materials demonstrated much higher capacities than expected based on the previously reported maximum lithium uptake of two moles of Li per mole of Bi-2212 (~60 mAh/g). The highest discharge capacity (441 mAh/g) was demonstrated by the unmilled and undoped material though the milled materials retained more of their capacity on cycling. The initial discharge capacities of the milled doped and undoped materials were all approximately 300 mAh/g. After cycling however the capacity of the doped BM190 material was higher than that of the other materials. The charge and discharge capacities of the undoped BM190 material after ten cycles as well as the specific surface area are approximately half those of the doped BM190 material. The electrochemical properties of the doped and undoped materials were similar despite the specific surface area of the doped material (63 m$^2$/g) being over two times that of the undoped material (30 m$^2$/g).

5. REFERENCES