Fabrication procedure for $LiMn_2O_4$/Graphite-based Lithium-ion Rechargeable Pouch Cells

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The following procedures were developed at LBNL specifically for making electrodes and batteries of $LiMn_2O_4$ (spinel) and MCMB (meso carbon micro beads) graphite for high-power applications (HEVs). Electrode performance can be very dependent on the materials used so it is pointed out that Toda M809 was used for the cathode active material and MCMB 10-28 from Osaka Gas was used for the anode active material. The conductive additives were Dankon black, an acetylene black, and SFG-6, a micron-size graphite. The binder used was PVdF (Kureha 1100). More details of these procedures can be found in the lab notebook of Gao Liu. These procedures are documented here but are continuously being refined, and should therefore be considered a work in progress.

I. Cathode

1. Slurry for both electrodes (Reference to Liu 5 notebook page 11. 9-19-06)

This slurry making procedure is optimized for both the spinel cathode material TodaM809 and the MCMB10-28 anode material.

Composition:
The cathode electrode for a spinel cell is composed of 81.6% $LiMn_2O_4$ active material, 6.4% acetylene black, 4% SFG-6 graphite, and 8% PVDF binder.

- Materials and % w/w
  - Toda spinel M809 $Li_{1.15}Mn_2O_4$ – 81.6%
  - Denkon acetylene black – 6.4%
  - Timcal Ltd. SFG-6 graphite – 4%
  - Kureha 1100 PVdF – 8%

Binder solution:
5% wt. PVDF in NMP solution is made and stored in the glove box. Kureha #1100 PVDF is dried at 120 ºC under high vacuum for 12 hours prior to mixing. Bio-grade anhydrous NMP solution is from Sigma-Aldrich.

- Materials and % w/w
  - Kureha #1100 PVdF – 5%
  - Simga Aldrich NMP – 95%

Conductive glue:
Dankon ™ black is dried at 190 ºC under high-vacuum for 24-hours prior to use. An appropriate amount of carbon black is mixed with the binder solution to make a carbon

black to PVDF weight ratio of 4:5. The mixture is sonicated for 30-minutes at 70% power using a Branson 450 Sonicator to improve the carbon black dispersion. The process is performed in a glove box.

- Materials and % w/w
    - Dankon black – 4 g
    - PVdF solution – 100 g
- Equipment and settings and time
    - Branson 450 sonicator – 70% power – 30 min.

Slurry:
20.36 g of the conductive glue is mixed with 10 g $LiMn_2O_4$ and 0.49 g SFG-6. The mixture is homogenized using Polytron PT10-3S Homogenizer at 3000-5000 RPM for 5 minutes. A viscous slurry is acquired. This process is performed in a glove box.

- Materials and % w/w
    - Conductive glue – 20.36 g
    - Toda Spinel – 10 g
    - SFG-6 – 0.49 g
- Equipment and settings and time
    - Polytron PT10-3S Homogenizer – 3000 to 5000 rpm – 5 min.

2. Casting Electrode:

Equipment and current collector preparation:
The Mitutoyo doctor blade is set at a height of 250 μm for casting; the draw down coater (manufacturer: Yoshimitsu Seiki; Model: YOA-B) casting speed is set at 5. (The ratio of the height of the blade and the final electrode thickness (in dry state) is set ca. 3:1 of the final target thickness.) Trace NMP solvent is spread on the perforated glass table top of the casting machine before Al foil (28 μm thick) is spread across the top. The Al foil is then tightly held to the glass by vacuum and the trace NMP. Trace NMP is also spread on the surface of the Al foil to improve the wettability of the slurry with Al foil. The trace NMP on the Al surface is allowed to evaporate before casting an electrode.

(Suggestion 1: In the future we may consider trying to improve the adhesion of the laminate to the Al or Cu foil and hence reduce the electrode resistance, by roughening the foil surface after it has been placed on the coater surface with memory cloth and then cleaning the surface with NMP solvent. The roughening may remove the oxidation film on the Al/Cu foil and increase the contact area of active material with the current collector.)

- Materials and wt%
    - Aldrich NMP – trace
    - Al foil – 1 m
- Equipment and settings and time
    - Doctor blade – 250 μm
    - Yoshimitsu Seiki drawdown coater – 5

Casting:

The slurry is poured adjacent to the doctor blade holder and spread out across the blade; the casting is started at a constant speed of 5. After the casting arm has stopped, the IR lamps are turned on for an hour to bake out the NMP solvent. The laminate is then dried at 120°C for an additional 12-hours under high-vacuum. This process is performed in the glove box and the antechamber affixed to the glove box.

- Materials and wt%
    - Slurry – 12 ml
- Equipment, settings, time
    - Three IR lamps – 250 W – 1 hour
    - Antechamber – full vacuum – 12 hours

Electrode Initial Characterization:

A portion of the cathode electrode is weighed and the total weight, including current collector, is recorded. It should be *ca.* 20 mg/cm^2, which translates to 0.94 mAh/cm^2 based on the density of the aluminum foil, the formulation proposed, and the manufacturer's reported a 1st charge capacity of 90 mAh/g, 1st discharge capacity of 89 mAh/g, and efficiency of 98.3%. A Swagelok cell with electrode area of 1.27 cm^2, with lithium as counter and reference electrodes, is assembled to test the capacity of the electrode. LP40 electrolyte from Ferro, America is used. The initial capacity test is performed at C/25 charge and discharge current densities based on the capacity calculated above. The first charge capacity we find for this material is 0.97 mAh/cm^2, and the first discharge capacity is 0.90 mAh/cm^2. This translates to a first cycle efficiency of 92%. (Liu5-Pg 33) The Swagelok cell is assembled in a glove box and tested at ambient conditions.

- Materials and size
    - Cathode laminate – 1.27 cm^2
    - Lithium foil (high purity from Cyprus Foote Mineral) – 1.6 cm^2
    - LP40 electrolyte – enough to wet all components
- Equipment, settings, and time
    - Swagelok cells

3. Calendaring

Electrode cutting:
Once satisfied with the capacity of the laminate, it is cut into 3 cm by 4 cm rectangles with a 1cm by 0.5cm tab on the upper right side of the electrode with a punch. The electrode material on the tab region is scraped away with a flat head knife, and may further cleaned with hot NMP. At this point, each electrode should be weighed and the weight recorded. Warning: use of NMP at this stage should be done with great caution as residual NMP is known to lead to delamination of electrodes.

- Materials and size
    - Cathode laminate – 3 cm by 4 cm
    - Aldrich NMP – 5 ml
- Equipment, settings, time
    - Customer built punches by Lanval Poinçons et Matrices Ltée in Canada.

Calendaring:
The target porosity of a spinel-based electrode for an HEV application is 40%. This results in a target thickness of 91 μm, including current collector.

The calendaring machine (manufacturer: International Rolling Mills) temperature control is left off. The electrode is sandwiched between two sheets of Al foil to prevent contamination of the rollers. The distance between rollers should be adjusted to the desired thickness, taking into account the thickness of the two aluminum sheets. The rolling speed is sit at a low speed 2. The electrodes are fed through the rollers two or three times until the desired thickness is achieved.

Each electrode should be measured for thickness using a micrometer and weighed again with the total capacity calculated and recorded.

- Materials and amount
    - Laminates
- Equipment, settings, time
    - IRM calendaring machine – temperature control off, roller speed at dial 1.

II. Anode
The procedures for making anode laminates are similar to those for the cathode above. Differences are spelled out below.

1. Slurry: (Reference to Liu5-pg24)

Composition:
Anode electrode for the spinel cell is composed of 92% MCMB10-28 graphite active material, 8% of PVDF binder (Kureha 1100). MCMB is a gift from Osaka Gas, Japan.

7.8 g of the MCMB10-28 powder is mixed with 13.5 g PVDF (Kureha 1100, 5%) binder solution. The mixture is homogenized at 3000-5000 RPM for 5 minutes. This process is performed in a glove box.

- Materials and wt %
    - Osaka Gas MCMB 10-28 – 92%
    - Kureha #1100 PVdF – 8%
- Equipment, settings, and time
    - Polytron homogenizer – 3000 to 5000 rpm – 5 minutes

2. Casting Electrode: (Reference to Reference to Liu5-pg24)

Preparation:
Doctor blade set at 150 μm high for casting, drawdown coater casting speed set at 5. Trace NMP solvent is spread on the glass surface of the coater table top before Cu foil (30 μm thick) is spread across it. The Cu foil is tightly held down by applying the vacuum in the presence of the NMP. Trace NMP solvent is also spread on the Cu foil

surface to improve the wettability of the slurry. The trace NMP is evaporated before casting.

Special note: The Cu foil of 28 μm appears to be too thick for calendering. Its mechanical properties (particularly stiffness) are not compatible with the dried anode laminate. The laminate is easily stripped off of the current collector after calendaring. Perhaps 15 μm Cu foil would work better.

- Materials and amount
  - Cu foil – 30 μm by 1 m
  - Aldrich NMP – trace (5 ml)
- Equipment and settings
  - Doctor blade – 150 μm

Casting:
The height of the doctor blade in relation to the final electrode thickness (in dry state) is set at a height of *ca.* 2:1. Immediately after stopping the homogenization, the slurry is spread out across the blade, and the casting stared at a constant speed of 5. After the casting arm stops, the IR lamps are turned on for an hour to bake out the NMP solvent. The laminate is dried at 120 °C for an additional 12 hours under high vacuum. This process is done in a glove box and the antechamber affixed to the glove box.

- Materials and amount
  - Anode slurry – 12 ml
- Equipment, settings, time
  - Yoshimitsu Seiki drawdown table – 5
  - Three IR lamps – 250 W – 12 hours

Electrode Initial Characterization:
The electrode is weighed and the total weight including current collector is recorded. It should be *ca.* 38.1 mg/cm^2. The manufacturer of MCMB (Osaka Gas, Japan) does not provide a specific capacity nor other electrochemical test data for this material. A Swagelok cell with electrode area of 1.27 cm^2, lithium as counter and reference electrodes, is assembled to assess the capacity of the electrode. LP40 electrolyte from Ferro, Japan is used. The first charge capacity is measured at 340 mAh/g and the first charge capacity is 277 mAh/g. The irreversible capacity is 23%. (Liu5-Pg 27) The cell is assembled in a glove box and tested at ambient conditions. (Recent results with coin cells show a reduced first irreversible efficiency, down to around 10%.)

- Materials and size
  - Anode laminate – 1.27 cm2
  - Lithium foil (high purity from Cyprus Foote Mineral) – 1.6 cm^2
  - LP40 electrolyte – enough to wet all components
- Equipment, settings, and time
  - Swagelok cells

4. Calendaring

Electrode cutting:

The laminate is cut into 3.15 cm by 4.15 cm rectangle with a 1 cm by 0.5 cm tab on the upper right side of the electrode. This procedure is carried out with a pouch. The electrode material on the tab is scraped away with a flat-head knife, and may further be cleaned with hot NMP (see note of warning under cathode). At this point, each electrode should be weighed and the weight recorded. This process is performed in a glove box.

- Materials and size
    - Cathode laminate – 3 cm by 4 cm
    - Aldrich NMP – 5 ml
- Equipment, settings, time
    - LPM punch

Calendaring:
The anode thickness is targeted such that the void volume is 40%. This should result in an electrode of 61 microns, including Cu current collector.

The temperature of the calendaring machine is left at ambient conditions for pressing. The electrode is sandwiched between two sheets of Al foil to prevent contamination of the rollers. The distance between the rollers is adjusted to the desired thickness with consideration of the additional thickness contributed by the Al sheets. The rolling speed is sit at a low speed of 2. The electrodes are fed through the two rollers two or three times until the desired thickness is achieved. This process is performed in a glove box.

Each electrode is weighed again, and the weight recorded, total capacity calculated, and the thickness measured with a micrometer.

- Materials and amount
    - Laminates
- Equipment, settings, time
    - IRM calendaring machine – temperature control off, roller speed dial at 1

III. Tab lead welding

An Al tab is used for the cathode and a Ni tab for anode. The tab lead is manufactured by Showa, Japan. A piece of thermal plastic glue is attached to each of the tab leads by the manufacturer for better adhesion between the pouch and the lead. The Al tab lead is ultrasonically welded to the Al current collector such that the lower edge of the plastic glue is 2 cm from the top edge of the electrode. This process is performed in a glove box.

- Materials and amount
    - Ni tabs and Al tabs with glue – 1 for the anode and 1 for the cathode
    - Cathode and anode laminates
- Equipment, setting, time
    - AM Tech Ultra Weld 40 ultrasonic welder

IV. Electrode assembly

The electrodes are dried at high-vacuum at 60 C for 12 hours. The separator is cut into a 3.5 cm by 4.5 cm rectangle and dried under high-vacuum at room temperature for the

same amount of time. Cathode/separator/anode are stacked one upon the other with the laminates facing each other through the separator. The separator is positioned such that all four sides stick out. Since the anode is slightly larger than the cathode, the anode should over lap all four edges of the cathode. A 3.5 cm by 4.5 cm by 2 mm thick Teflon sheet is set behind the anode electrode to provide mechanical strength for the cell. This process is performed in a glove box.

- Materials and amounts
    - Electrodes with tabs and separator - ~3cm x 4cm pieces

V. Pouch cell assembly

A Fuji vacuum sealer is used to seal the pouch cells. The electrode feedthroughs need to be sealed in place first. The opposite edge of the pouch is then sealed. Only one side is left open for electrolyte filling. The sealer is pressed all the way down for 10 seconds for each sealing.

0.25mL of electrolyte is added between the cathode, anode, and separator. Two to five minutes are allowed to pass for the electrolyte to permeate throughout the entire electrode assembly before the cell is completely sealed under vacuum.

- Materials and amount
    - Pouch cell
- Equipment, settings, and time
    - Fuji vacuum sealer, vacuum and heat settings at the maximum 10, 10 s per side

The pouch cell is put in a test fixture and 10 psi pressure applied. The cell is put through formation cycles at 30°C in an oven.

- Materials and amount
    - Pouch cell
- Equipment
    - Cyclers

After the formation is finished, the pouch is cut open, cell degassed under vacuum of the cell sealer and the cell re-sealed.

- Materials and amount
    - Pouch cell
- Equipment, settings, and time
    - Fuji vacuum sealer, vacuum and heat settings at the maximum 10, 10 s per side

The cell is transferred out of the glove box for EV and HEV testing.

- Materials and amount
    - Pouch cell
- Equipment
    - Cyclers