SURFACE VEHICLE RECOMMENDED PRACTICE

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(R) Recommended Practice for Determining Material Properties of Li-Battery Cathode Active Materials

RATIONALE

The rapid electrification of the automobile market has spurred an increase in the production of lithium ion batteries. The cathode active material—the energy storage material on the positive electrode of the battery—is a critical component of the battery, occupying a substantial fraction of its weight and cost. Accordingly, understanding the cathode active material's chemical and physical properties are vital to engineering an appropriate battery and, ultimately, vehicle. In this SAE Recommended Practice, a set of characterization methods is provided to evaluate different cathode active materials under a uniform framework. Pass/fail criteria is not included in this document as it is under the discretion of the individual manufacturer to establish their internal benchmarks.

INTRODUCTION

The most prevalent lithium ion battery cathode active materials are transition metal oxides. These materials can be divided into two classes:

- Layered structures (e.g., $LiNiO_2$ [identified as LNO], $LiNi_xCo_yAl_zO_2$ [identified as NCA], and $LiNi_xMn_yCo_zO_2$ [identified as NMC], where x, y, and z sum to 1), and

- Non-layered structures such as olivine (e.g., $LiFePO_4$ [identified as LFP]) and spinel (e.g., $Li_4Ti_5O_{12}$ [identified as LTO]).

While differentiation between these materials is beyond the scope of this document, the market is generally advancing towards high energy materials utilizing elements with less market volatility.

Due to the difference in chemical composition and synthesis conditions, the chemical and physical properties of the cathode active material can vary substantially. Accordingly, in this document, a set of characterization techniques is provided which can be applied to all cathode active materials. A manufacturer can use these techniques to obtain material parameters necessary to evaluate a supplier, set benchmarks for internal engineering, and for product road mapping.

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1. SCOPE

This SAE Recommended Practice provides a set of test methods and practices for the characterization of lithium ion battery cathode active material.

It is beyond the scope of this document to establish criteria for the test results, as these are usually established between the vendor and customer. It should be noted that materials properties can vary substantially between classes of materials (e.g., LNO and LFP) and caution should be exercised when attempting to directly compare their chemical and physical properties. While these distinctions are important for the manufacturer, this document focuses on the techniques to measure the materials properties and not their absolute or relative values. Future materials such as solid-state batteries and sulfides are beyond the scope of this document.

It is beyond the scope of this document to examine the rheological properties of the cathode material dispersed in a coating slurry since such properties are influenced by the conductive additive, binder, and solvent, which are determined by the coating process.

It is beyond the scope of this document to examine the electrochemical properties of cathode materials since these are influenced by electrode and ultimately cell design. Due to the difference in electrical and electrochemical properties of the cathode material, it is unrealistic to establish an electrode and cell design that would justly compare different cathode active materials.

2. REFERENCES

2.1 Applicable Documents

The following publications form a part of this specification to the extent specified herein. Unless otherwise indicated, the latest issue of SAE publications shall apply.

2.1.1 SAE Publications

Available from SAE International, 400 Commonwealth Drive, Warrendale, PA 15096-0001, Tel: 877-606-7323 (inside USA and Canada) or +1 724-776-4970 (outside USA), www.sae.org.

SAE J1715	Hybrid Electric Vehicle (HEV) and Electric Vehicle (EV) Terminology
SAE J1715/2	Battery Terminology

2.1.2 ASTM Publications

Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, Tel: 610-832-9585, www.astm.org.

ASTM C1274-10	Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption
ASTM D618-00	Standard Practice for Conditioning Plastics for Testing
ASTM D6304-07	Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils and Additives by Coulometric Karl Fischer Titration
ASTM D7481-09	Standard Test Method for Determining Loose and Tapped Bulk Densities of Powders Using a Graduated Cylinder
ASTM D7785-12	Standard Test Method for Water in Lint Cotton by Oven Evaporation Combined with Volumetric Karl Fischer Titration
ASTM E70-07	Standard Test Method for pH of Aqueous Solutions with Glass Electrode
ASTM E203-08	Standard Test Method for Water Using Volumetric Karl Fischer Titration

ASTM E537-12	Standard Test Method for the Thermal Stability of Chemicals by Differential Scanning Calorimetry
ASTM E1981-98	Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry
ASTM E2550-11	Standard Test Method for Thermal Stability by Thermogravimetry
ASTM E2651-10	Standard Guide for Powder Particle Size Analysis

2.1.3 External Organizations

International Centre for Diffraction Data, http://www.icdd.com/.

3. DEFINITIONS

Except as noted below, all definitions are in accordance with SAE J1715 and SAE J1715/2.

4. SAMPLE PREPARATION

Samples should be handled and/or conditioned following the manufacturer's recommended safety data sheet.

The tests in this recommended practice are to be performed at standard laboratory atmosphere, defined in ASTM D618-00 (Section 3).

5. PHYSICAL PROPERTIES

5.1 Bulk and Tap Density

The method as described in ASTM D7481-09 is recommended, with the following clarification:

Prior to analysis, the material should be passed through a sieve to prevent agglomeration.

5.2 Surface Area

The methods as described in ASTM C1274-10 are recommended.

5.3 Particle Size (Primary and Secondary Particle, Distribution)

The methods as described in ASTM E2651-10 are recommended.

6. THERMAL PROPERTIES

6.1 Thermal Stability (Powder Only; Powder in Electrolyte)

The thermal stability of the material by itself or in electrolyte may not provide a complete picture of the thermal stability of a full cell.

For the purposes of this document, the state of charge (SOC) of the active material is not changed. The material is tested as synthesized (generally, this means fully lithiated in the cathode of $LiMO_2$, LiM_2O_4, and $LiMXO_4$). To adjust SOC requires definition of electrode formulation, formation protocols, instructions for cell assembly and disassembly, and instructions on rinsing of electrodes to prevent changes to surface layers. Some of these procedures are material (electrode formulation, formation) dependent while others (rinsing while preventing damage to surface layer) are not yet defined. As a result, procedures to modify the SOC of the materials are beyond the scope of this document.

6.2 Thermogravimetric Analysis (TGA) (Not to be Used with Electrolyte)

ASTM E2550-11 provides general information on the usefulness of the technique and operating principles.

Instrument heats the material at a constant rate until a desired final temperature is reached. The rate of temperature increase is set by the user. The atmosphere should be selected so that it is inert to the material (i.e., nitrogen or argon atmosphere).

The upper temperature limit is often limited by the pan material. Aluminum oxide pans are typically used up to 600 °C, while platinum pans can be used up to 1000 °C. The maximum temperature should be chosen to examine the phases of interest of the cathode material.

The instrument keeps a continuous record of the mass of the material in the sample pan. Any change to the material resulting in a change in mass will be detected.

6.3 Suggested Test Parameters

- Initial sample size: 10 to 50 mg (follow instructions for particular instrument)
- An open pan can be used to hold the sample
- Temperature ramp: 1 °C/min

Ideally, the gaseous species evolved from the sample are routed to a mass spectrometer for identification. Alternately, post TGA analysis, such as XRD, could be used to identify crystalline phases in the resulting material and so indirectly help identify the evolved gaseous species.

6.4 Differential Scanning Calorimetry (DSC)

ASTM E537-12 provides general information on the usefulness of the technique and operating principles.

The DSC measures heat flow to and from a sample as a function of temperature. As a result, it can measure thermal energy generated by the reaction of electrode with electrolyte.

6.4.1 Samples without Electrolyte

This test is often run simultaneously with the TGA technique detailed in 6.2 to measure the heat flow into the material. Accordingly, the same sample preparation can be followed. The heat flow of the material will show peaks indicating phase changes of the material as the temperature is increased.

6.4.2 Suggested Test Parameters

- Initial sample size: 10 to 50 mg (follow instructions for particular instrument)
- An open pan (with no cover) can be used to hold the sample
- Temperature ramp: 1 °C/min

6.4.3 Samples with Electrolyte

A hermetically sealed pan should be used to prevent reaction of electrolyte with air (particularly water). Pan will open when gaseous components cause sufficient increase in pressure—temperature data beyond this point is no longer meaningful. Hermetic pans can open energetically, as a result users are cautioned to perform a careful review of the experimental setup, including compatibility of the different materials. Ideally, this test should be performed in equipment that is housed in an enclosure.

Samples should be prepared in an inert environment.

6.4.4 Test Parameters

- Initial sample size: 10 to 50 mg (follow instructions for particular instrument)
- Temperature range: 25 to 400 °C
- Temperature ramp: 1 °C/min

6.5 Accelerating Rate Calorimetry (ARC)

ASTM E1981-98 provides general information on the usefulness of the technique and operating principles.

ARC is adiabatic system which increases sample temperature at a user set heating rate until an exothermic reaction is detected, at which point the heat flow out of the sample is measured.

ARC data can generally be correlated to DSC data.

ARC samples use more material than DSC samples. ARC samples allow the use of significant amounts of excess electrolyte which influence the test results.

Users interested in measuring the heat flow from a material are encouraged to first investigate using DSC. If ARC is pursued, users should define an appropriate amount of electrolyte to be used. The comments made at the beginning of 6.1 regarding changes in SOC of the material apply to preparation of samples for ARC.

7. CHEMICAL PROPERTIES

7.1 Chemical Content (Li, Transition Metal, Ratio of Li/TM, Impurities)

Inductively coupled plasma atomic emission spectroscopy—also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES)—is recommended for quantification of the elemental content, except carbon and sulfur, of the materials. ICP methods are not recommended for carbon and sulfur quantification because these may not be discernible from the inherent background levels.

If the cathode active material does not completely dissolve in the matrix or in acid, microwave-assisted acid digestion can be used to solubilize the cathode active material in a suitable ICP matrix. It is recommended to refer to the instrument application guidelines, but typically the cathode active material is added to a mixture of hydrochloric acid and nitric acid and heated in the microwave cavity to fully dissolve the cathode active material.

For quantification of the carbon or sulfur content, a combustion/evolved gas analyzer for carbon and sulfur content could be used. Combustion techniques will measure organic carbon content. Users wanting to quantify elemental content down to the parts per billion level are advised to use ICP-mass spectrometry (ICP-MS).

In all cases, ICP-OES, ICP-MS, and combustion/evolved gas measurement is to be performed per instrument guidelines.

7.2 Residual Lithium Content

Cathode active materials are typically synthesized with an excess of lithium to ensure that the main particle is fully lithiated. To approximate the soluble amount of lithium on the surface of the material, the following technique is used:

- A few grams of cathode active material are added to de-ionized water and stirred for 15 minutes
- The cathode active material is filtered out of the solution leaving a particle free solution behind
- The solution is diluted to appropriate sensitivities levels for the ICP instrument and the lithium content is measured (usually in ppm)
- The residual lithium content is then expressed as a weight percent to the original mass of cathode active material added

7.3 Water Content

Coulometric Karl Fisher titration method is recommended for water content determination, particularly for materials with water content <1000 ppm. Sample preparation and measurement is to be performed per instrument manufacturer guidelines.

NOTE: For materials where lower precision is acceptable, for example in a material with higher intrinsic water content, volumetric titration could be used. Volumetric titration has the additional benefit of shorter measurement time than coulometric titration. ASTM E203-08 describes a method for sample preparation and water content determination using volumetric titration.

NOTE: For some materials, oven evaporation may be necessary to remove all of the water from the sample. For coulometric titration, this is generally described in ASTM D6304-07. For volumetric titration, this is generally described in ASTM D7785-12.

NOTE: If oven evaporation is used, the user is cautioned to select a maximum temperature such that it does not lead to decomposition of the active material or any surface treatment/layer present on the particles.

7.4 pH

Excess soluble hydroxide and carbonate on the cathode material surface can lead to gelling of the electrode coating slurry. Measuring the pH increase from the cathode material helps in developing a slurry mixing process.

ASTM E70-07 specifies the apparatus and procedures for the electrometric measurement of pH values of aqueous solutions with the glass electrode.

Most cathode materials rapidly react with an aqueous solution. Lithium ions in the cathode material will exchange with protons in the solution, thereby leading to an increase of the pH of the solution. Accordingly, it is critical that when comparing the pH of different materials, the time the cathode material contacts the solution remain fixed amongst all the different materials. In addition, the ratio of the cathode material to solution must be fixed amongst the different materials to ensure a fair comparison. To mitigate the ion exchange between lithium and protons, a nonaqueous solvent (e.g., methanol) can be used.

7.4.1 Equipment and Supplies

The following equipment is required to measure the pH of the cathode material:

- Benchtop pH-meter
- Double-junction pH electrode with built-in reference and temperature compensation probe (ATC)
- pH 4, 7, and 10 calibration standards
- pH = 9.0 verification standard
- Beaker 150 mL
- Spatula
- Spinning rod
- Magnetic stirrer with rotation speed controller
- Demineralized water (minimum 5 MΩ * cm^{-1})

7.4.2 Calibration of pH Meter

The pH meter should be calibrated per the instrument manufacturer recommendation. Typically this is at least once a day and at minimum involves a three point calibration using pH standards 4, 7, and 10. Instruments/electrode performance acceptance criteria after calibration:

- Slope: 97 to 102%
- Offset: ±15 mV

7.4.3 Sample Preparation and Measurement

It is important that a sufficient amount of solvent is used to ensure complete dissolution of any residual LiOH, Li_2CO_3, or Li_3PO_4 on the surface of the cathode material. The solubility of Li_2CO_3, LiOH, and Li_3PO_4 in cold water is 1.54 g/100 g H_2O, 12.7 g/100 g H_2O, and 0.034 g/100 g H_2O, respectively. The surface species present are dependent on the material composition and synthetic method. The following procedure uses a large excess of water to guarrante complete dissolution of all the species.

- Add 2.00 g of active material into a 150 mL beaker
- Add 100 mL of demineralized water and add a spinning rod to the mixture; alternatively, a mixture of an aqueous and non-aqueous solvent (e.g., methanol) can be used
- Set up rotation speed of the stirrer at 500 rpm
- Put the beaker on the magnetic stirrer and let it mix for a predetermined, constant time (e.g., 5 minutes)
- Stop stirring and plunge the pH probe into the cathode active material/water mixture
- Wait until stability condition has been reached
- Record the pH value

Repeat the process with a second sample of the same lot; average the measurements. Report results with ±0.1 pH-unit accuracy.

8. CRYSTALLOGRAPHIC AND MORPHOLOGICAL PROPERTIES

8.1 Phase Purity/Crystallographic Structure (e.g., XRD; refer to Rietveld)

Purpose: Determine that the material has the desired crystal structure.

Powder X-ray diffraction is recommended as the method to determine purity of the crystallographic structure. Both the positions (corresponding to lattice spacing) and the relative intensity of the measured intensity peaks are indicative of a particular phase and material.

NOTE: XRD cannot detect ppm levels of impurities or amorphous phases.

Test parameters for a coupled 2θ-ω Bragg-Brentano scan:

- 2-Theta scan region from 10 to 90 degrees
- At a maximum, the step size should be 0.05 degrees
- A minimum signal-to-noise (S/N) ratio of five is recommended, where the signal-to-noise ratio is defined as the peak signal intensity of the weakest peak of interest divided by the average signal intensity of the noise