SAE INTERNATIONAL

SURFACE VEHICLE RECOMMENDED PRACTICE

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(R) Measuring Properties of Li-Ion Battery Electrolyte

RATIONALE

As the market for lithium-ion batteries continues to grow, new electrolyte concepts are being proposed for incorporation into these batteries. A variety of physical and chemical properties can be measured with a variety of testing methodologies. This SAE Recommended Practice provides a set of test methods to characterize lithium-ion battery electrolytes. These methods can enable comparisons of supplier materials to assure a consistent and fair analysis for sourcing selection. Pass/fail criteria is not included in this document, as it is the decision of each manufacturer to establish their limits for desired material properties.

INTRODUCTION

Most electrolytes are composed of solvents and salts. Through optimized composition of solvents and salts, batteries can achieve good low-temperature performance and high power. Ionic liquids are beginning to be used in addition to, or as a replacement for, solvents. Ionic liquids enable improved performance for flammability issues. Additives are used to extend cycle life and enhance safety. In addition, additives can improve the interface on the cathode and/or anode surface.

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1. SCOPE

This SAE Recommended Practice provides a set of test methods for characterizing lithium-ion battery electrolytes. These test methods are applicable to existing electrolyte materials and allow different facilities to conduct testing in a common manner.

Solid electrolytes are expected to be commercially used for large scale batteries in the future. However, characterizing solid electrolytes may require methods different from those contained in this document. Such methods are not addressed in this document.

It is not within the scope of this document to establish acceptance criteria for test results, as this is usually established between the vendor and customer. It is also not within the scope of this document to examine the electrochemical properties of an electrolyte, since these are influenced by electrolyte composition. In addition, establishing an electrolyte composition appropriate for all applications is not feasible.

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 J1715/2	Battery Terminology

2.1.2 ISO Publications

Copies of these documents are available online at http://webstore.ansi.org/.

DIN EN ISO 3104:1999-12	Determination of Kinematic Viscosity and Calculations of Dynamic Viscosity of Transparent and Opaque Liquids

2.1.3 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 D445-17a	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
ASTM D618-13	Standard Practice for Conditioning Plastics for Testing
ASTM D664-17a	Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
ASTM D891-18	Standard Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemical
ASTM D1125-14	Standard Test Methods for Electrical Conductivity and Resistivity of Water
ASTM D1209-05	Standard Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
ASTM D4052-18	Standard Test method for Density, Relative Density and API Gravity of Liquids by Digital Density Meter
ASTM D4447-15	Standard Guide for Dissposal of Laboratory Chemicals and Samples

ASTM D5386-16	Standard Test Method for Color of Liquids Using Tristimulus Colorimetry
ASTM D7042-16e3	Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)
ASTM D7111-16	Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Couple Plasma Atomic Emission Spectrometry (ICP-AES)
ASTM D7867-13	Standard Test Methods for Measurement of Rotational Viscosity of Paints, Inks and Related Liquid Materials as a Function of Temperature
ASTM E260-96	Standard Practice for Packed Column Gas Chromatography
ASTM E502-07	Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods
ASTM E537-12	Standard Test Method for the Thermal Stability of Chemicals by Differential Scanning Calorimetry
ASTM E681-09	Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)
ASTM E918-83	Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature
ASTM E1064-16	Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer titration
ASTM E1184-10	Standard Practice for Determination of Elements by Graphite Furnace Atomic Absorption Spectrometry
ASTM E1981-98	Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Calorimetry
ASTM UOP714-07	Metals in Miscellaneous Samples by ICP-OES
ASTM UOP389-15	Trace Metals in Organics by ICP-OES

3. DEFINITIONS

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

ELECTROLYTE: The medium that provides ion transport between the positive and negative electrodes of a cell. Electrolyte may also participate directly in the charge and/or discharge reactions.

4. SAMPLE PREPARATION

Typically, lithium-ion battery electrolytes are extremely sensitive to moisture. Specifically, fluorinated salts contained in the electrolyte will hydrolyze on contact with moisture, resulting in the formation of hydrofluoric acid (HF).

Prior to testing, samples should be handled and/or conditioned using the manufacturer's procedures. If manufacturer procedures are not available, the tests in this recommended practice are to be performed at standard laboratory atmosphere, defined in ASTM D618-13.

When preparing samples and performing testing, care should be taken to use clean and dry equipment, and to use procedures that minimize exposure of the sample to moisture. At no time during preparation for, or performance of, the measurement should the water content of the electrolyte exceed the manufacturer's specification. Users should consider performing the test in the dry room/dry box. After testing, samples should be disposed of through appropriate waste streams and equipment should be cleaned and dried.

5. ELECTROLYTE MATERIALS PARAMETERS

5.1 Chemical Content (Lithium, Impurities)

Prior to making an electrolyte, the purity and chemical composition of the solvents are typically checked against the manufacturer's specifications by using gas chromatography (GC). The solvents are each tested separately, as the combined chromatogram can be convoluted with overlapping peaks. ASTM E260-96 provides guidance on the application of gas chromatography with packed columns for the separation and analysis of vaporizable organic and inorganic compounds.

For analysis of the final electrolyte, elemental composition may be determined by application of a suitably sensitive analysis technique, such as ion-coupled plasma optical emission spectroscopy (ICP/OES). ASTM D7111-16 describes ICP-OES applied to fuels. The techniques described in ASTM D7111-16 are applicable to electrolytes, with appropriate modification to standard solutions. Alternatively, graphite furnace atomic adsorption (ASTM E1184-10) could be selected.

ASTM UOP714-07 is recommended to determine the metal in samples.

NOTE: Concentrations determined generally cover the range of 0.02% to several mass percent.

NOTE: Barium and silicon cannot be determined by this method due to the acid treatment of sample.

ASTM UOP389-15 is recommended to determine the metals in organic matrices.

5.2 Water Content

Coulometric titration is recommended for the determination of water content of electrolytes. ASTM E1064-16 describes an automated coulometric titration procedure which allows for the determination of water, from 0 to 2.0% mass, in most liquid organic chemicals with Karl Fischer (KF) reagent.

Conventional titrants can be used with most electrolytes. In some cases, the electrolyte additives (e.g., vinylene carbonate) may not be compatible with the titration reagents, as indicated by a failure to reach an endpoint. In these cases, the user may measure water content on the electrolyte without the additive. Discuss with the KF titrant supplier to select an appropriate titrant.

5.3 Free Acid (Neutralization)

Potentiometric titration method (i.e., neutralization titration) as described in ASTM D664-17a is recommended for the measurement of free acid (e.g., hydrofluoric acid), with the following comments:

- ASTM D664-17a provides guidelines regarding sample preparation which may not be applicable to electrolytes. The user should prepare samples according to the manufacturer's recommended guidelines and/or modify the sample preparation methods so that free acid amount does not increase as a consequence of the measurement system (e.g., solvent selection).

- If there is no manufacturer's recommended titration systems/practice, then the user should evaluate the contribution of each component of the electrolyte separately to determine if there is potential interference as a result of reaction with the titration system. If a component is not compatible with the titrant system, as could be evidenced by the inability to reach endpoint stabilization, then alternative titrants and/or solvents should be explored.

5.4 Color (Platinum-Cobalt Color)

The color of an electrolyte is measured by comparison to known color reference materials or by correlation of spectroscopic response upon controlled illumination. Color is an indication of potential product degradation.

ASTM D1209-05 describes a procedure for the visual measurement of color for light colored liquids. The color of the liquid is compared to the color of platinum-cobalt standard solutions.

ASTM D5386-16 describes an instrumental method for the measurement of the color of near clear liquid samples. The measured color is converted to a color rating of the platinum-cobalt scale. This is the preferred method due to the less subjective nature of the analysis and better precision.

Prepare samples per the manufacturer's guidelines.

5.5 Density/Specific Gravity

Density is often measured from the direct measurement of a sample mass with known fixed volume.

NOTE: Density and specific gravity values should only be compared when conducted at the same measurement temperature (±1 °C). Most electrolytes will generate hydrofluoric acid (HF) in the presence of water. It is not expected that HF generation would significantly change the measured density of the electrolyte. However, the generated HF could damage equipment.

ASTM D891-18 describes a method of determining specific gravity of a liquid by pycnometry. The volume of the material is held constant by the measurement system, and when combined with the measured mass allows for the calculation of density. The method provides for using the same sample tube to first measure the volume of the pycnometer with water (using the known density of water as a function of measurement temperature to calculate the volume from the measured mass of water).

ASTM D4052-18 describes an instrumental method of determining density and specific gravity of a liquid by introducing the liquid into an oscillating sample tube. This method uses the change in oscillation frequency caused by the change of the mass of the tube to determine density.

5.6 Viscosity

Viscosity is often determined by measuring the flow properties of materials in relation to a reference material. Viscosity varies as a function of temperature. The user should record the temperature at which the measurement is performed. For situations where users are trying to evaluate whether an electrolyte would be appropriate for an application, the users should evaluate the sensitivity of viscosity at select temperature points within the expected temperature operating regime.

If a temperature bath is used to maintain the test temperature, the user should use an aprotic solvent with low vapor pressure within the temperature range of interest. Further, the solvent must remain liquid within the temperature range.

NOTE: To characterize the material under a controlled shear, dynamic viscosity should be used. If shear does not need to be controlled, kinematic viscosity techniques can be used. Kinematic techniques are generally applied to Newtonian fluids.

5.6.1 Dynamic Viscosity (Also Known as Absolute Viscosity or Shear Viscosity)

Absolute viscosity, or the coefficient of absolute viscosity, is a measure of the kinematic resistance. Dynamic (absolute) viscosity is the tangential force per unit area required to move one horizontal plane with respect to the other at unit velocity when maintained a unit distance apart by the fluid.

ASTM D2196-18e1 describes a method of determining viscosity using rotational techniques.

5.6.2 Kinematic Viscosity

Kinematic viscosity is the ratio of absolute or dynamic viscosity to density. It is a quantity in which no force is involved.

ASTM D445-17a describes the general methodology for determining kinematic viscosity.

ASTM D7042-16e3 applies the methods of D455-17a within a specific instrument.

For either ASTM D445-17a or ASTM D7042-16e3, solvents used for cleaning of the apparatus should be miscible with the electrolyte.

ISO 3104 (1999), which describes a method for determining kinematic viscosity and the calculation of dynamic viscosity, is offered as an alternative to the ASTM documents referenced above.

5.7 Ionic Conductivity

Ionic conductivity is typically determined by measuring the alternating current resistance of a material between two electrodes. Conductivity varies as a function of temperature. The user should record the temperature at which the measurement is performed.

The methods described in ASTM D1125-14 are generally recommended, with consideration for the following:

- The temperature bath should not use water. The bath should contain an aprotic solvent with low vapor pressure within the temperature range of interest. The solvent must remain liquid within the temperature range.
- Equipment preparation should allow for parts that contact the electrolyte to be dried.
- Solvents used for cleaning of the apparatus should be miscible with the electrolyte.
- Formation of hydrofluoric acid (HF) due to exposure to moisture could cause variability in the measured conductivity. If the user observes atypical variability in the conductivity measurement, they should consider placing the equipment in a dry box/dry room.

For situations where users are trying to evaluate whether an electrolyte would be appropriate for an application, the users should evaluate the sensitivity of conductivity at select temperature points within the expected temperature operating regime. For example, electrolytes developed for automotive applications should, at a minimum, have conductivity measured between -30 °C and 60 °C. Alternately, in a quality control situation, conductivity may only need to be measured at one temperature.

5.8 Thermal Stability

Thermal stability is typically determined by monitoring changes in the physical properties of a material as a function of temperature.

NOTE: The thermal stability of the material by itself will not provide a complete picture of the thermal stability of a full cell.

NOTE: Samples must be prepared in an inert, dry environment.

5.8.1 Differential Scanning Calorimetry (DSC)

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

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 an electrode with an electrolyte.

- A hermetically sealed pan should be used to prevent reaction of the electrolyte with air (particularly water). The pan will open when gaseous components cause a sufficient increase in pressure; therefore, temperature data beyond this point is no longer meaningful. As hermetic pans can open energetically, 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.

NOTE: ASTM E537-12 section 12.3 briefly discusses self-pressurization of the hermetic container and the impact of increased partial pressure on the enthalpy. The increased partial pressure is a drawback to using this technique.

Recommended 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

5.8.2 Accelerating Rate Calorimetry (ARC)

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

ARC is an 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.

- The user should make judicious choices for:
  - initial temperature setpoint,
  - self-heating rate (SHR), and
  - heat/wait/search (HWS) profile.
- Only data measured under the same conditions/parameters will be comparable.
- ARC units can be equipped with pressure relief systems, which will avoid the partial pressure change observed when performing DSC measurements in hermetic systems.

ARC data can generally be correlated to DSC data.

5.8.3 Flammability

Flammability of a material is typically determined by monitoring a substance for evidence of combustion as a function of temperature and concentration. ASTM E918-83 describes methods for the determination of the lower and upper concentration limits of flammability of vapor-oxidant mixtures at temperatures up to 20 °C. This method provides a method for introducing a liquid fuel into the test chamber.

ASTM E681-09, while similar to ASTM E918-83, looks at the lower and upper concentration limits of flammability of chemicals with sufficient vapor pressure to form flammable mixtures in air at atmospheric pressure at the test temperature.

5.8.4 Flash Point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed.

NOTE: Since lithium battery electrolyte salts react with water, open cup measurement techniques are not recommended for measuring the flash point of electrolytes.

NOTE: The flash point of a material is an empirical measurement rather than a fundamental physical parameter. The measured value will vary with equipment and test protocol.

There are different types of closed cup testers. When reporting flash point results, the user should also report the flash point method used.

ASTM E502-07, provides general information on the usefulness of the technique and operating principles.