STANDARD OPERATING PROCEDURE

Four-Electrode Electrical Conductivity Probe & Incremental Immersion Calibration

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Target Application:	Liquid Electrolyte & Corrosive Salt EC Measurement	**Methodology:**	Calibration-Free Incremental Immersion (g-Factor)

1. Purpose & Principle of Operation

This Standard Operating Procedure defines the field and laboratory protocol for measuring the electrical conductivity (k) of liquid electrolytes using a four-electrode probe and the incremental immersion technique. Traditional two-electrode conductivity cells suffer severe measurement bias in reactive or high-temperature liquids due to electrode polarization, contact wetting variations, and parasitic field fringing. The four-electrode incremental immersion method overcomes these limitations by isolating voltage sensing from current injection and deriving solution conductivity directly from the linear derivative of conductance ($C = I / \Delta V$) with respect to electrode immersion depth (Δz).

The probe array consists of four parallel 316 stainless steel wire electrodes (diameter $2a_E = 2a_S = 2.35\ mm$). Outer current injection electrodes are situated at $x_E = \pm 10\ mm$, while inner voltage sensing electrodes sit at $x_S = \pm 5\ mm$. Because wetting effects at the liquid surface and lower end-effect fringing remain invariant during incremental immersion, the geometric cell factor (g) is obtained without requiring reference solution calibration equations.

2. Required Equipment & Setup Specifications

- **Potentiostat / EIS Analyzer:** Gamry Interface 1000 or equivalent supporting 4-electrode EIS (1 Hz to 1 MHz, 5 mV AC amplitude).
- **Probe Assembly:** 4-electrode 316 stainless steel wire array mounted in a rigid non-conductive fixture.
- **Micrometer Drive:** Precision manual or motorized linear drive with ±0.01 mm positioning accuracy.
- **Sample Vessel & Thermal Bath:** Plastic beaker (internal diameter $D = 52.05\ mm$, solution depth $L \geq 25\ mm$) in an ice bath held at 0.0 °C ± 0.1 °C.
- **Reference Thermometer:** Certified RTD temperature standard (0.01 °C resolution).

3. Step-by-Step Field Execution & Measurement Protocol

3.1 Sample Thermal Stabilization

1. Cool the electrolyte solution to approximately 4 °C, invert 20 times to homogenize, and pour into the plastic beaker to a depth of $L = 25\ mm$.
2. Immerse the beaker into the ice bath and monitor temperature until stabilized at **0.0 °C ± 0.1 °C** (approx. 45 minutes).

3.2 Contact Surface Detection (z_0)

1. Connect outer wires to potentiostat Counter/Working cables and inner wires to Sense cables.
2. Monitor Open Circuit Potential (OCP) while lowering the probe with the micrometer drive.
3. Mark position $\boldsymbol{z_0}$ the exact instant OCP shifts, confirming initial liquid electrical contact.

3.3 Incremental Immersion & EIS Impedance Acquisition

1. Lower probe in steps of **Δz = 1.0 mm** from 1.0 mm to 20.0 mm immersion depth.
2. At each depth, run Electrochemical Impedance Spectroscopy (EIS) from 1 Hz to 1 MHz.
3. Extract real solution resistance R from the Bode plot where phase angle approaches 0° at high frequency, and calculate conductance $C = 1 / R$.
4. Apply displacement volume correction factor $A / (A - 4A_e)$ to adjust effective immersion depth.

4. Data Fitting & Geometric Factor Calculation

Plot conductance *C* against immersion depth Δz. Identify the linear least-squares region between **1.0 mm ≤ Δz ≤ 15.0 mm** (confirm $R^2 > 0.999$). The slope *dC/dz* yields the geometric cell factor: ***g = (dC/dz) / k***. Experimental validation across KCl solutions (0.01 to 1.0 molal) establishes a mean geometric factor of ***g = 2.275 ± 0.051*** (varying by ±2% across 3 orders of magnitude), agreeing within 0.04% of Finite Element Analysis (FEA) COMSOL modeling.

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