Screen-Printed Electrode Information

**Carbon and Ceramic Electrode Information**

Pine Research Instrumentation offers aqueous, screen-printed carbon electrodes (e.g. Pine Research Part#: RRPE1001C or RRPE1002C) and ceramic screen-printed electrodes for non-aqueous use (e.g. Pine Research Part#: RRPE2001AU or RRPE2001PT). The article herein aims to provide information on how to activate, prepare, use, and clean screen-printed electrodes while also detailing system compatibility, reference electrode stability, and example voltammetric response.

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1. **Description**

Screen-printed electrodes (SPEs) offer some advantages over traditional electrodes in the areas of cost, solution volume, and operating temperature. Due to these advantages, SPEs have been employed in biosensor applications, teaching laboratories, and systems that require small volume or high temperature.

In the production of SPEs, mineral binders or insulating polymers are often added to carbon and gold or platinum inks to improve the ink’s adhesion onto plastic and ceramic substrates, respectively. The proprietary binder compounds found in the ink may introduce stray (but small) features in voltammograms, and the heterogeneous kinetics at these electrode surfaces may be a bit sluggish (especially for screen-printed carbon electrodes, see section 2). Additionally, the surfaces of SPEs are rough and not as pristine as more traditional electrodes fashioned from glassy carbon, pyrolytic graphite, or pure metal rods and sheets. Consequently, the exact determination of electrode area for an SPE is difficult. For academic teaching purposes and routine experiments, these problems do not pose any great concern; however, the electrochemical purist is likely to find fault when comparing SPEs to more expensive, traditional electrodes.

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2. **Screen-Printed Carbon Electrodes (SPCEs)**

2.1 **Background**

Conductive carbon inks have been employed for many years in a variety of biosensor applications—most notably in disposable blood glucose detectors due to their low-cost and accuracy. Typically, analyte-reactive enzymes are placed on the working electrode (either by coating the electrode or pre-mixing the ink with the enzyme) to enhance the electrochemical response for a given analyte. For example, a modified form of glucose oxidase is present on the working electrode of most blood glucose detectors and, as this redox enzyme mediates the oxidation of glucose, the electrochemical signal for glucose is boosted.

2.2 **Available Electrode Patterns**

Pine Research Instrumentation offers SPCEs in two different patterns; these patterns differ only with respect to the working electrode geometry (2 mm diameter disk and 5 mm x 4 mm rectangle, see Figure 1). The card, composed of polyethylene terephthalate (PET) plastic and a conductive silver track, has the dimensions: 15 x 61 x 0.36 mm. The carbon working electrodes (disk or rectangles), Ag/AgCl reference electrode (thin grey line), and carbon counter electrode (thick black line) are adhered to the conductive silver layer in a recessed, insulating layer of the electrode (see Figure 2).

![Figure 1. Rectangular (left) and Disk (right) Carbon Screen-Printed Electrodes](image)
Figure 2. a) Reference Electrode, b) Working Electrode, and c) Counter Electrode for a SPCE

The disk-shaped electrode is suitable for routine use in an educational setting. The rectangular working electrodes offer a larger area to those researchers wishing to drop coat an appreciable amount of enzyme on to the working electrode. A blue insulating layer surrounds and also coats the extreme outside perimeter of the carbon working electrode. The thickness of the carbon, silver, and insulating layers is typically $7-13 \mu m$.

2.3 Screen Printed Silver-Chloride Reference Electrodes

The demand for commercial blood glucose detectors has also driven the development of silver/silver chloride inks suitable for printing stable reference electrodes. Printed Ag/AgCl reference electrodes are most stable when used in an aqueous solution of chloride ions (such as 1.0 M KCl) but can also be used in nitrate-based electrolyte solutions (such as 0.1 M KNO₃). When using a printed Ag/AgCl reference electrode, it is important to allow the electrode to equilibrate with the test solution for at least 60 seconds before experimenting.

2.4 Compatibility

SPCEs are only compatible with aqueous systems; the carbon ink used to print SPCEs will react with non-aqueous solvents. Additionally, SPCEs are stable up to 80°C.

**Chemical Compatibility:**

Screen-printed carbon electrodes are for aqueous use only.

**Thermal Stability:**

Screen-printed carbon electrodes can be used from 10°C to 80°C.

2.5 Mounting the Screen-Printed Electrodes

The Compact Voltammetry Cell Kit (Pine part #: AKSPEKIT) is designed for use with both the carbon and ceramic SPEs. Since the carbon SPEs are thinner than the ceramic SPEs (0.36 mm vs 0.67 mm, see sections 2.2 and 3.2), one or more “spacers” are needed to mount the carbon SPE so that it can maintain a proper grip within the cell cap (spacers are included upon purchase). Like the SPCE, the spacers are composed of polyethylene terephthalate, an inert polymer, and it is approximately one-third the length of the SPCE. It is important to keep the spacer above the solution level, as solution contact will create solution buildup between the spacer and SPCE by capillary action, leading to a possible short of the electrode circuit and eventual corrosion of the grip. For this reason, it is not recommended that two SPCEs be used back-to-back.
The Compact Voltammetry Cell features a custom cap with a built-in edge card connector into which the carbon electrode card may be inserted. A mini-USB style connector on the top of the custom cap permits electrical connection to be made to the electrode card. To connect to the card, always use the mini-USB style port which is on the left when viewing the top of the card (see Figure 3). Connect the banana cables to their respective colors on the potentiostat with which experiments are being performed.

![Figure 3. Mounting a Screen-Printed Carbon Electrode](image)

2.6 Typical Electrochemical Response

While the electrochemical response of different systems may vary wildly, there are two common factors seen in many cyclic voltammograms performed with SPCEs: peaks in the background scan and slow electrode kinetics.

2.6.1 Background Scans

Hexaamineruthenium(III) chloride $$[\text{Ru(NH}_3)_6\text{Cl}_3]$$ is a common source for the popular electroactive ion hexaamineruthenium(III). This ion exhibits a well-behaved, reversible redox couple at about $$-0.44 \, V$$ vs Ag/AgCl (recall that the Ag/AgCl reference electrode is printed on the same substrate). A potassium chloride electrolyte solution can be used to prepare a solution of hexaamineruthenium(III) $$[10 \, \text{mM} \, \text{Ru(NH}_3)_6\text{Cl}_3]$$ in $$0.1 \, \text{M} \, \text{KCl}$$. If a background scan is taken using a SPCE, small features are revealed on both the anodic and cathodic scans (see Figure 4a). The features are characteristic of the carbon ink itself and, in the presence of a reasonable concentration of the target analyte (e.g., $$10 \, \text{mM}$$), these background features tend to be dwarfed by the voltammogram of interest (see Figure 4b). The electrochemical behavior of the hexaamineruthenium(III) ion at the SPCE electrode is well suited for teaching cyclic voltammetry.
2.6.2 Slow Electrode Kinetics

Many other popular electroactive ions (including hexacyanoferrate(III), dopamine, and ascorbic acid) are not as well-suited for teaching purposes because sluggish heterogeneous kinetics significantly distort the shape of the voltammogram. For example, the peak splitting on a cyclic voltammogram of dopamine may be as large as 400 mV (much greater than the expected 59 mV, see Figure 5).

Researchers and laboratory instructors who still wish to use ions with sluggish heterogeneous kinetics are directed to activate the carbon surface to improve electron transfer (see section 2.7).

2.7 Activating the Carbon Surface

Slow electrode kinetics are due (in part) to carbon ink binding factors that shelter electroactive carbon particles. Over the years, researchers have developed many methods to activate the carbon electrode surface including
potential cycling to extreme anodic potentials,2,3 heat treatment,4,5 and oxygen plasma treatment.6–8 Only potential cycling will be discussed herein due to its simple and cheap procedure.

Potential cycling, or pretreatment, is an effective method to remove organic link-crossings from the carbon ink while also increasing surface roughness and functionality. Best of all, it can be performed with minimal additional supplies, making it perfect for teaching laboratories.

To activate an SPCE, cycle it via cyclic voltammetry in sulfuric acid at extreme anodic and cathodic potentials (0.1 N H₂SO₄ will suffice, see Table 1 for specific parameters). During the pretreatment, oxygen and hydrogen gas bubbles evolve on the carbon surface (see Figure 6a for a typical voltammetric response). After pretreatment, the heterogeneous electron transfer kinetics of many electroactive ions are improved. To illustrate, the electron transfer kinetics of a solution of dopamine (1 mM, sweep rate = 200 mV/s) are quite sluggish before surface activation but much faster after surface activation as evidenced by smaller peak-to-peak separation (see Figure 6b).

<table>
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Table 1. Bulk Electrolysis Parameters to Activate Screen-Printed Carbon Electrode Surfaces

**Figure 6. Cyclic Voltammograms of the a) Pretreatment and b) Dopamine Before (Red) and After (Blue) Activation**
2.8 Cleaning the Screen-Printed Carbon Electrodes

SPCEs are designed with low-cost materials and have a fairly short lifetime. For example, one SPCE is likely useful for a single analysis in a research setting or a full laboratory period in a teaching setting. Research conditions will dictate the lifetime of the SPCE and users should determine lifetime experimentally.

3. Ceramic Screen-Printed Electrodes

3.1 Background

The ceramic screen-printed electrodes offered by Pine Research Instrumentation are perfect for high temperature and non-aqueous applications. With proper care, the ceramic SPEs can be reused many times, making them ideal for routine electrochemistry.

3.2 Available Electrode Patterns

Ceramic SPEs have three electrodes on a single surface (see Figure 7). For all ceramic SPEs, the working electrode is a 2.0 mm OD disk surrounded by a large counter electrode. Both the working and counter electrodes are available in gold or platinum. There are two inks used to prepare the reference electrode (Ag and Ag/AgCl), but a pattern that does not include a reference electrode is also available for purchase. All patterns share the same basic electrode geometry with unit dimensions: 15 x 61 x 0.67 mm (see Figure 8).

Figure 7. Gold (left) and Platinum (right) Ceramic Screen-Printed Electrodes

Figure 8. a) Reference Electrode, b) Working Electrode, and c) Counter Electrode for a Ceramic SPE

3.3 Reference Electrode Options

The reference electrode on a ceramic SPE is a small disk located between the working electrode and the counter electrode. While the working and counter electrodes are fabricated from a noble metal (such as gold or platinum), the reference electrode is silver (Ag) or silver/silver chloride (Ag/AgCl). When using Ag or Ag/AgCl reference electrodes, it is important to allow the reference electrode to equilibrate with the solution for about 60 seconds before use.

For work in aqueous solutions, the silver/silver chloride redox pair is the best reference electrode material. It is quite stable when used in an aqueous solution containing chloride ions.

For work in non-aqueous solutions (or in cases where chloride ion may interfere with the electrochemical experiment), Pine Research Instrumentation offers a silver “pseudo-reference” electrode. This electrode must be standardized against a known redox couple. Typically, ferrocene (or one of its derivative compounds) is added to the test solution as an internal standard, and potential measurements against the silver pseudo-reference are corrected with respect to the known position of the ferrocene redox couple.
The reference electrode has the shortest lifetime of the ceramic SPE. Depending on the conditions in which the SPE is used, users should be aware of potential drift due to the screen printed $Ag/AgCl$ reference electrode response decline. While this reference electrode deterioration will limit the immediate lifetime of the reference electrode, it is quite easy to use a more typical reference external electrode instead of the reference spot on the SPE. Pine Research Instrumentation offers $Ag/AgCl$ reference electrodes.

### 3.4 Compatibility

Ceramic SPEs can be used in aqueous and non-aqueous systems. They are compatible with systems up to 200°C.

**Chemical Compatibility:**

Ceramic screen-printed electrodes are stable in aqueous and non-aqueous solvents.

**Thermal Stability:**

Ceramic screen-printed electrodes can be used from 10°C to 200°C.

### 3.5 Mounting Ceramic Screen-Printed Electrodes

The Compact Voltammetry Cell Kit (Pine part #: AKSPEKIT) is designed for use with both carbon and ceramic SPEs. The ceramic SPEs are thicker than the carbon SPEs (0.67 mm vs 0.36 mm, see sections 2.2 and 3.2), and therefore a “spacer” is not needed to mount the ceramic SPE.

The Compact Voltammetry Cell features a custom cap with a built-in edge card connector into which the ceramic electrode card may be inserted. A mini-USB style connector on the top of the custom cap permits electrical connection to be made to the electrode card. To connect to the card, always use the mini-USB style port which is on the left when viewing the top of the card (see Figure 9). Connect the banana cables to their respective colors on the potentiostat with which experiments are being performed.

![Figure 9. Ceramic Screen-Printed Electrode Cell Connection](image)
3.6 Typical Electrochemical Response

Ceramic SPEs can be used to perform electrochemical experiments in solutions that are classically known to undergo slow heterogeneous kinetics on a screen-printed carbon electrode (e.g., dopamine, potassium hexacyanoferrate(III), and ferrocene) without electrode activation.

3.6.1 Potassium Hexacyanoferrate(III) Electrochemistry on a Gold Ceramic Screen-Printed Electrode

Potassium hexacyanoferrate(III) \( (K_3Fe(CN)_6) \) is a common source for the electroactive ion hexacyanoferrate(III). This ion exhibits a well-behaved redox couple at \( \sim +0.22 \, V \) vs Ag/AgCl on the ceramic, gold-patterned substrate; its well-behaved kinetics can be evidenced by peak-to-peak separation of approximately 60 mV and a nearly linear current dependence upon concentration (see Figure 10, sweep rate = 100 mV/sec). As a reminder, slow heterogeneous electron transfer from a screen-printed carbon electrode to a substrate like dopamine or hexacyanoferrate(III) typically manifests itself through large peak-to-peak separation (see Figure 5).

![Graph showing cyclic voltammogram](image)

**Figure 10.** \( K_3Fe(CN)_6 \) Solution Electrochemistry on a Gold Screen-Printed Electrode a) Cyclic Voltammogram of Varying Concentration and b) Cathodic Current as a Function of Concentration

3.6.2 Ferrocene Electrochemistry on a Platinum Ceramic Screen-Printed Electrode

Ferrocene is often used as a non-aqueous internal standard for solutions that require the absence of silver or chloride ions. The Ceramic SPEs produced by Pine Research Instrumentation can be used in conjunction with ferrocene internal standard solutions and behave well at multiple scan rates (see Figure 11, sweep rate = 100 mV/sec). Interested readers are directed to Bard and Faulkner’s book\(^{15}\) for more information on current and concentration interdependency.
3.7 Activating and Cleaning the Ceramic Screen-Printed Electrode

Before a sensitive, electrochemical experiment is performed, or if the electrode surface becomes fouled, it may be desirable to clean and/or activate the electrode surface. One way to do this is via repeated cycling of the working electrode potential in a dilute sulfuric acid solution (for specific parameters, see Table 2).

Repetitive cycling removes surface contamination and improves subsequent cyclic voltammetry results. As a result, the cyclic voltammogram obtained with each scan evolves over time, often manifesting in the resolution of peaks that were previously unresolved and/or the reduction of other peaks. Clean gold and platinum surfaces have characteristic peaks; a clean gold surface typically shows an onset of gold oxidation around 1100 mV vs. Ag/AgCl and a sharp reduction peak around 900 mV vs. Ag/AgCl (see Figure 12a) while a clean platinum surface typically shows an onset of platinum oxidation around 600 mV vs. Ag/AgCl, a sharp reduction peak around 450 mV vs. Ag/AgCl, and two hydrogen adsorption and desorption peaks (sometimes called the “butterfly region”) at near zero negative potential. (Figure 12b). When performing an electrochemical cleaning, be sure to compare the cycled cyclic voltammogram output to the signature response; once they match, the electrode has been refreshed/cleaned.

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<th>Gold Electrode</th>
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Table 2. Parameters to Clean Ceramic Screen-Printed Electrodes by Cyclic Voltammetry
Figure 12. Characteristic Features of Ceramic SPEs with a) Gold and b) Platinum Working Electrodes

4. References


5. Support

If you have any questions about the screen printed electrode materials described in this document, please contact us via the means provided below:

5.1 Email

Reach us by emailing the entire sales department: pinewire@pineresearch.com.

5.2 Website

There is a contact us form on our website. There may also be additional resources for the products mentioned here: http://www.pineresearch.com