

Probing Fuel Cell Electrocatalyst Properties Using Pine Rotated Disk and Ring-Disk Electrodes

Overview of the Nafion Thin-Film RRDE Technique

This technical note discusses some practical aspects of using rotating electrodes to study fuel cell electrocatalyst materials. Specifically, a method utilizing Nafion to immobilize platinum-bearing catalysts on electrode surfaces is described. This approach has been successfully employed by many researchers to probe both the (desired) kinetic and (undesired) peroxide generating properties of electrocatalysts used for the reduction of dioxygen. A representative bibliography of formal research papers on this topic is also provided.

Introduction

Recent trends in fuel cell research and production have increased the demand for fundamental information about the behavior of fuel cell electrocatalysts. Particular attention to those catalysts involved in the oxygen reduction reaction (ORR) has been driven by interest in H_2/O_2 fuel cells based on polymer electrolyte membranes.¹ Because ORR electrocatalysts typically make use of very expensive metal particles (most notably, nanoscale structures involving platinum), a key issue in fuel cell research is the search for lower cost catalyst materials.

Investigators from a wide variety of backgrounds are bringing their efforts to bear on this economic issue, developing catalytic materials with less noble metal content (*i.e.*, a dilution approach) and/or a more efficient use of the existing noble metal content (*i.e.*, engineering particle morphology). Regardless of the approach taken, these researchers generally end up producing a large number of candidate ORR catalysts which must be screened. The two screening criteria of most interest are the ORR kinetics (which should be as fast as possible) and the amount of peroxide formed (which should be as low as possible). Rotating electrodes^{2,3} provide a convenient and well-established way to probe both criteria.

For over three decades, Pine has provided electrochemical researchers with a reliable line of rotating electrode products. Both our rotated disk (RDE) and rotated ring-disk (RRDE) electrodes (see Figures 1 & 2) have proven to be quite popular tools for probing electrocatalyst behavior. This technical note assimilates much of the practical feedback that



Figure 1: Pine Rotating Disk Electrodes

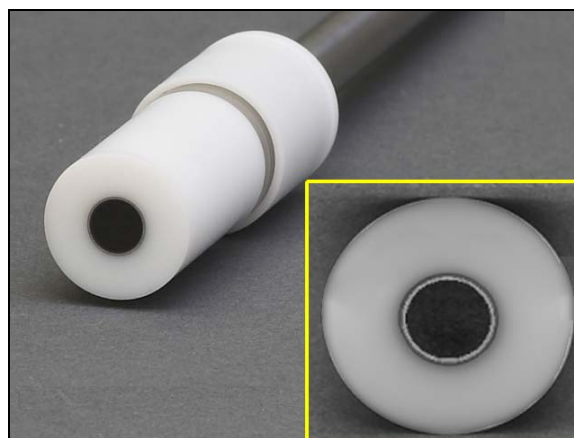


Figure 2: A Pine Rotating Ring-Disk Electrode

we have received from fuel cell researchers who use our products to screen electrocatalysts. Particular attention is paid to techniques involving the immobilization of thin ORR electrocatalyst films on glassy carbon RDEs and RRDEs. A bibliography of related research publications is also provided.



Figure 3: Pine AFMSRX Electrode Rotator

Rotating Electrodes

There are two principle rotating electrode geometries which are useful for studying the ORR process. The simplest geometry is the rotating disk electrode (see Figure 1), consisting of an electrode material (usually glassy carbon) fashioned into a disk shape and shrouded by an inert insulating material (such as Teflon or PEEK). This disk is mounted (coaxially) on a rigid shaft and typically rotated at rates between 200 and 2500 RPM using an electrode rotator (see Figure 3). For ORR studies, glassy carbon is used as the disk material and catalyst support because carbon is electrochemically inert over the range of electrode potentials relevant to ORR study.

The rotating ring-disk electrode (see Figure 2) is a more complex geometry in which a ring electrode (typically platinum) is placed around the disk electrode with ring, disk, and shaft all sharing the same axis of rotation. In appearance, an RRDE electrode does not look much different than a simple RDE electrode, however, an RRDE may be two to four times more expensive and is a much more delicate research tool. A thin insulating ring forms the “gap” between the disk and the ring electrode (keeping them electrically isolated), and the outer diameter of the ring is also shrouded by an insulating material. The surfaces of the ring, disk, gap, and shroud are all ideally polished and coplanar. For ORR studies, the ring material is usually platinum to allow for easy detection of any peroxide formed by the catalyst on the disk electrode.

Basic Concepts

Using the RDE and RRDE to study ORR electrocatalysts requires understanding of a few basic ideas. For the RDE, the key point is understanding the combined effects of mass transport (*i.e.*, how fast

does oxygen travel to the disk electrode?) and fundamental kinetics (*i.e.*, how fast is the oxygen reduced once it reaches the electrode?). For the RRDE, the key point is realizing that the ORR products (hydroxide and peroxide) generated at the disk must subsequently travel past the ring electrode. While the disk produces (generates) the products, the ring detects (collects) the products. This “generator-collector” geometry allows direct detection of any peroxide formed by the catalyst.

RDE Kinetic Measurements. A glassy carbon rotated disk electrode coated with a thin layer of an ORR electrocatalyst may be used to reduce dissolved oxygen in an electrolyte solution.^{4,7} By gradually increasing the rotation rate of the RDE, the rate of mass transport of the dissolved oxygen to the electrode surface increases. Initially, the cathodic (reduction) current at the disk electrode is governed by this mass transport (*i.e.*, the rate at which oxygen is arriving at the electrode). As the rotation rate increases, the current increases as the amount of oxygen arriving at the electrode surface increases.

Eventually, at a high enough rotation rate, the rate at which oxygen arrives at the electrode surface approaches the rate at which the electrocatalyst reduces the oxygen. At this point, the current signal measured at the disk electrode begins to be governed (or more precisely, *limited*) by the kinetic properties of the catalyst. It is at these higher rotation rates that the measured disk current begins to yield kinetic information. This category of RDE experiment is usually called a *Koutecky-Levich* experiment, and the reader is referred to textbook explanations^{2,3} of this method for further theoretical details.

RRDE Peroxide Detection. The solution flow pattern induced by a rotating electrode continually mixes the test solution and draws fresh solution toward the center of the disk electrode. The chemical species of interest, dissolved oxygen in this case, is drawn by the flow toward the disk electrode, and upon encountering the catalyst coated electrode surface, it is reduced. The ORR process yields some ratio of hydroxide to peroxide as products, depending on whether the catalyst favors the so-called *four electron* pathway versus the *two electron* pathway. The two electron pathway (leading to peroxide) is disadvantageous in a fuel cell context, as peroxide generally goes on to damage other critical materials comprising the fuel cell.

The solution flow pattern at a rotating electrode tends to sweep away products generated at the disk electrode in an outward (radial) direction. These

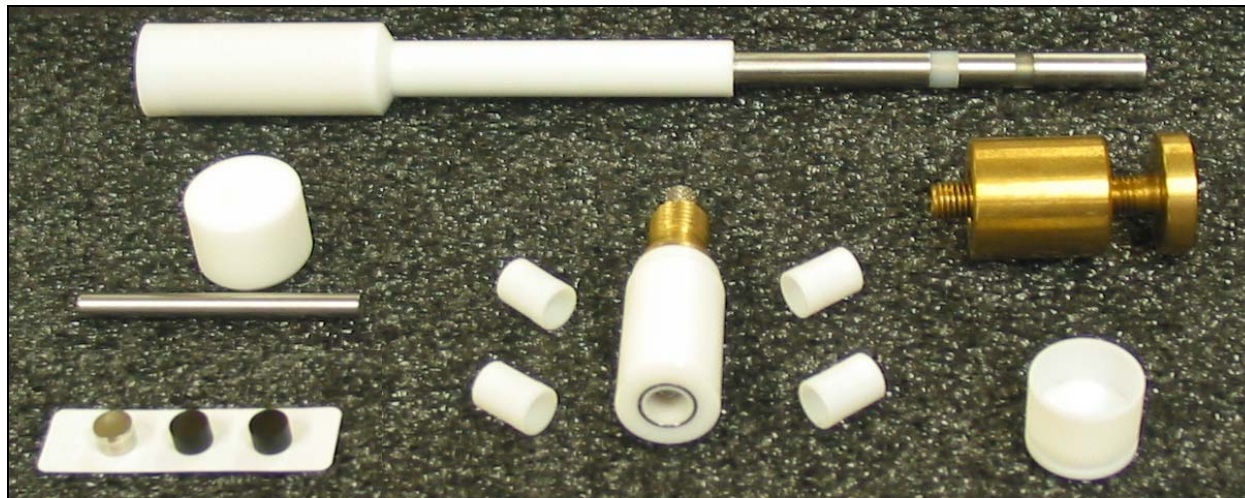


Figure 4: Many Pine RRDE Designs May Be Completely Disassembled to Facilitate Polishing

products can be detected if a suitable ring electrode is placed around the disk electrode. Peroxide is conveniently detected electrochemically using a platinum ring electrode. By comparing the amount of oxygen reduced at the disk (as indicated by the disk current) to the amount of peroxide detected at the ring (as indicated by the ring current), it is possible to deduce the fraction of oxygen which was reduced via the *two electron* pathway versus the *four electron* pathway. This use of an RRDE is often called a “collection” experiment, and the reader is again referred to textbook explanations^{2,3} and to specific research reports⁴⁻⁷ for further details.

Practical Matters

While textbooks and research reports provide theoretical background for Koutecky-Levich and RRDE Collection experiments, the technical aspects of actually conducting the experiment often go unmentioned. This section contains hints and advice gleaned from several researchers who have used Pine electrodes in their ORR research projects.

Polishing Electrodes. The glassy carbon disk electrode (whether on an RDE or an RRDE) should be clean and mirror polished prior to use. It should also be completely dry. Routine polishing of glassy carbon RDEs is fairly straightforward, but for an RRDE, it is generally best to polish the disk separately from the ring. Attempting to polish the ring and the disk at the same time is likely to cross-contaminate the disk with platinum debris from the ring. This can be a not so obvious source of error in an ORR study as such debris will likely also behave as an ORR catalyst. Many Pine RRDE designs permit the disk material to be ejected from the RRDE

assembly for separate polishing. The glassy carbon disk insert, once ejected, can be mounted in a separate holder for hand polishing (see Figure 4).

Coating Catalyst on to a Disk Electrode. The most popular way to immobilize an ORR electrocatalyst uses Nafion as the “glue” which sticks the catalyst particles to the glassy carbon disk. A suspension of catalyst particles and Nafion is prepared in a suitable solvent, and then a portion of this suspension is drop coated on to the disk. The solvent is allowed to evaporate, leaving behind a thin film of Nafion with embedded catalyst particles.

The catalyst dispersion is prepared by quantitatively dispersing a known amount of catalyst in a known volume of solvent (500 to 1000 μg of catalyst per milliliter of solvent). In general, this dispersion can be prepared in a common 20 mL disposable vial.

Because the catalyst will not actually dissolve, ultrasonication is required to create a uniform dispersion of catalyst particles in the solvent. When possible, pure water should be used as the solvent, but some hydrophobic catalysts may require the use of 20% to 40% isopropyl alcohol as the solvent. In general, the amount of alcohol should be kept to a

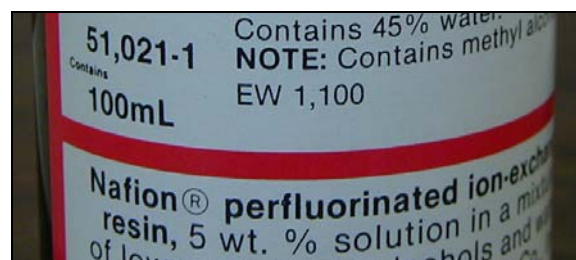


Figure 5: Typical 5% Nafion Solution

minimum as it may frustrate the drop coating procedure (see below).

Nafion is generally available as a 5% (by mass) solution in alcohol and water (see Figure 5). To introduce Nafion into the catalyst dispersion, use a micropipette to add 200 μL of 5% Nafion solution for every 50 mL of catalyst dispersion. Additional mixing and sonication is required after adding the Nafion. The elapsed time between this final ultrasonication step and the subsequent drop coating step should be minimized to avoid undue settling of the dispersion.

The drop coating step is by far the most difficult step. The idea is to use a micropipet to transfer a known volume of the catalyst dispersion on to the disk electrode, and only on to the disk electrode. For a 5.0 mm OD glassy carbon disk electrode, about 20 μL of the dispersion should be placed on to the disk. After evaporation of the solvent, a thin Nafion film ($\sim 0.1 \mu\text{m}$ thick) should remain on the disk. From the concentration of the catalyst in the dispersion and the known volume dispensed on to the disk electrode, it should be possible to estimate the amount of catalyst in the thin film. Thick films (more than 0.5 μm) should be avoided as these may interfere with ideal solution flow at a rotating electrode.

Drop coating on to an RRDE is a bit more tedious. Here, the close proximity of the ring to the disk can make it difficult to coat just the disk and not the ring. One factor which aids in this regard is the fact that the “gap” between the disk and the ring is often made from Teflon, which is somewhat hydrophobic. This tends to help confine the drop to the glassy carbon disk as long as the solvent is predominately water. However, when additional alcohol is used to prepare the dispersion, the drop is more prone to wetting the Teflon as well as the glassy carbon disk, and this may frustrate drop coating efforts.

After drop coating, many researchers accelerate the drying process by placing the electrode in an oven. Extreme temperatures should be avoided when heating Pine electrodes, and baking a rotating electrode may cause it to leak (*i.e.*, breaking the seal between the disk and the insulating shroud). Another problem with evaporating the solvent in a “bone dry” environment is that concentric rings of catalyst particles may form on the glassy carbon disk (rather than a uniform film). Some researchers have suggested that it is better to dry the film slowly in a somewhat humid environment. This may help

alleviate concentric segregation of the catalyst particles in the resulting film.

Rotation Rates. In Koutecky-Levich experiments, the range of useful rotation rates is typically between 100 and 3000 RPM. Be sure that the RDE being used is rated for this range of rotation rates. For the RRDE Collection experiments, a rotation rate between 1500 and 2000 is generally sufficient. Again, be sure to check the range of allowable rotation rates for the particular RRDE being used.

Collection Efficiency. In an RRDE Collection experiment, not all the product generated at the disk electrode will make the trip to the ring electrode. The flow pattern at a rotating electrode generally sweeps anywhere from 20% to 30% of the disk products past the ring electrode. The percentage of material which is collected (detected) at the ring electrode is often called the “collection efficiency” of the RRDE.

While theoretical equations for computing the collection efficiency are available, it is always best to empirically measure the collection efficiency of a specific RRDE before using it for any quantitative work. This is normally done using a well-behaved electrochemical system such as the ferricyanide-ferrocyanide redox couple. This system can be used to measure a stable collection efficiency at rates between 200 and 2500 RPM. The reader is referred to the appropriate reference⁶ for more details.



Figure 6: Pine High Temperature RDE

Elevated Temperatures. Because ORR research is driven in large part by automotive fuel cell target applications, there is a need to characterize electrocatalyst behavior at elevated temperatures. Unfortunately, most RDE and RRDE designs are not stable at elevated temperatures. Pine does offer an RDE design which is stable up to 80°C (see Figure 6). Many researchers use this electrode at a series of

elevated temperatures (from 50 to 80°C) in a set of related *Koutecky-Levich* experiments. After extracting the kinetic rate constants at each temperature, an Arrhenius extrapolation is used to predict the kinetic behavior at still higher temperatures.

Finally, against Pine's recommendations, many researchers⁴⁻⁷ have used Pine RRDEs at temperatures up to 80°C in an effort to determine the amount of peroxide formation at higher temperatures. Although not designed for such work, these researchers report that up to a dozen experiments at elevated temperature can be accomplished with a Pine RRDE before damaging the electrode. Such damage (usually a leak) can often be repaired by simply replacing the Teflon spacer between the disk and the ring electrode. This piece is called the "Teflon U-Cup", and while the U-Cup is itself fairly expensive, it is still much less expensive than replacing the entire RRDE assembly.

Reprints

Reprints of this document are available upon request from Pine Research Instrumentation, 5908 Triangle Drive, Raleigh, North Carolina 27617 (www.pineinst.com)

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