The Ag/AgCl Reference Electrode

RESOURCES > REF ELECTRODES > SILVER-SILVER CHLORIDE

- **The silver/silver chloride or Ag/AgCl reference electrode** is many electrochemists' reference electrode of choice. It is easily and cheaply prepared. It is stable, and quite robust. It is sometimes referred to as "SSCE" (Silver/Silver Chloride Electrode) but that abbreviation has been used for Sodium Saturated Calomel Electrode also.

- Construction
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- Conditioning or reviving Ag/AgCl electrodes
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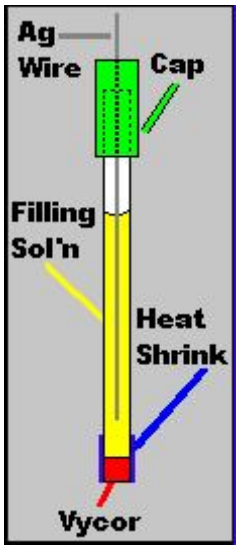
Construction:



The figure to the right shows an easily constructed Ag/AgCl reference electrode. The body of the electrode is made from 4 mm glass tube. Vycor® porous glass is available in 4 mm diameter rod and serves as the ionicly conducting electrical pathway between the inside of the reference electrode and the bulk of your cell. It has low electrical resistance (under 10 kohm for the common filling solutions) and a modest leak rate. The electrical resistance of the reference electrode 'frit' is an important factor in determining the stability and speed of your potentiostat in actual use. (See the GAMRY and PAR notes mentioned in the resource on potentiostat stability for more information.) The leak rate may be important because of possible contamination of your solution by the reference electrode filling solution and *vice versa.*

The Vycor® frit (about 1/8" long) is attached to the glass tube by 'heat shrink' Teflon tubing. The heat-shrink tubing should be cut flush with the end of the Vycor frit to prevent trapping any air bubbles. Pre-cut Vycor® frits and heat shrink tubing are available from Gamry, PAR, BAS, and probably other electrochemistry suppliers. The cap is conveniently made out of scrap Teflon or plastic cap or protector made to fit 5/32" OD tubing. It should be snug, but easily removable for replenishing the filling solution.

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Filling solutions:

A variety of filling solutions can be used. The most commonly used are saturated KCl or 3.5*M* KCl. KCl has the uncanny ability to 'creep' and form a crusty layer of solid KCl where the solution is exposed to the air. This author has seen 'beards' of KCl emanating from a Vycor® frit that were several cm long. If perchlorate electrolytes are to be studied, $KClO_4$ may precipitate in the pores of the frit, and for these electrolytes NaCl (either sat'd or 3*M*) is preferred. The author routinely uses NaCl filled electrodes, but has used LiCl in special instances.

Saturated solutions of KCl or NaCl have the advantage that the concentration is reproducible even if the temperature changes (if solid salt is present) and are immune to the effects of water evaporation. However, the solid salts harden into an impenetrable block which may lead to a high impedance electrode. A "nearly saturated" solution (3.5*M* KCl or 3*M* NaCl) can change concentration due to evaporation.

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Conditioning or reviving a Ag/AgCl electrode:

If an electrode needs to be 'revived' after abuse or prolonged storage, the first step is to disassemble the electrode and remove the silver wire from the electrode shell that surrounds it. The 'frit' which electrically connects the inside filling solution to the outside world should be replaced (if it is Vycor®) or cleaned to insure that ionic transport across the inside/outside interface is facilitated.

The procedure, below, is the one generally followed by this web site's author, but a similar procedure is outlined in Sawyer, Sobkowiak, & Roberts.

The old silver chloride coating can be removed by soaking the wire in conc. ammonium hydroxide. Nitric acid may be used to roughen the silver surface. Once the wire has been cleaned and rinsed, the electrode must be anodized or re-coated with AgCl. If a 'low resistance' (*i.e.*, high leak rate) frit is used this anodization can be done after the electrode is reassembled and refilled with fresh filling solution (the author's preference!) This not only coats the silver wire, but also insures that the filling solution is saturated with AgCl. The assembled electrode (or just the silver wire) should be placed in a beaker containing the filling solution. For a wire that is a few cm long and 0.05 cm diameter, a current of about 10 uA applied overnight is generally adequate. A platinum counter electrode completes the circuit. A galvanostat can be used if one is handy: A 9V battery in series with a 1Megohm resistor will also suffice. Be sure that the silver wire is at a **positive** voltage with respect to the counter electrode to anodize (oxidize) it! In the author's experience the resulting coating should be a smooth, dull, and slightly off-white.

If you have not already done so, reassemble the electrode and allow the renewed reference electrode to 'equilibrate' overnight for best stability. Store the electrode with the frit in the filling solution. If a low leakage 'fiber plug' or cracked glass junction is used, DI water can be used to store the electrode. However, this is not recommended for storage if Vycor® or other 'high leak rate' junctions are employed since that can lead to the dilution of the filling solution!

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Enemies of the Ag/AgCl electrode:

- **Light.** UV light decomposes AgCl to give silver(0) which gives the electrode a black appearance. Normal lab fluorescent lights are OK, but don't store your electrodes on the window sill!

- **Base.** Ag_2O or AgOH will form if the [OH^-] is on the order of 0.1 *M* and the electrode potential will be a mixed Ag/AgCl/Ag_2O potential and will depend on the pH. Ag_2O will also form in the pores of the frit used.

- **NH_3 Buffers.** NH_3 will complex silver and will dissolve AgCl.

- **Sulfide.** Silver sulfide is quite insoluble.

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Temperature range:

The references, cited below, contain several tables and equations representing the Standard Potential of silver-silver chloride electrodes at temperatures ranging from 0°C to 95°C. These tables and equations must be used with care, however. They generally refer to the potential of a cell without a liquid junction. Sawyer gives the potential (including junction potential) from 10° to 40°. Around 25°, the potential can be estimated from the linear approximations, below.

[KCl]	Potential *vs.* NHE, E in mV, T in °C
3.5*M*	E = 205 - 0.73 * (T - 25°C)
sat'd	E = 199 - 1.01 * (T - 25°C)
From the data in Table 5.3 of Sawyer, 2nd Ed.	

I have seen references to an operating range of -5° to 100° for the Ag/AgCl electrode with intermittent use up to 130°. The practical temperature limits may be more restrictive, depending on the materials used to make the electrode. Generally, isolating the reference electrode with a bridge-tube and keeping the reference electrode at laboratory ambient may be the easiest answer for high temperature work!

If you need a really high temperature reference electrode, check here.

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REFERENCES

Further information can be found in Ives & Janz, and in Sawyer, Sobkowiak, & Roberts, section 5.2.