Instrumentation for amperometric and voltammetric measurements:

Two electrode configurations---can use only when reference is large area relative to working---so no $\eta_{\text{conc}}$ occurs!

$$V_0 = -iR_f$$
Three electrode potentiostat arrangement:---used when reference electrode is small, and/or $iR_{\text{soln}}$ will be large (large area working electrode)--hence significant error in $E_{\text{WE}}$ will exist due to $iR_{\text{soln}}$ drop!

**first generation:**

$E_{\text{in}}$ $R_1$ $S$ $R_2$ $E_{\text{ref}}$

point S is virtual ground
counter electrode
working electrode grounded

$i_{R1} + i_{R2} = 0$ ; no current can pass through amplifier---point S is virtual grd.

therefore:

$E_{\text{in}}/R_1 + E_{\text{ref}}/R_2 = 0$ Amplifier will put out voltage to make sure this always occurs
if $R_1 = R_2$ then $E_{in} = -E_{ref}$

but each voltage is with respect to common ground—
which is what $E_{WE}$ is kept at

Thus: $E_{in} = -(E_{ref} - E_{WE}) = E_{WE} - E_{ref}$

as you change $E_{in}$ you change $E_{WE} - E_{ref}$ ---since
summing amplifier will need to output enough
voltage to drive a current into the solution---so that
the potential of the solution is changed---to a value
where the potential of the reference electrode with
respect to ground (the working electrode) changes!

for example---if $E_{in}$ is made very negative---
from an initial value----
whenever \( E_{\text{ref}}/R_2 \neq E_{\text{in}}/R_1 \) then summing amplifier will force current to flow into solution via a faradaic reaction at counter electrode---
e.g., \( \text{H}_2\text{O} - 2\text{e}^- \longrightarrow 2\text{H}^+ + 1/2\text{O}_2 \)

At electronic equilibrium, output voltage of amplifier applies enough voltage to counter electrode so that polarization occurs to an extent that \( I_{\text{total}}=0 \) at point S.

If faradaic reaction takes place at working electrode due to potential difference between it and solution being great enough---then amplifier will continue to put charge into solution via oxidation (or reduction at counter electrode) to allow faradaic current to flow across interface of working electrode and solution.

Problem with first generation design is that current can flow through reference electrode---until--electron equilibrium is reached----thus reference electrode could become polarized during this current flow---

Solve this by using Voltage follower amplifier---before \( R_2 \)
Typical potentiostat arrangement:--2nd generation

\[ E_{in} \]

\[ R_1 \]

\[ S \]

\[ E_{ref} \]

\[ R_2 \]

\[ + \]

\[ - \]

\[ + - \]

\[ R_f \]

\[ \text{voltage follower} \]

\[ \text{current follower} \]

\[ V_o = -iR_f \]
\[ V_o = -iR_f \]

\[ E_1/R_1 + E_2/R_2 + E_3/R_3 + E_{\text{ref}}/R_{\text{ref}} = 0 \]