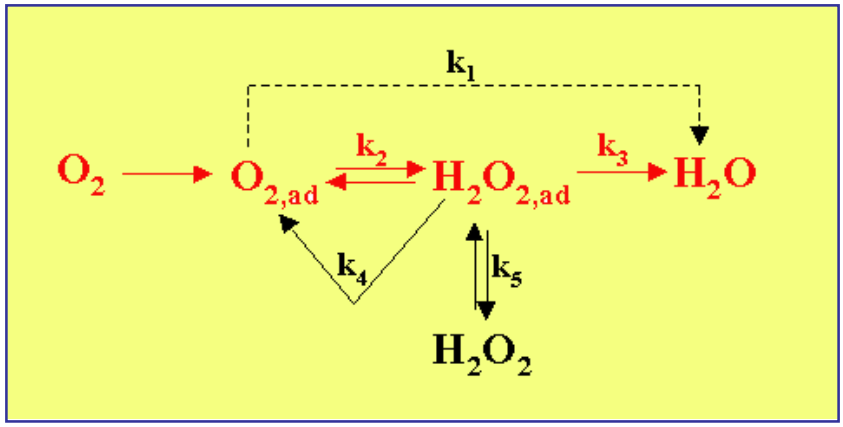


Oxygen Reduction Reaction

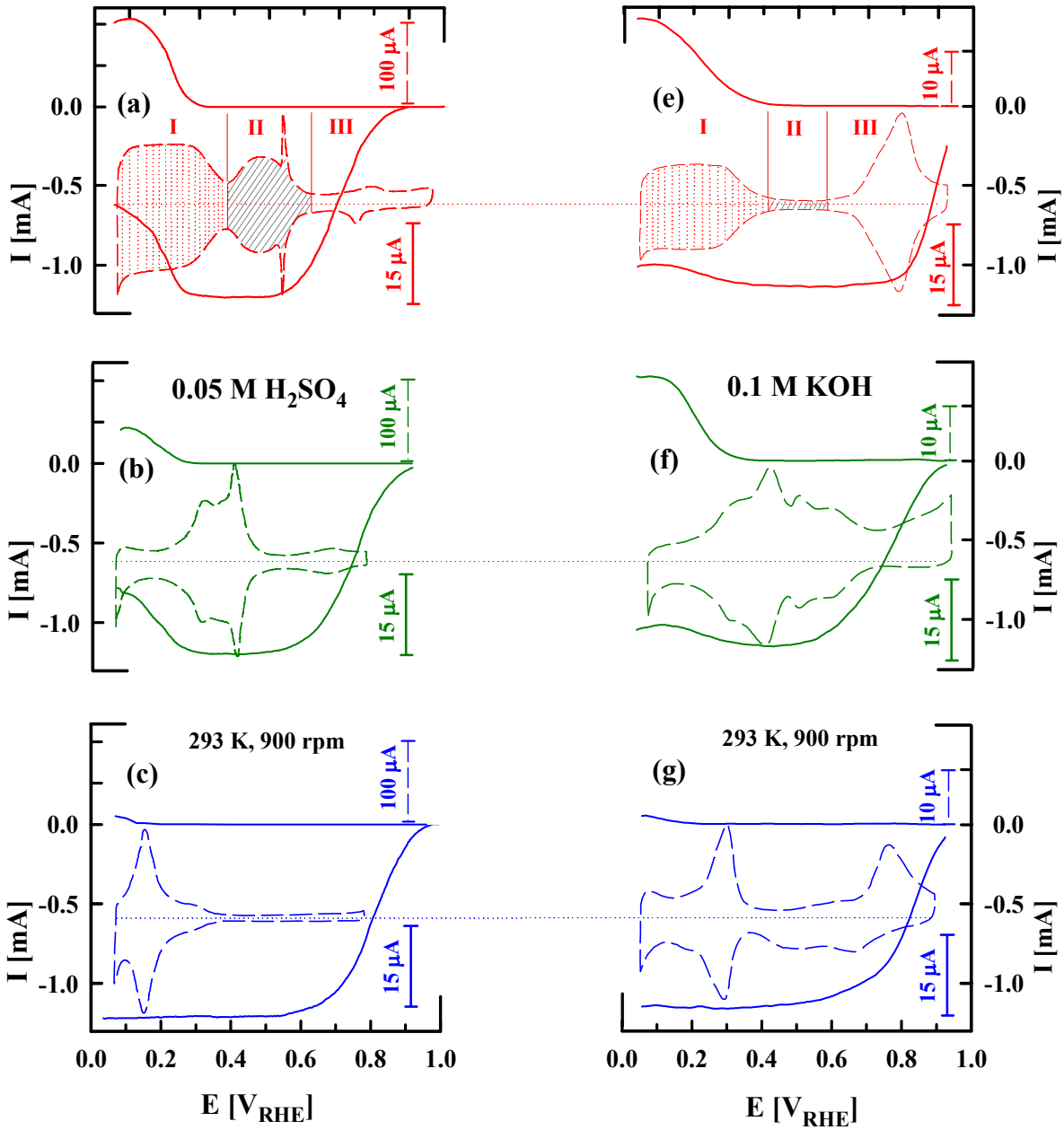
$O_2 + 1\ e^- + M = M(O_2^-)_{ad}$ (rds)

$M(O_2^-)_{ad} + H_3O^+ = H_2O + M(O_2H)_{ad}$

$M(O_2H)_{ad} + H_3O^+ + 1\ e^- + M = 2\ MOH_{ad}$

$M(O_2H)_{ad} + H_3O^+ + 1\ e^- = H_2O_2$

$[MOH_{ad} + H_3O^+ + 1\ e^- = H_2O]$ x2

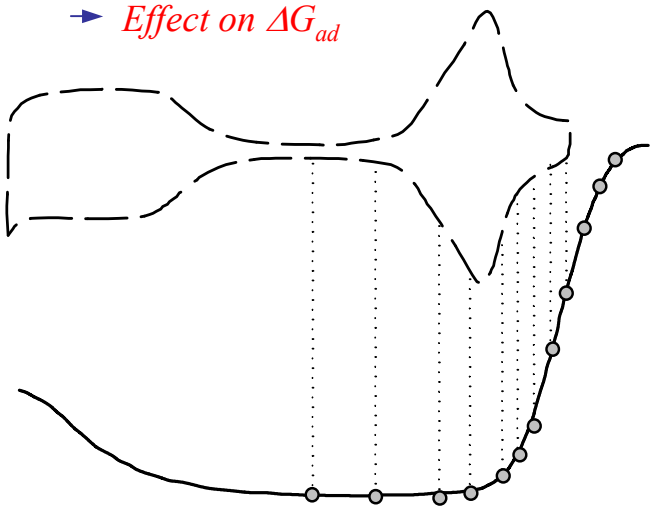

(a)
I
II
III
100 µA
15 µA
0.0
-0.5
-1.0
I [mA]
(e)
10 µA
15 µA
0.05 M H2SO4
(b)
0.1 M KOH
(f)
293 K, 900 rpm
(c)
(g)
0.0
0.2
0.4
0.6
0.8
1.0
E [VRHE]

$$i = nFKc_{O_2}(1-\Theta_{ad})^x \exp(-\beta FE/RT)\exp(-\Delta G^*_\Theta/RT)$$

$(1-\Theta_{ad})$ term

Θ_{ad} is mostly OH_{ad} and A_{ad}, not $(O_2^-)_{ad}$

- *Effect on availability of metal sites*
- *Effect on ΔG_{ad}*

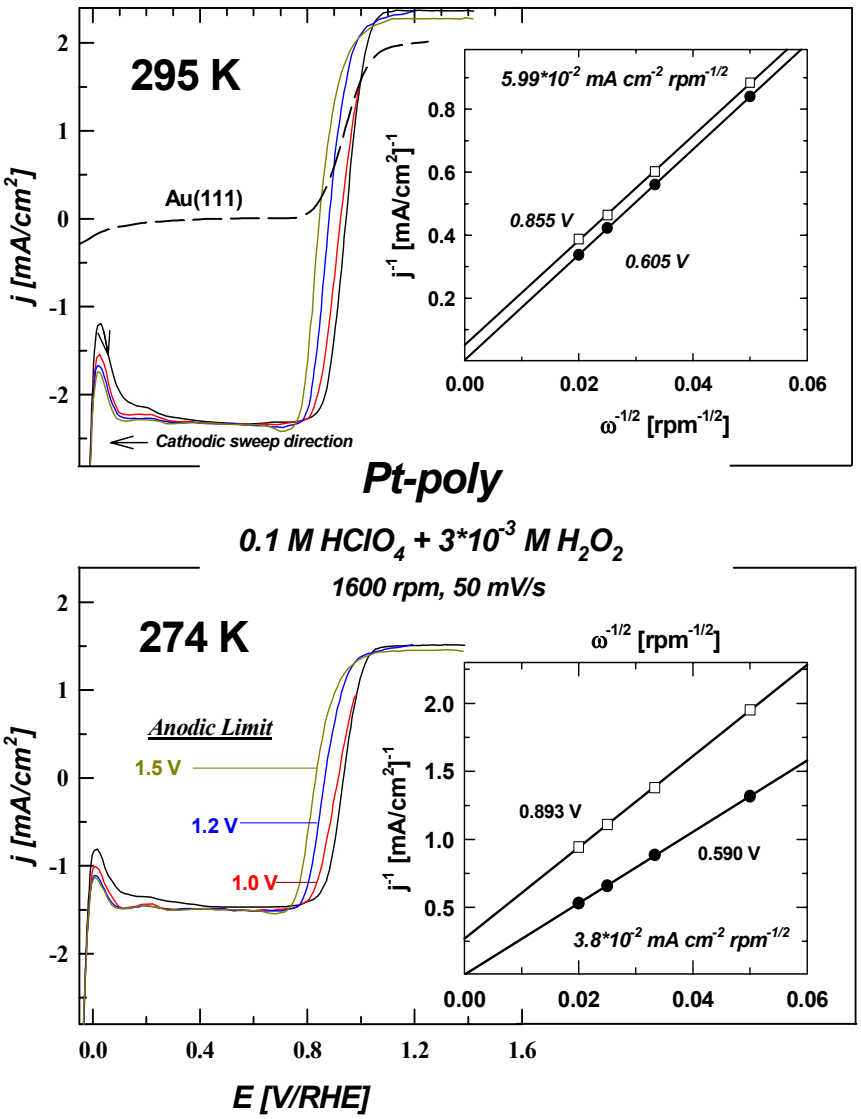


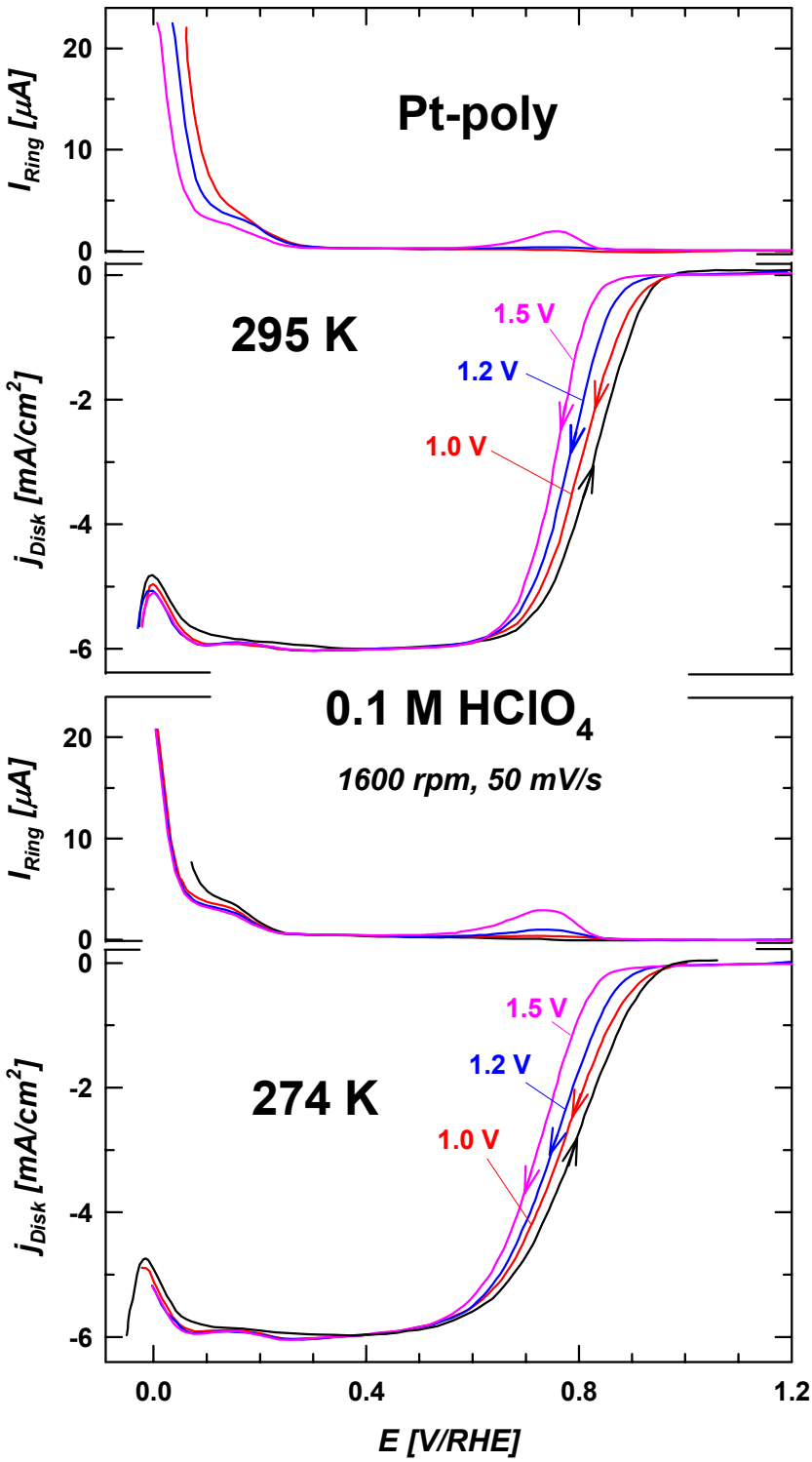
ΔG_{ad} term

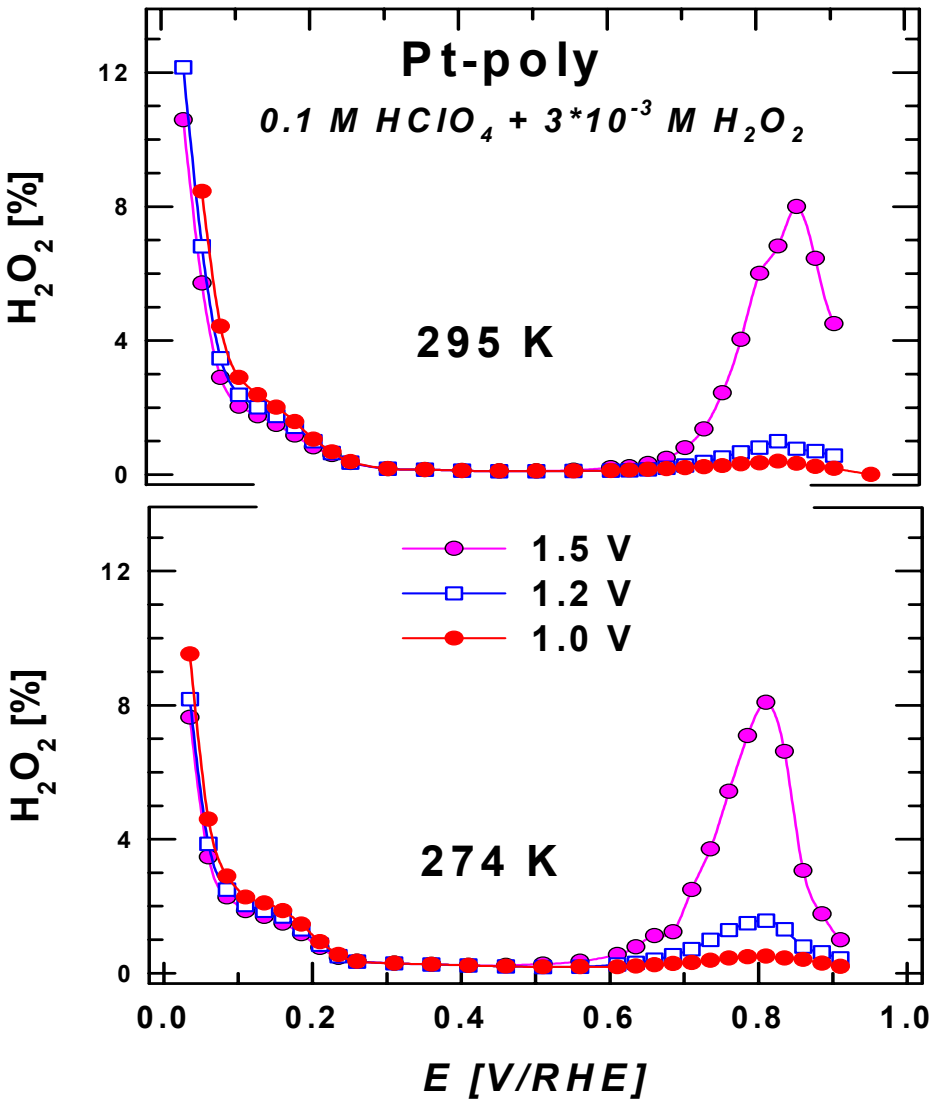
O_2 *adsorption strength is uniquely related to the electronic properties of the electrode material*

$Pt - O_2^- : \Delta G_{ad} = -0.87$ eV

$Au - O_2^- : \Delta G_{ad} = +0.24$ eV


295 K
Au(111)
Cathodic sweep direction
j [mA/cm²]
5.99*10⁻² mA cm⁻² rpm⁻¹/²
0.855 V
0.605 V
j⁻¹ [mA/cm²]⁻¹
ω⁻¹/² [rpm⁻¹/²]
Pt-poly
0.1 M HClO4 + 3*10⁻³ M H2O2
1600 rpm, 50 mV/s
274 K
Anodic Limit
1.5 V
1.2 V
1.0 V
ω⁻¹/² [rpm⁻¹/²]
0.893 V
0.590 V
3.8*10⁻² mA cm⁻² rpm⁻¹/²
E [V/RHE]


Pt-poly
295 K
1.5 V
1.2 V
1.0 V
0.1 M HClO4
1600 rpm, 50 mV/s
274 K
1.5 V
1.2 V
1.0 V
I_Ring [μA]
j_Disk [mA/cm²]
E [V/RHE]
20
10
0
-2
-4
-6
0.0
0.4
0.8
1.2


Pt-poly
0.1 M HClO4 + 3*10-3 M H2O2
295 K
274 K
1.5 V
1.2 V
1.0 V
H2O2 [%]
H2O2 [%]
0
4
8
12
0.0
0.2
0.4
0.6
0.8
1.0
E [V/RHE]

Conclusions

Operation at 274 K does not produce any more peroxide at either electrode than operation at higher temperatures

Primary source of peroxide is at the hydrogen electrode from reduction of oxygen permeating through the membrane