Oxygen Electro-reduction on C22 and C276 Nickel Metal Alloy

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Acknowledgement and Disclaimer

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Outline

- Objective: determine if O_2 is reduced on C22 and C276 in 1M KOH
- Materials and methods
  - C22 and C276 surface preparation
  - O_2 reduction by CPRM method: standardized to Au disc – Au ring
  - O_2 reduction by CPRM method for C22 and C276
- Estimate of rate constants for O_2 reduction on C22 and C276
- Future Research
  - FTIR of C22 and C276 surface oxides
  - O_2 reduction in presence of nitrates and chloride
- Additional Acknowledgments

Oxygen Electro-reduction on C22 and C276 Nickel Metal Alloy

- **Project Objective:**
  - To establish if O_2 reduction occurs on alloys C22 and C276 in aqueous alkaline electrolyte.
  - Determine conditions and extent (kinetics) of O_2 reduction on C22 and C276.
    - Determine the sustained O_2 reduction potential(s) on hastelloys in alkaline media
    - Identify products of O_2 reduction and their rates of formation
    - Provide experimental results in a form suitable for inputting to computational methods for predicting alloy corrosion processes

- **Approach:**
  - Measure electrochemical behavior of fresh and aged alloys in aqueous alkaline (KOH) electrolyte in the presence or absence of O_2, with and without additives (KNO_3, Cl-, particles) at various temperatures.
    - Voltammetry with electrode in still solution
    - Rotating ring-disc electrode (RRDE)
    - Electrochemical impedance spectroscopy (EIS)
    - Electrochemical Fourier Transform Infrared (Echem-FTIR)

Nickel Metal Alloy wt% Compositions

Alloy Designation	UNS#	C	Co	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	V	W
Hastelloy(R) C276	N10276	4e-3	**1.45**	**15.74**	n/a	**5.58**	0.50	**15.53**	**57.55**	0.008	0.003	0.02	0.163	**3.45**
Hastelloy(R) C22	N06022	4e-3	**0.72**	**21.00**	n/a	**3.90**	0.23	**13.30**	**57.90**	0.011	0.004	0.026	0.013	**2.90**
Hastelloy(R) C2000	N06200	1e-3	0.05	22.71	1.54	0.65	0.23	15.64	59.12	0.003	0.004	0.043	n/a	n/a

n/a – not reported on analysis certificate.

Approach

- **Planarized electrode** – Allied HiTech 8" polishing table: wet 800, 1200, 2400 grit SiC; wet 5um, 3um, 0.5um alumina
- **Mirror surface finish** – Hand polishing fixture: wet felt 1um, 0.3um, and 0.05um alumina slurry
- **Prior to Echem** – Random hand polish: wet felt 0.05um alumina slurry; rinse in 95% EtOH, then 18.2 MΩ H_2O

<u>Apparatus:</u>

- Pine rotator (in blue)
- Jacketed Pyrex 5-neck cell
- Configured with bridged SCE reference
- Spectroscopic graphite auxiliary electrode
- RRDE (Au ring, hastelloy disc)
- Sparging tube
- PAR VMP2 controller w/ ver. 9.13 software
- Circulating glycol-H_2O **(thermostat control: ±1° C)**

The Cyclic Potential Ring Measurement (CPRM) Method

Rotating Ring Disc Electrode (RRDE) technique:

- Continuously cycle the ring over a small potential range for oxidation;
- Concurrently, step potentiostatically the disc in a range for reduction.

Reproducible, "clean" ring surface for quantitative ring electrode detection; background subtraction for low level detection, and does not underestimate the role of H_2O_2 production.

N. R. K. Vilambi and E. J. Taylor,
J. Electroanal. Chem., **270** (1989) 61-77;
Electrochemica Acta., **34**, no. 10, (1989) 1449-1454.

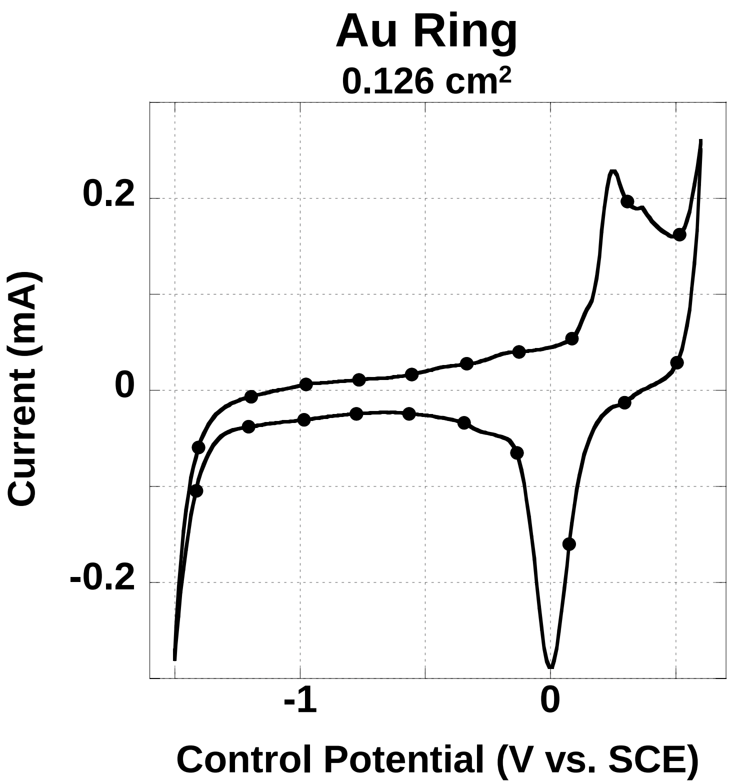
- **Quantitative description of peroxide formation during oxygen reduction on Au and Pt in alkaline media.**

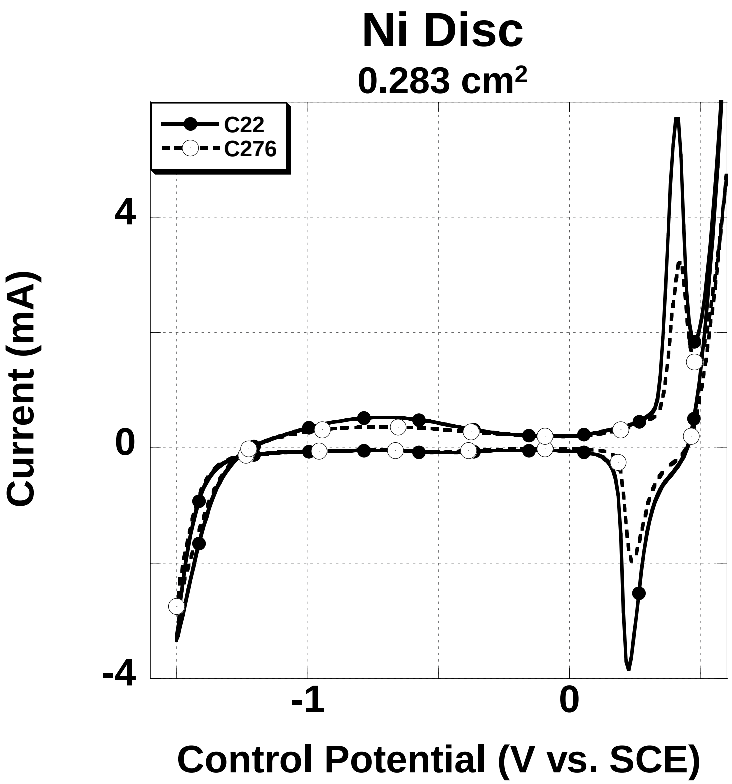
D. Gervasio, J. H. Payer,
in *"Fundamental Understanding of Electrode Processes, in Memory of Professor Ernest B. Yeager"*, Proceeding of the Electrochemical Society, Orlando, FL, J. Prakash, D. Scherson, M. Enayetullah and In-Tae Bae, Editors, (2003) 58–70.

- **Kinetics of oxygen electro-reduction on steel by CPRM in alkaline media were investigated.**

Cyclic Voltammetry Potential Range Surveys for CPRM Method

(Ar de-aerated 1M KOH @ 30°C, pH = 14, 500mV/s scan rate, 4900 rpm, 6th cycle)





- Little to no slope around 0 mA shows good RRDE configuration.
- C22 & C276 have very similar responses w/ C276 having less metal oxide formation and reduction than C22.

Cyclic Potential Ring Measurement (CPRM) Method – Timing for Au-Au RRDE

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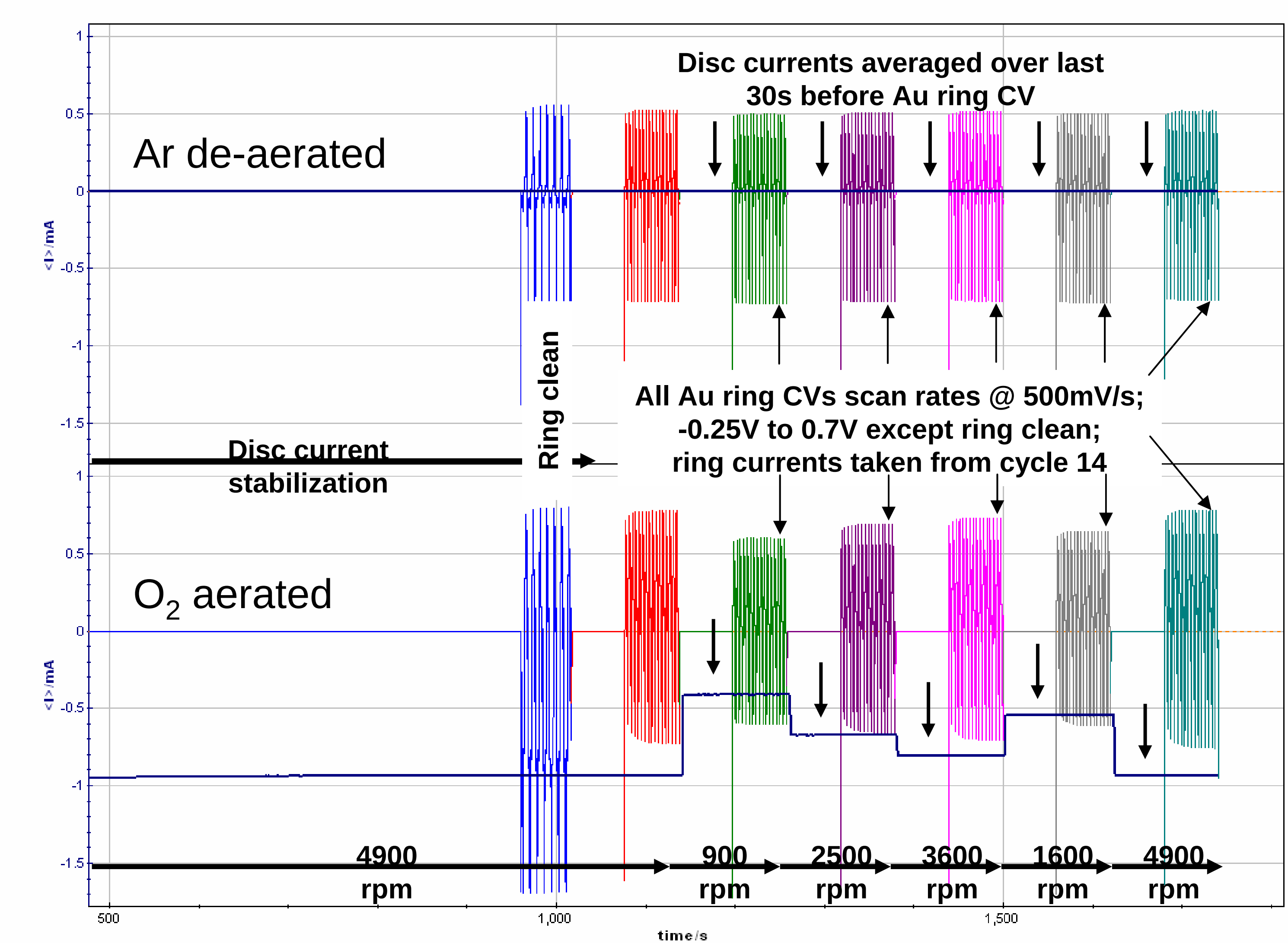

Cyclic Potential Ring Measurement (CPRM) Method

Series Reduction of O_2 on Au in 1M KOH @ 30° C, pH = 14

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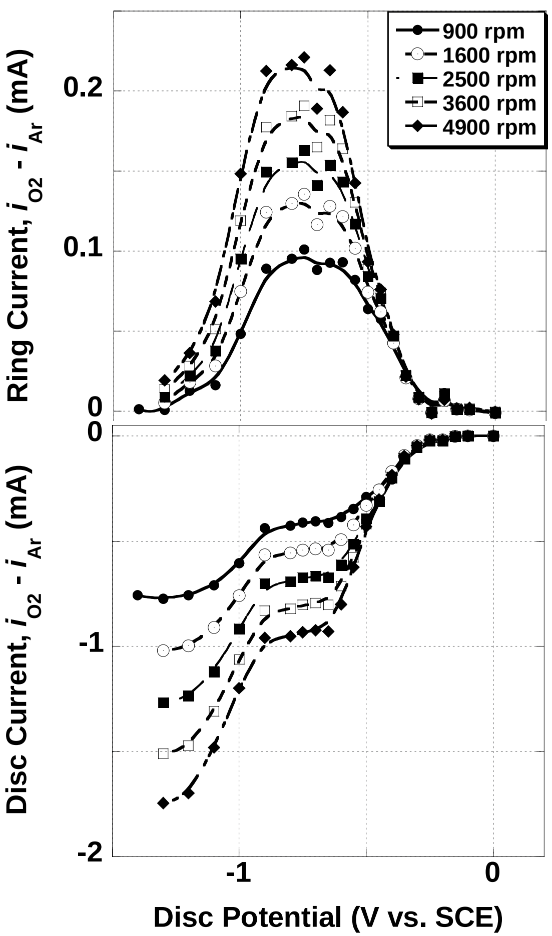
CPRM Plots

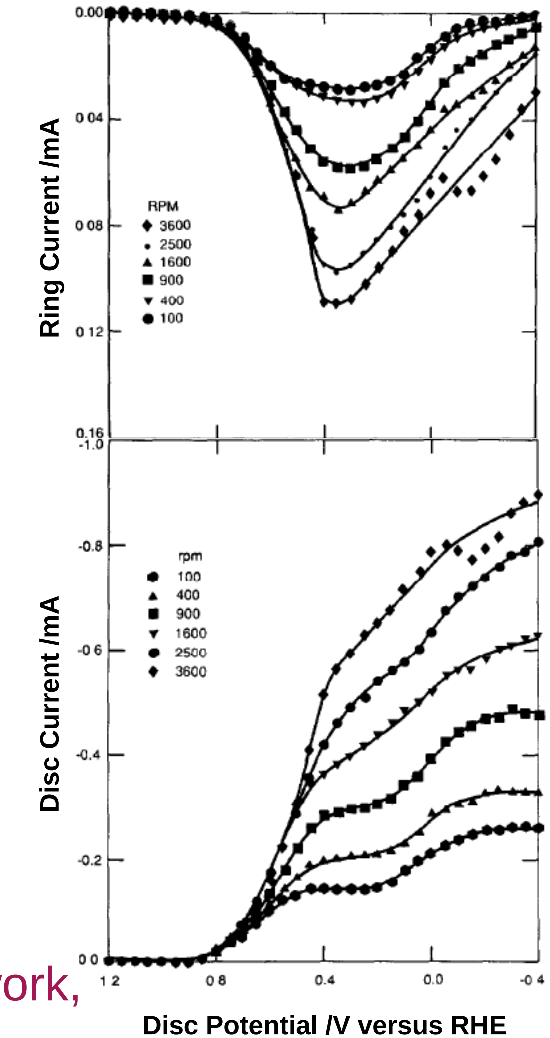
Current work at ASU



Au Ring (0.126 cm²) currents
(averaged from 0.5V to 0.6V on 14th cycle; scan: -0.25V to 0.7V @ 500mV/s)

Au disc (0.283 cm²) currents

Taken from Vilambi and Taylor, *J. Electroanal. Chem.*, 270 (1989) 61-77



- Our findings are very similar to those of Vilambi's work, calibrating our methodology.

Cyclic Potential Ring Measurement (CPRM) Method

for O_2 Reduction to H_2O_2 in 1M KOH @ 30° C, pH = 14

Levich Plots

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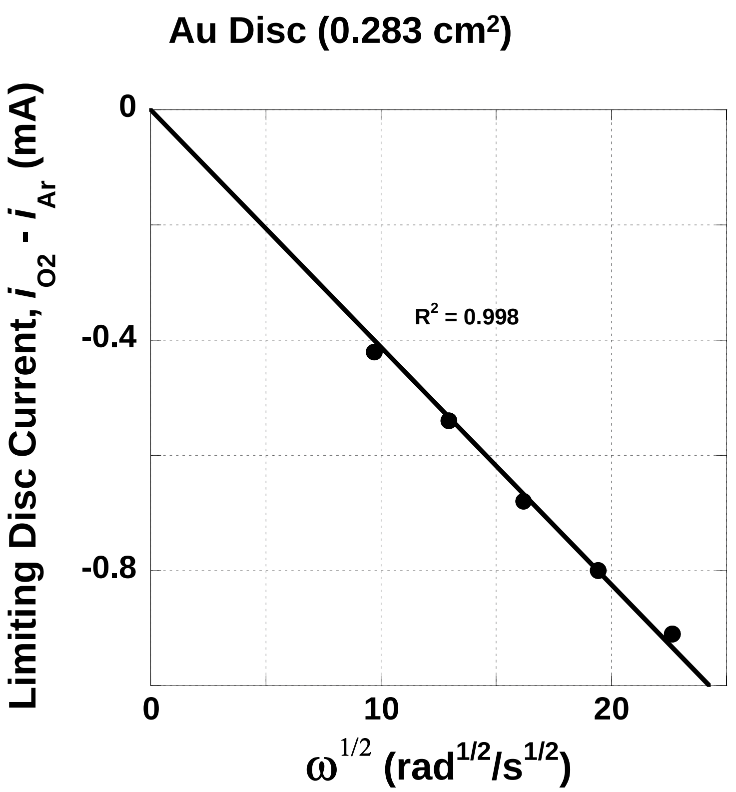
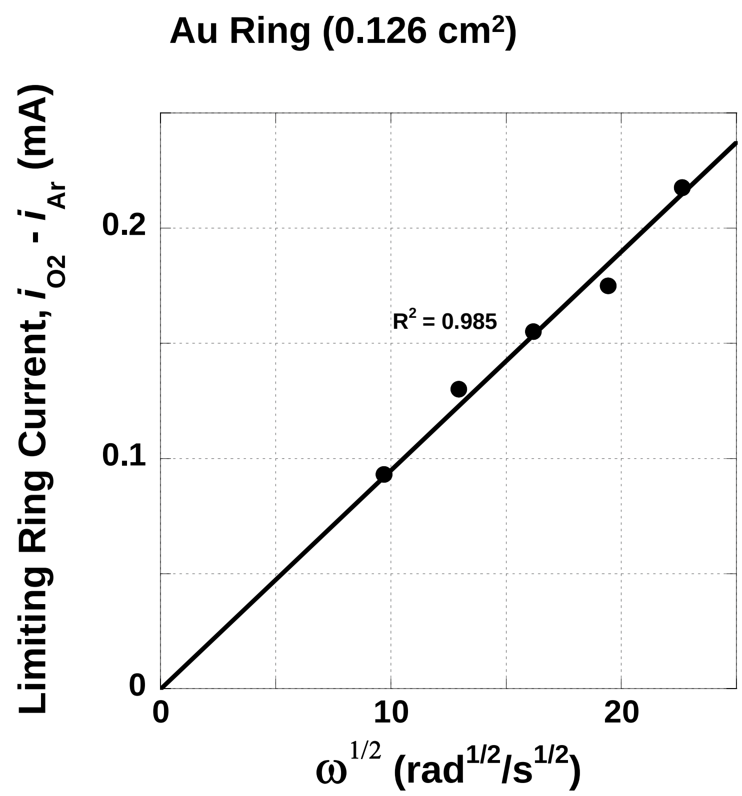
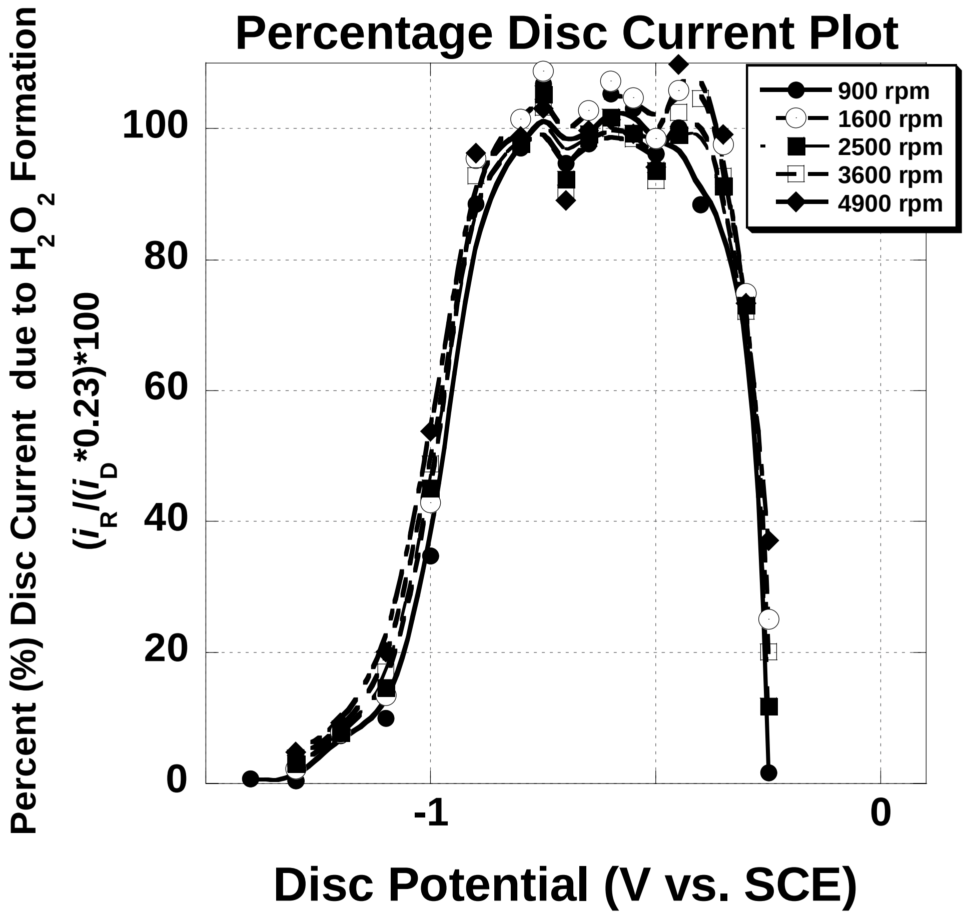




- As the rotation rate increase, the limiting currents increase linearly with the square root of the rotational speed in accordance with Levich's equation.

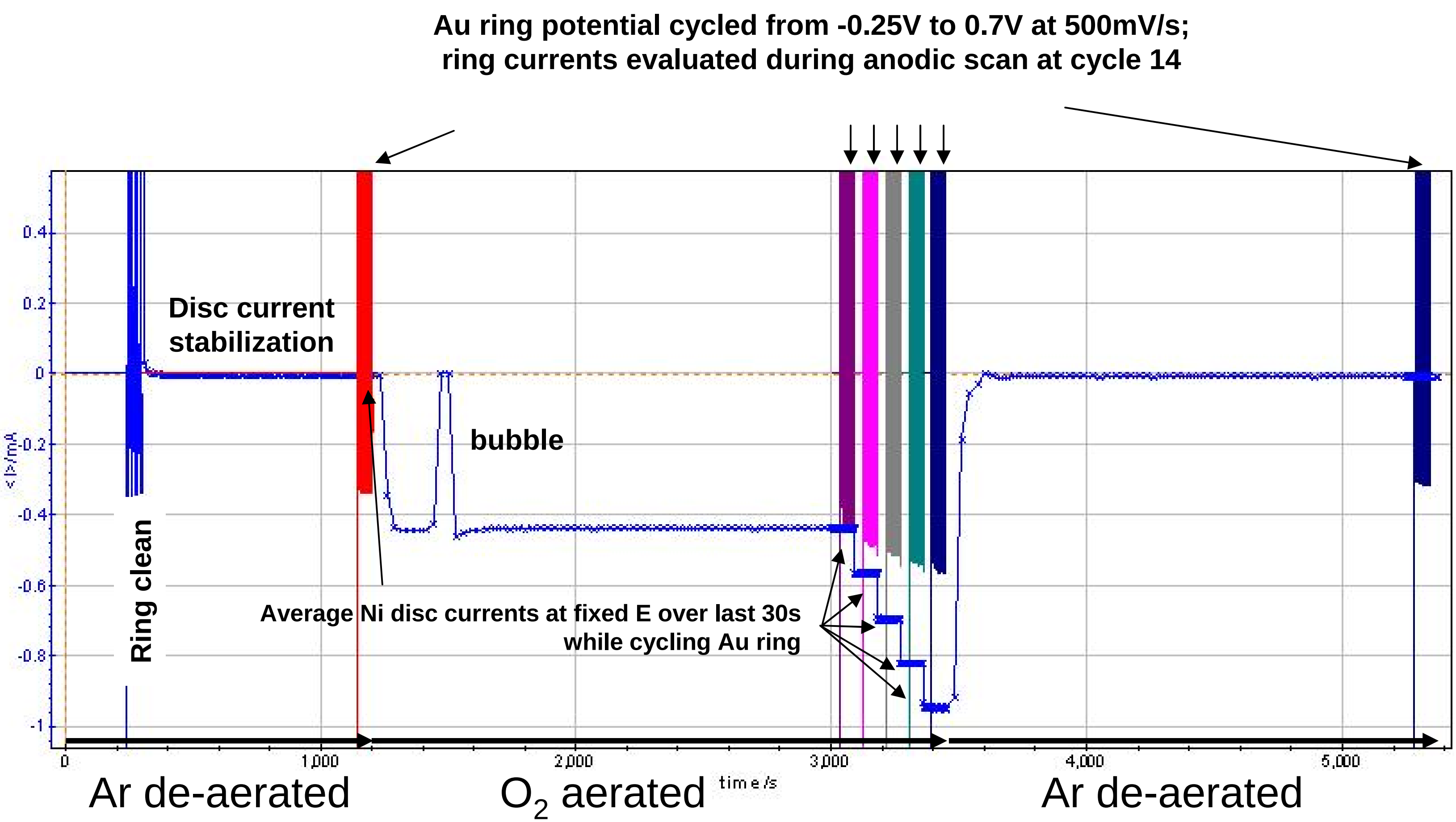
Cyclic Potential Ring Measurement (CPRM) Method

for O_2 Reduction to H_2O_2 in 1M KOH @ 30° C, pH = 14



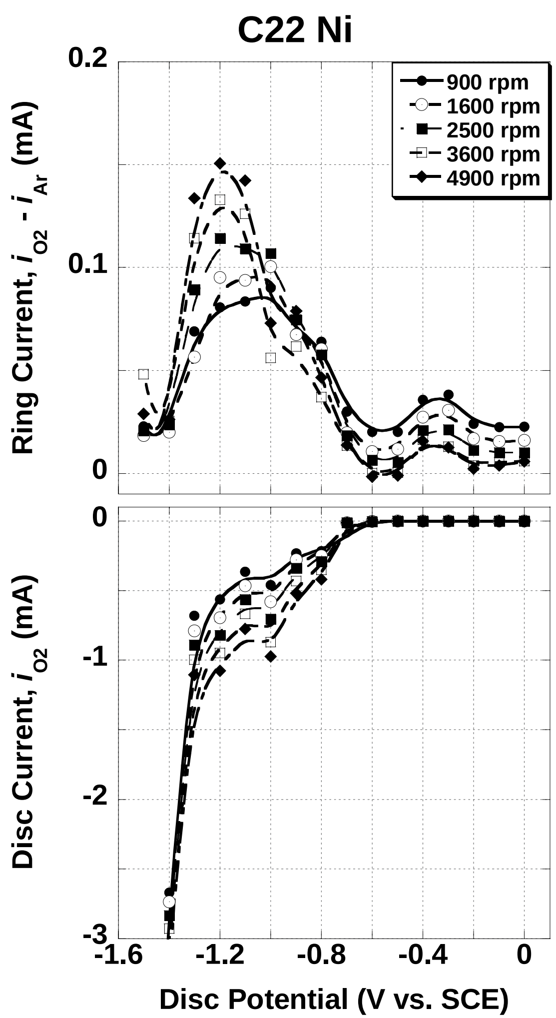
- Our CPRM experiment repeats Vilambi's findings of 100% current collection in the potential range (-0.4V to -0.8V) for the first reduction in the series mechanism for O_2 on Au, and validates our methodology.

Cyclic Potential Ring Measurement (CPRM) Method –
Timing for Au-Ni RRDE



Cyclic Potential Ring Measurement (CPRM) Method

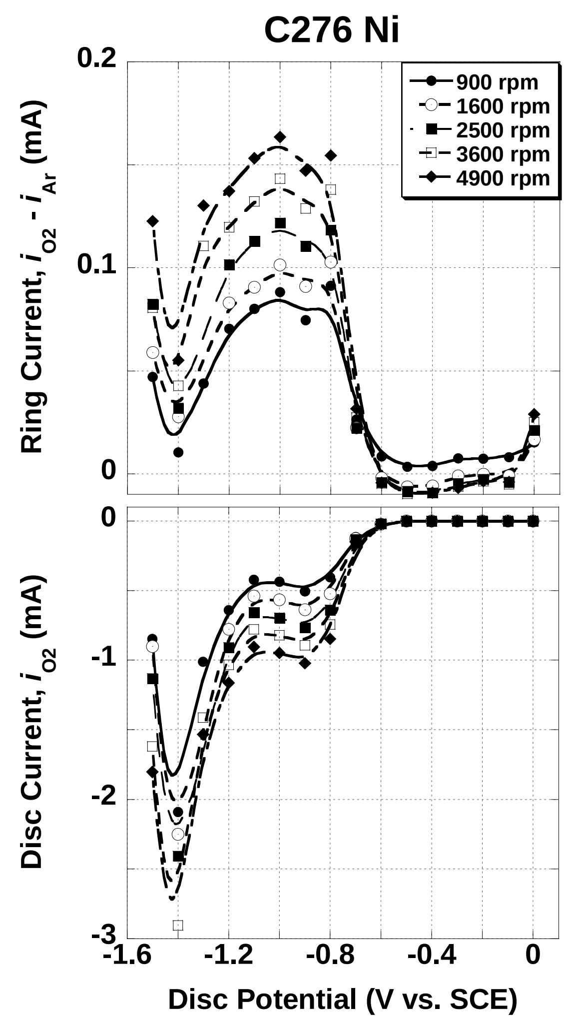
Series Reduction of O_2 on Hastelloys in 1M KOH @ 30° C, pH = 14



CPRM Plots

Au Ring (0.126 cm²) currents
(averaged from 0.5V to 0.6V on 14th cycle; scan: -0.25V to 0.7V @ 500mV/s)

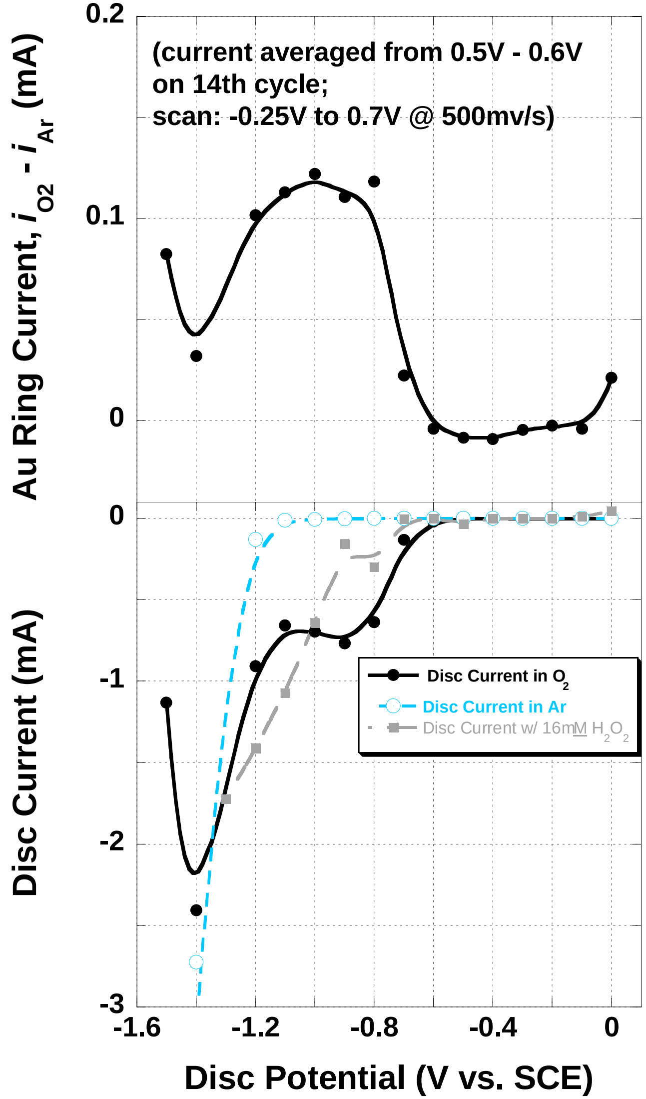
Ni disc (0.283 cm²) currents
(averaged over 30s during the Au ring cyclic voltammetry)



- A difference of ~0.1 V for H_2O_2 formation between C22 & C276.

Cyclic Potential Ring Measurement (CPRM) Method

C276 Ni; 1M KOH @ 30° C, pH = 14; 2500 rpm

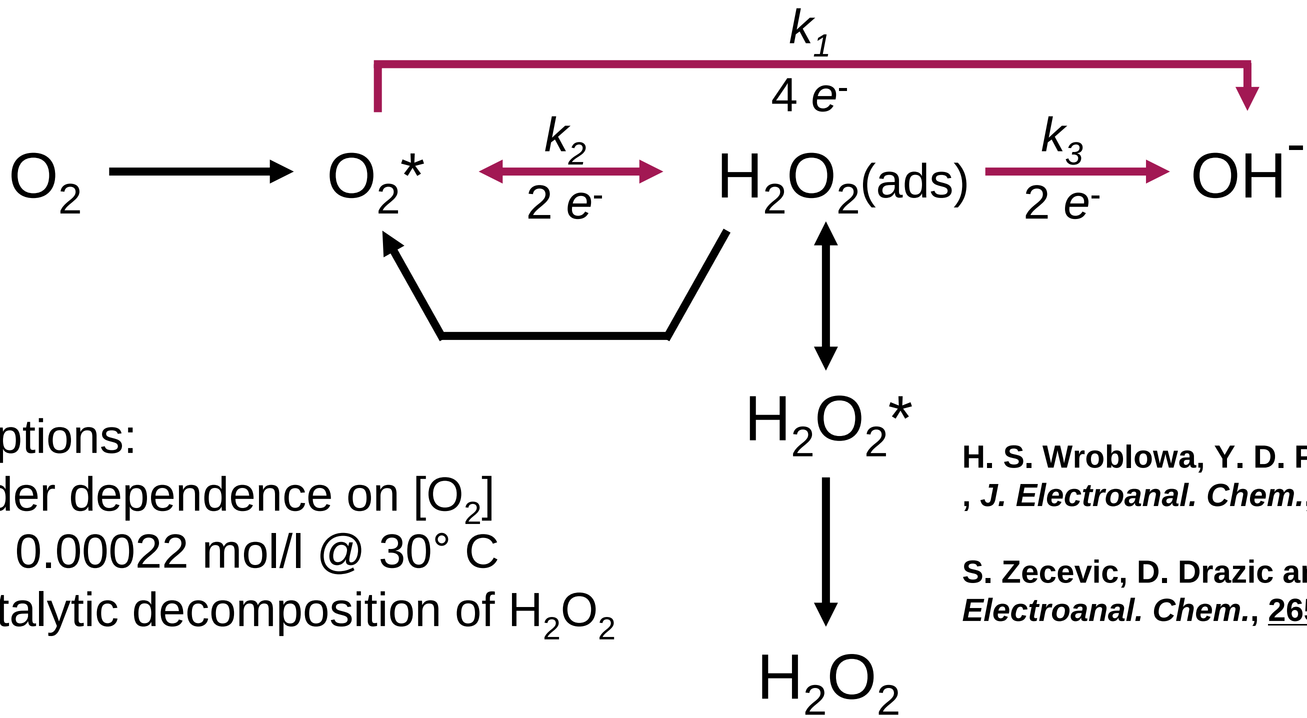


Disc currents on C276 in 1M KOH equilibrated with:

- **Ar,**
- **O_2,**
- **H_2O_2 under Ar**

- **O_2 reduction occurs in two waves (-0.5 to -1; -1 to -1.4);**
- **H_2O_2 reduction occurs in one wave (-1 to -1.4);**
- **Indicates a 2-step series reduction path for O_2 reduction to H_2O:**
  - **first: $O_2 \rightarrow H_2O_2$**
  - **second: $H_2O_2 \rightarrow H_2O$.**

Rate Constant Evaluation



Assumptions:

- 1^{st} order dependence on $[O_2]$
- $[O_2]$ = 0.00022 mol/l @ 30° C
- no catalytic decomposition of H_2O_2

H. S. Wroblowa, Y. D. Pan, and G. Razumney, *J. Electroanal. Chem.*, 60, (1976) 195.

S. Zecevic, D. Drazic and S. Gojkovic, *J. Electroanal. Chem.*, 265, (1989) 179.

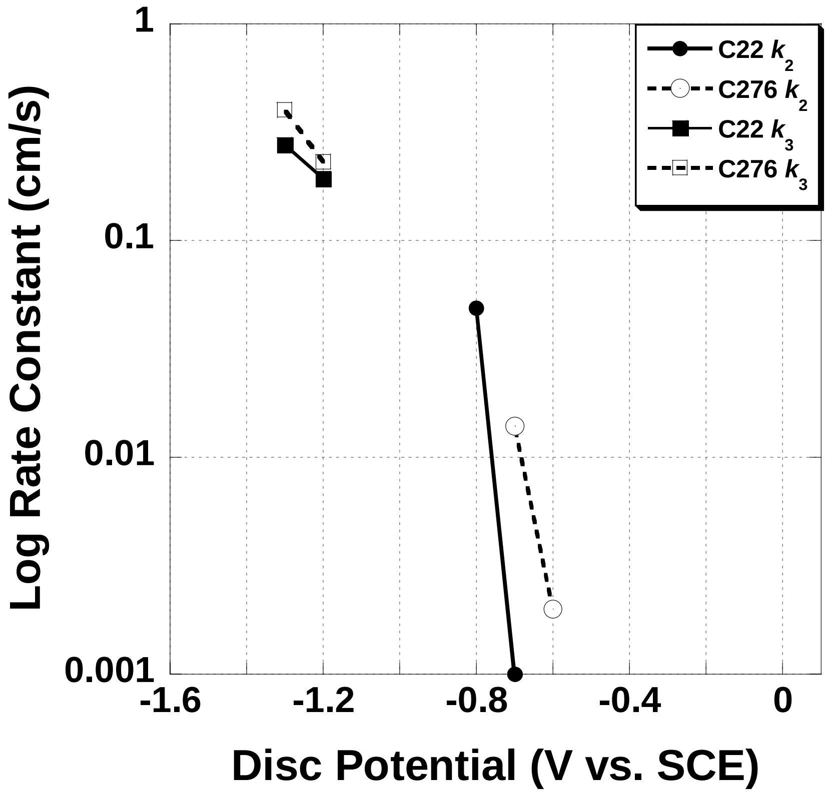
CPRM data applied to

$$j_{kinetic} = j_L\, j/(j_L - j)$$
$$j_{kinetic} = k_{exp} n [O_2]^1$$

→ Estimated rate constants k_2 & k_3

Estimated Rate constants for O_2 Reduction on C22 & C276
in 1M KOH @ 30° C; pH =14

- ***Assuming a series mechanism; &***
- ***Using CPRM disc data & the relations*** $j_{kinetic} = j_L j/(j_L - j)$, $j_{kinetic} = k_{exp} n[O_2]$.



- The estimated rate constants for H_2O_2, k_2, and H_2O, k_3, formation are greater for C276 than C22 for the same potential.

Summary

- Standardized and calibrated RRDE approach for O_2 reduction kinetics on hastelloy discs using the CPRM method of Vilambi & Taylor that used Au ring – Au disc;

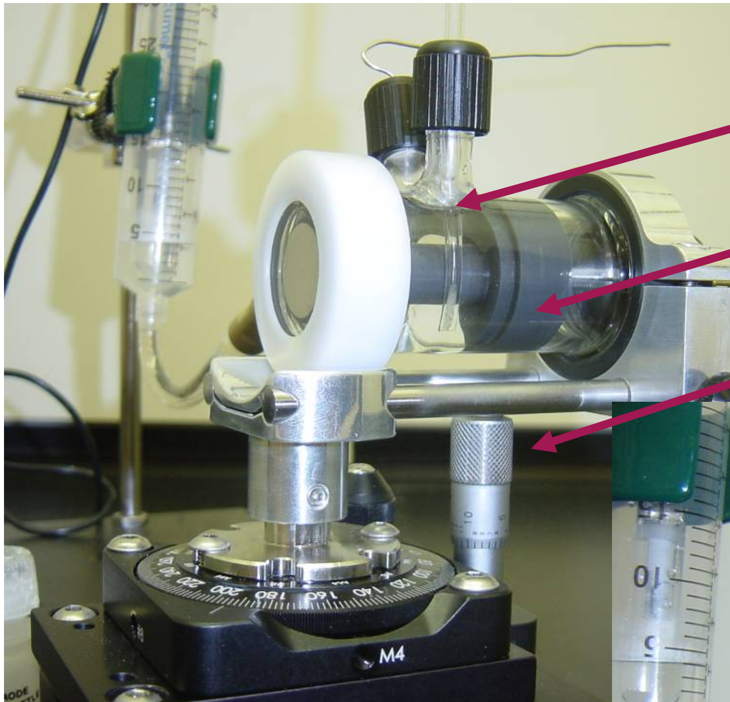
- Oxygen reduction on C22 & C276 in alkaline water to peroxide onsets at about -0.6V; continues to -1.4V; maximizes at -1.1V (on C22) and -1.0V (on C276) vs. SCE;

- The $H_2O_2 \rightarrow H_2O$ onset at -1V vs. SCE; the limiting H_2O_2 current was ill-defined due to overlap with H_2 generation at more negative potentials;

- Estimated rate constants, k_2 and k_3, from CPRM data for:

		C22	C276	
i) $O_2 \rightarrow H_2O_2$	@ -0.7V	0.001	0.013	(cm/s)
ii) $H_2O_2 \rightarrow H_2O$	@ -1.2V	0.193	0.232	(cm/s)

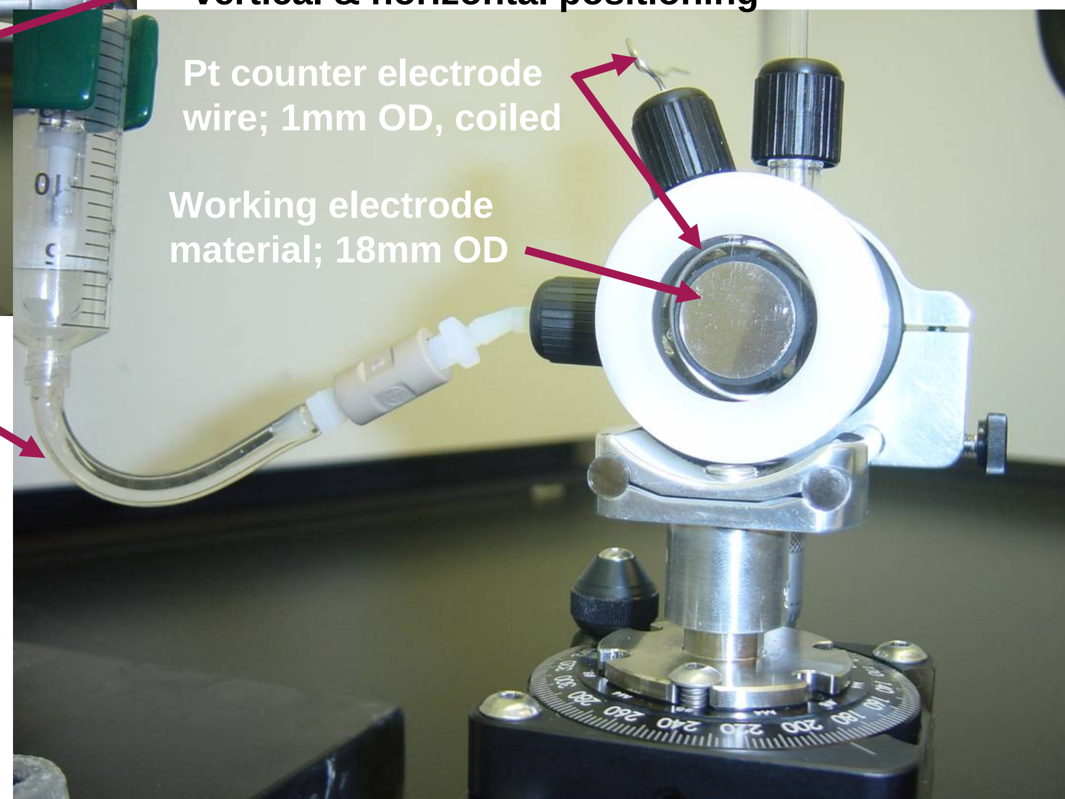
EChem-FTIR



Gas inlet/diffusion tube

PEEK plunger

FTIR box mount w/ rotation, tilt, vertical & horizontal positioning



Pt counter electrode wire; 1mm OD, coiled

Working electrode material; 18mm OD

Reference electrode reservoir to Luggin tip

- Standard window size (32mm OD x 2mm thick) is easily exchanged;
- Can be completely disassembled

Additional Acknowledgements

Design and fabrication assistance on the EChem-FTIR cell was provided by scientific glassware designer **Janice Kyle**, Dept. of Chemistry & Biochemistry at Arizona State University and by Sr. designer & instrument maker **Zoltan Farkas**, Dept. of Physics at Arizona State University.