

C-cp-Ag Composite Electrodes: A New Approach for Metal Air Batteries

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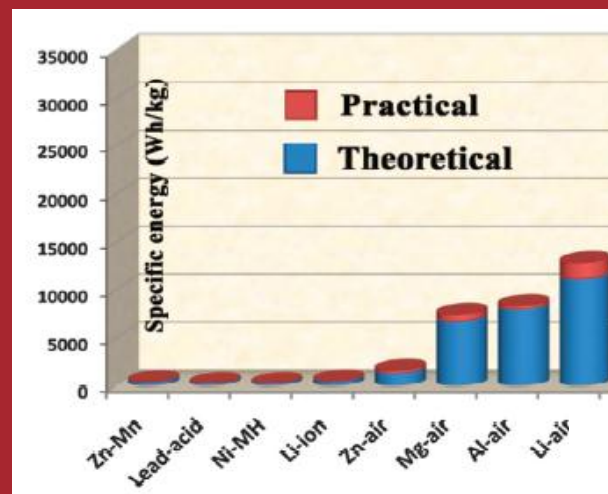
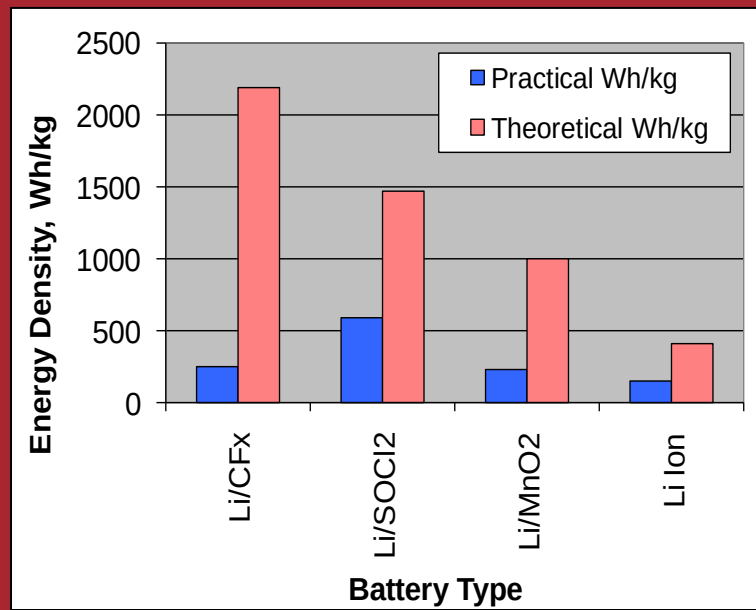
Stony Brook University

Sponsor: Air Force Office of Scientific Research
Program Officers: Dr. Joan Fuller, Dr. Ali Sayir
Award Number: FA9550-09-1-0334

Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE AUG 2012		2. REPORT TYPE		3. DATES COVERED 00-00-2012 to 00-00-2012	
4. TITLE AND SUBTITLE C-cp-Ag Composite Electrodes: A New Approach for Metal Air Batteries			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Stony Brook University, Materials Science and Engineering, Chemistry, Stony Brook, NY, 11794			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the 2nd Multifunctional Materials for Defense Workshop in conjunction with the 2012 Annual Grantees'/Contractors' Meeting for AFOSR Program on Mechanics of Multifunctional Materials & Microsystems Held 30 July - 3 August 2012 in Arlington, VA. Sponsored by AFRL, AFOSR, ARO, NRL, ONR, and ARL. U.S. Government or Federal Rights License					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 19	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

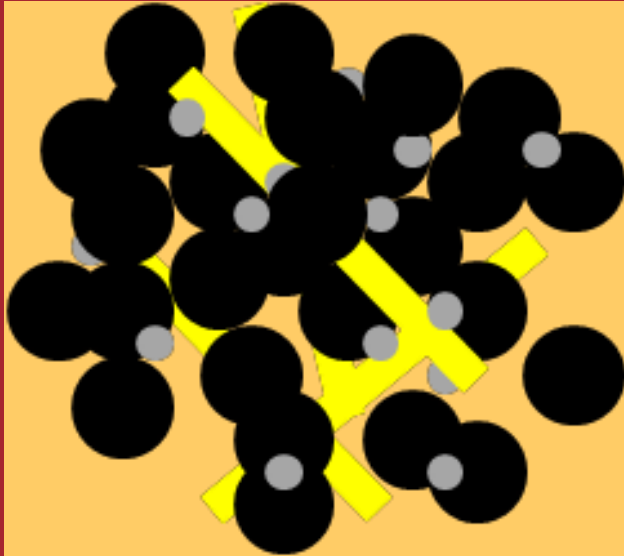
Metal-air batteries provide the opportunity for unprecedented energy density improvements

battery	theoretical		
	voltage (V)	capacity (Ah/kg)	energy (Wh/kg)
Li / (CF) _n	3.1	860	2,180
Li / SOCl ₂	3.7	450	1,470
Li / MnO ₂	3.5	310	1,010
Li-ion	3.8	150	570
Li / O ₂	3.4	3,860	13,000
Al / O ₂	2.3	2,990	6,900
Mg / O ₂	2.7	2,200	5,950
Zn / O ₂	1.3	820	1,070



Conventional electrode fabrication

conventional electrode



silver = active material

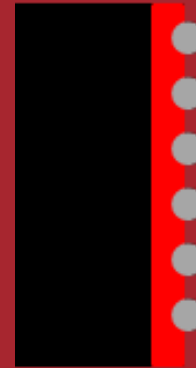
black = conductive additive

yellow = insulating binder

tan = metal foil current collector

novel composite electrode

planar (2D)



3D



black = conductive carbon

red = conductive polymer

silver = catalyst

Our composite electrode strategy offers several advantages

Electrochemical deposition of layers ensures good electrical contact among composite electrode components and electrolyte.

This is a transferrable concept that can be extended to prepare 2D and 3D layered composite electrodes.

Depending on the nature of the current collector (cc), and conducting polymer (cp), morphology and porosity of the layered composite can be tuned.

Due to the conductive nature of the composite, even small quantities of catalyst (Ag) should exhibit high oxygen reduction activity.

Project objectives

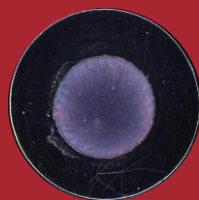
- i. Demonstrate new composite electrode based on carbon-conductive polymer-silver (C-cp-Ag) composite.
- ii. Evaluate composite oxygen reduction activity.
- iii. Assess roles of composite components.
- iv. Investigate non-aqueous oxygen reduction mechanism.
- v. Develop and investigate 3D C-cp-Ag composite.

Electrodeposition is desirable for fabrication

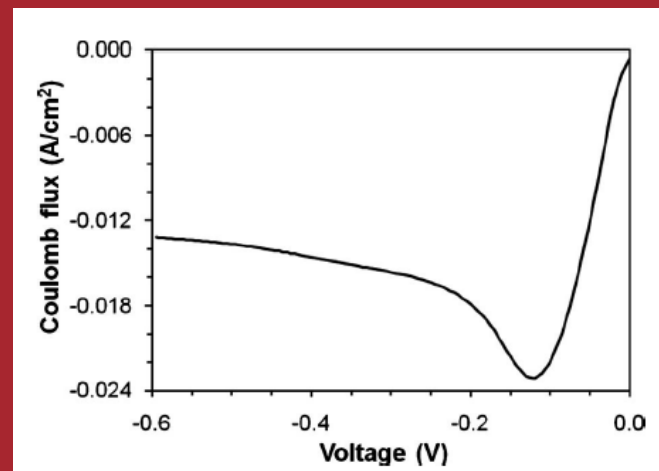
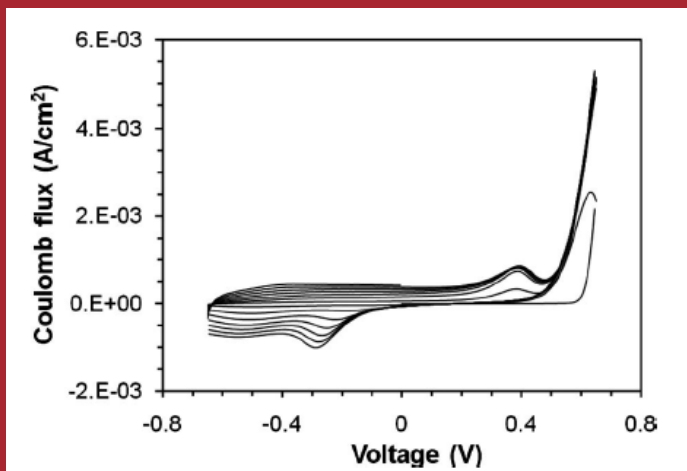
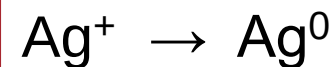
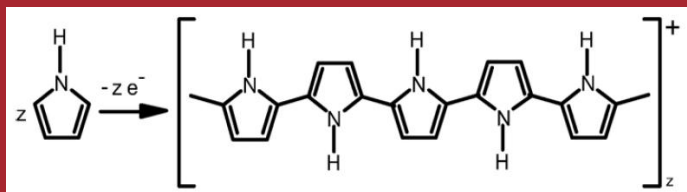
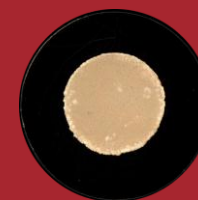
C



C-cp

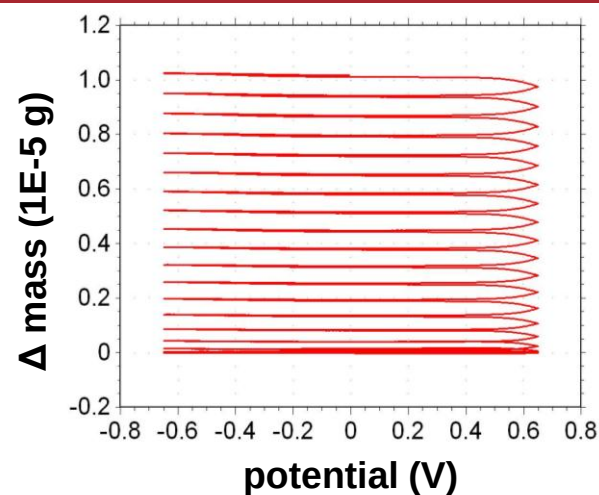
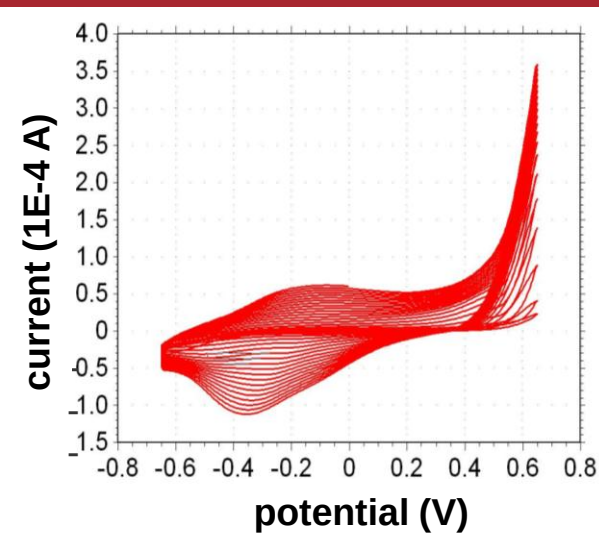


C-cp-Ag

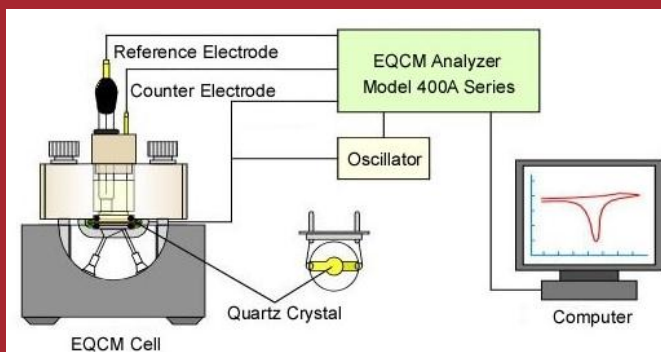
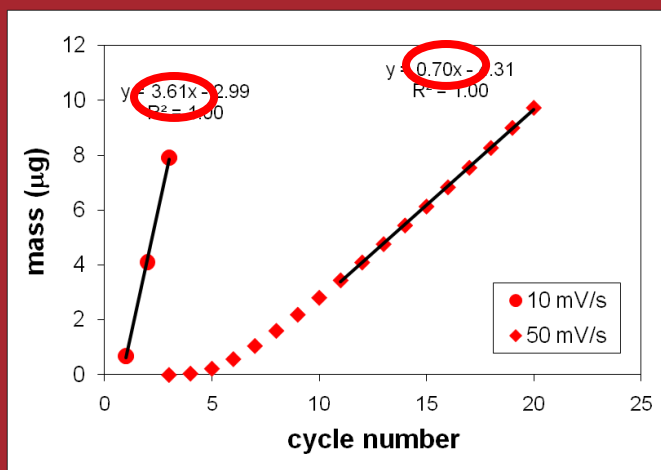


C-cp-Ag prep can be quantitatively controlled

cp deposition

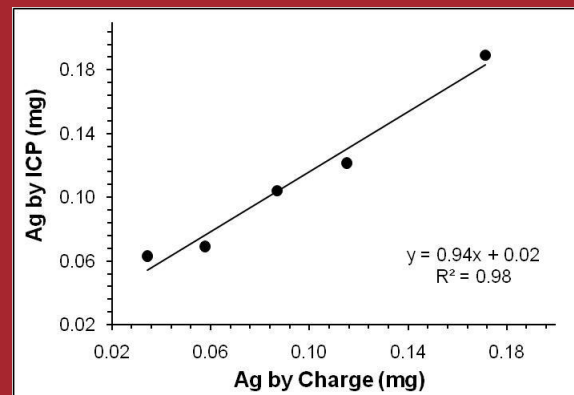


$$\Delta f = \frac{-2f_0^2}{A\sqrt{\mu\rho}} \Delta m$$

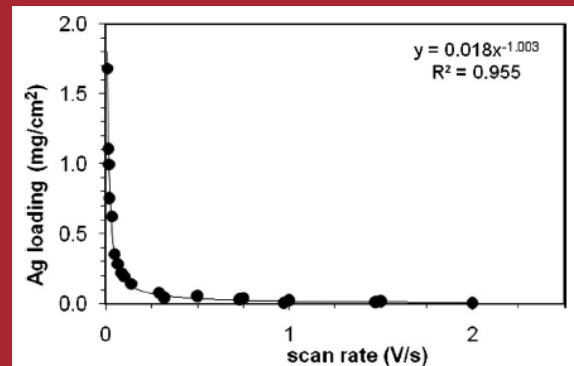


Ag deposition

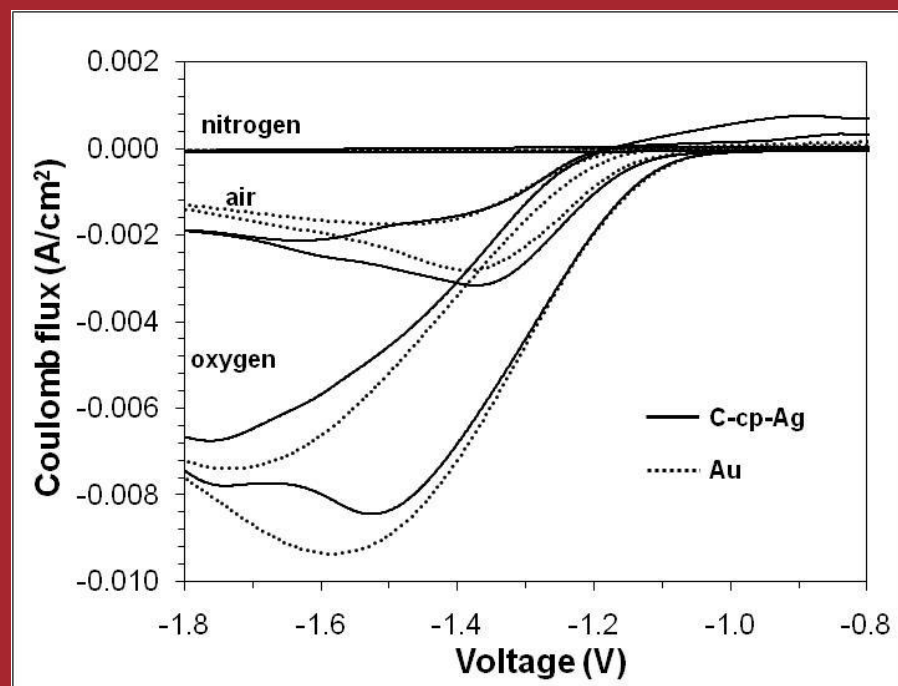
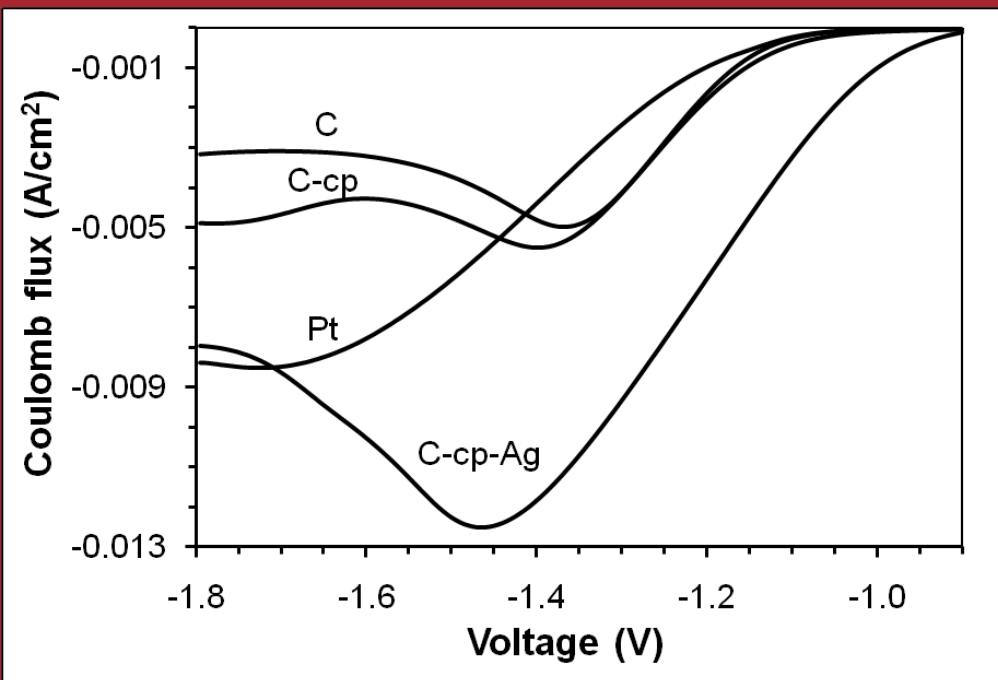
$$q = n \cdot F$$



	trial 1	trial 2
EQCM mass (μg)	19.0	5.94
Faraday mass (μg)	21.7	6.75
Δ (%)	12.5	12.0

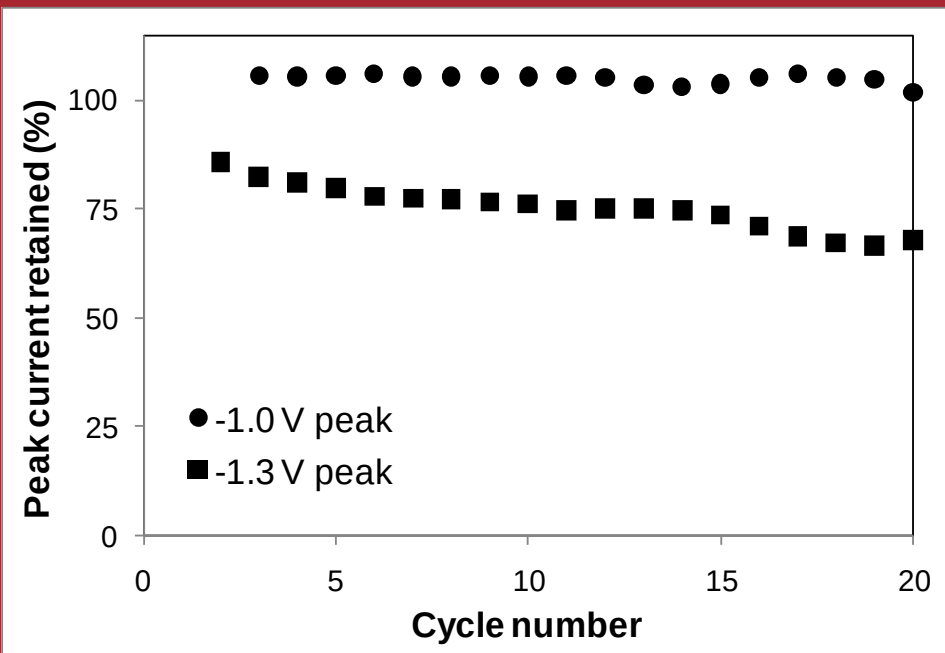
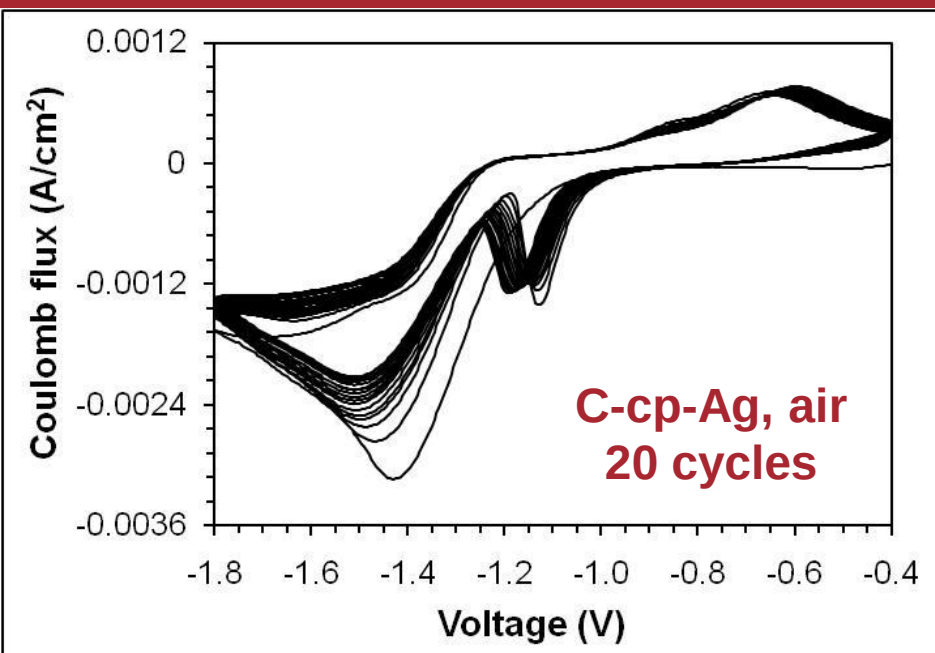


C-cp-Ag compares favorably to benchmarks



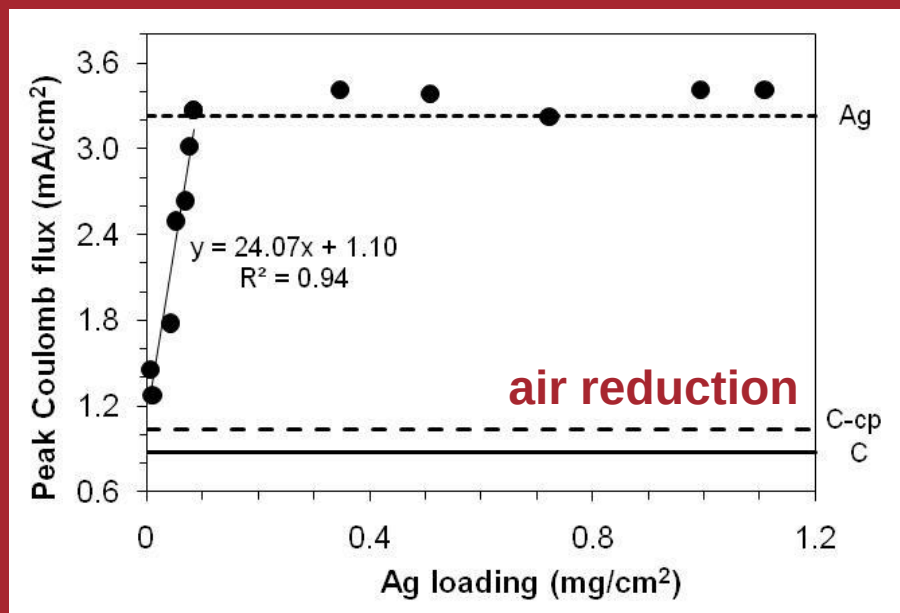
C-cp-Ag composite shows activity
2.6x higher than C
1.4x higher than Pt
comparable to Au

C-cp-Ag composite shows catalytic activity



C-cp-Ag composite electrodes retain high oxygen reduction capability on multiple cycling.

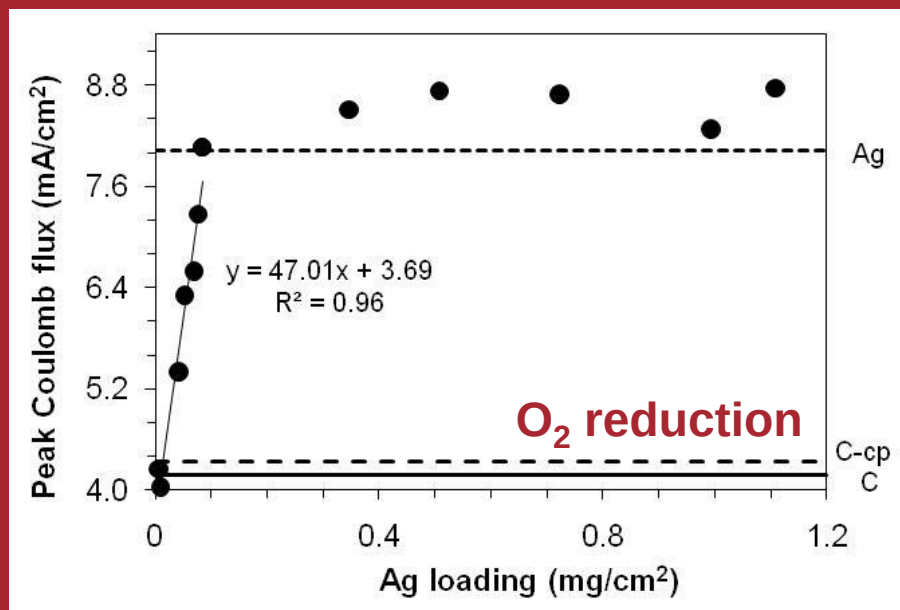
Low Ag loading is required for optimization



response optimized at Ag loading of 0.08 mg/cm²

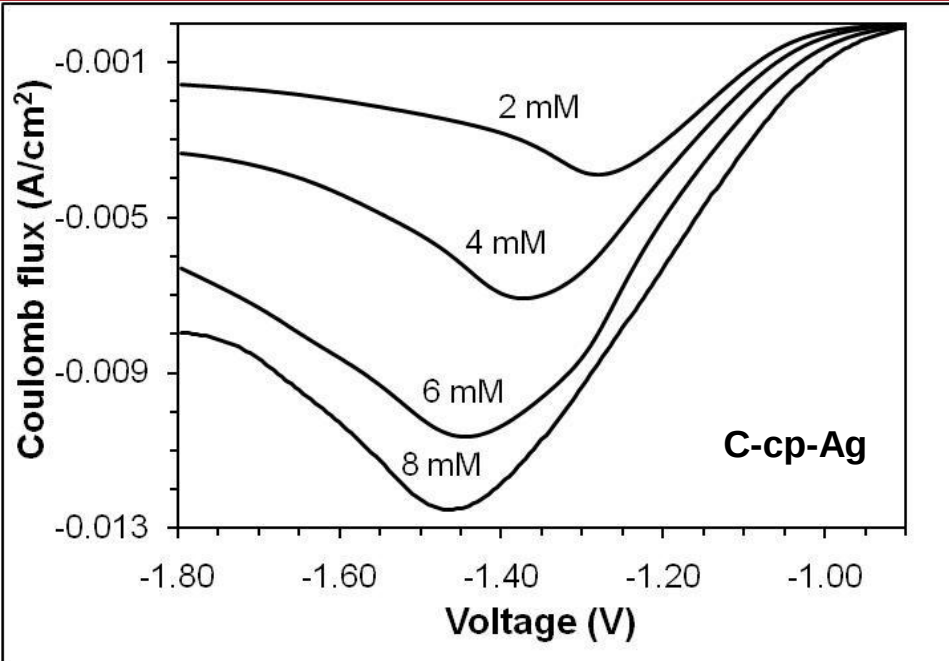
activity in air was 20 – 40% of the activity in pure oxygen

using density of Ag metal, suggests that 80 nm is minimum Ag thickness required



kinetics:

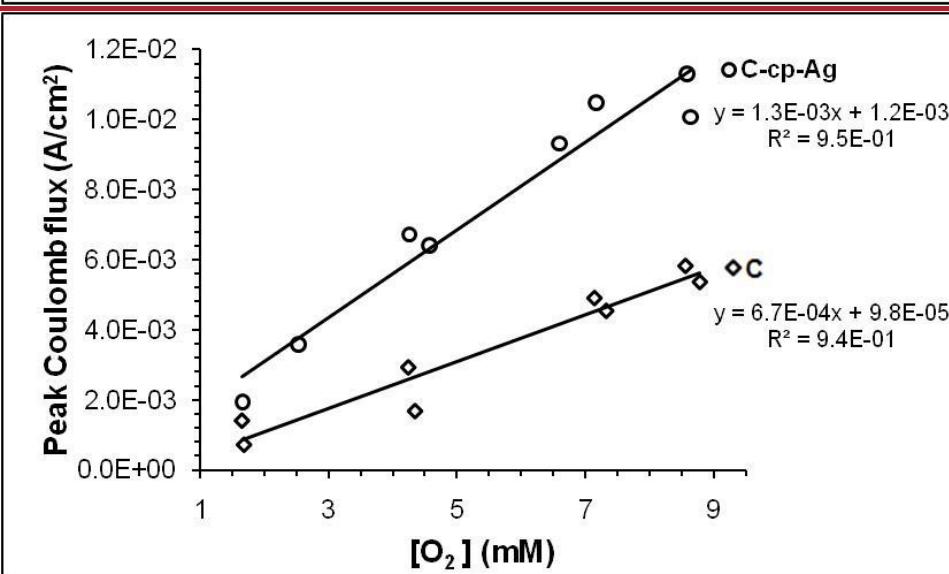
C-cp-Ag shows well behaved ORR



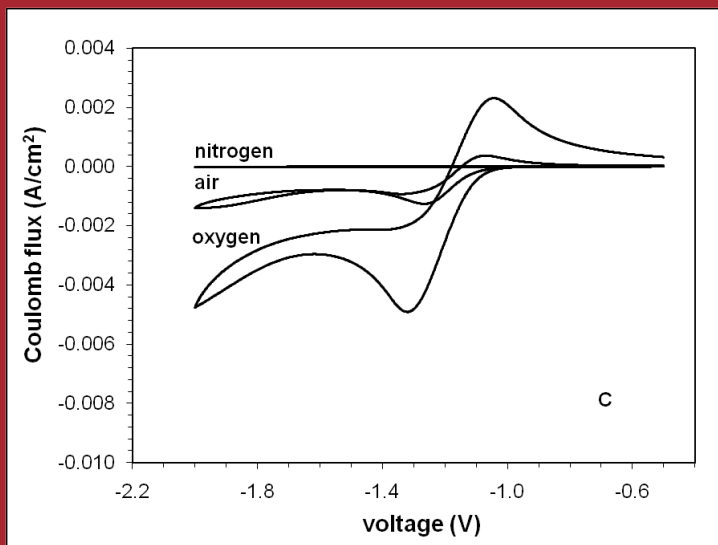
linear response to [O₂],
consistent with 1st order process

C-cp-Ag shows enhanced
activity at all [O₂]

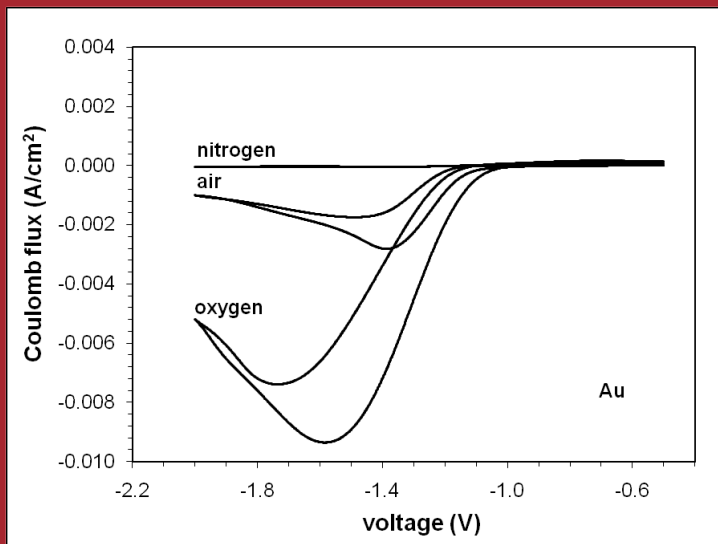
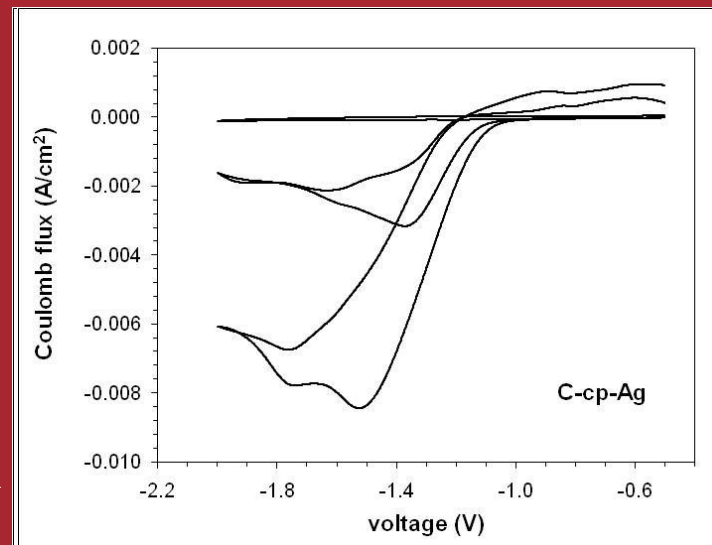
Ag loading of 0.3 mg/cm² for
C-cp-Ag composite



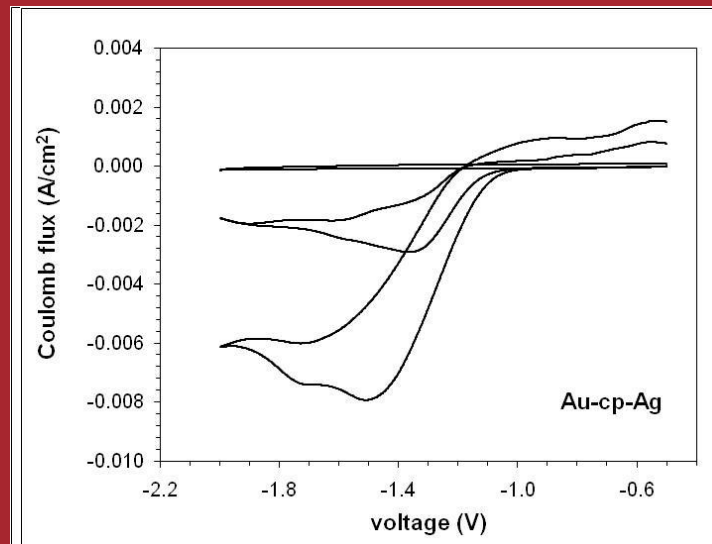
C-cp-Ag and Au-cp-Ag show similar profiles



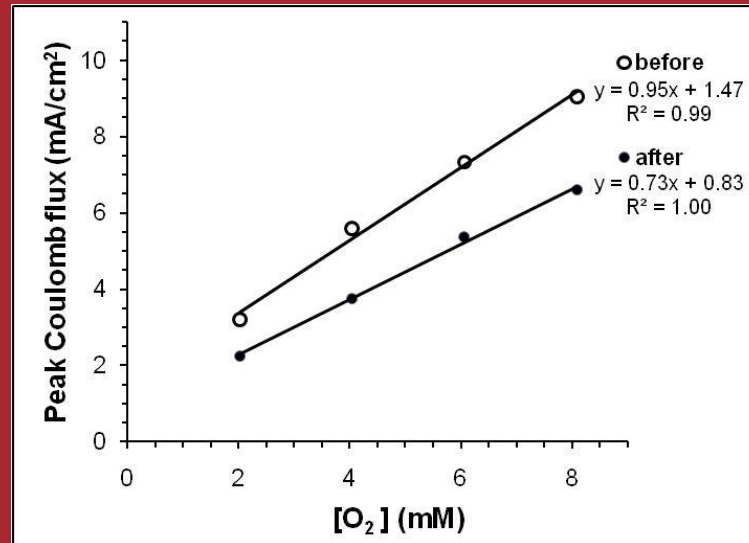
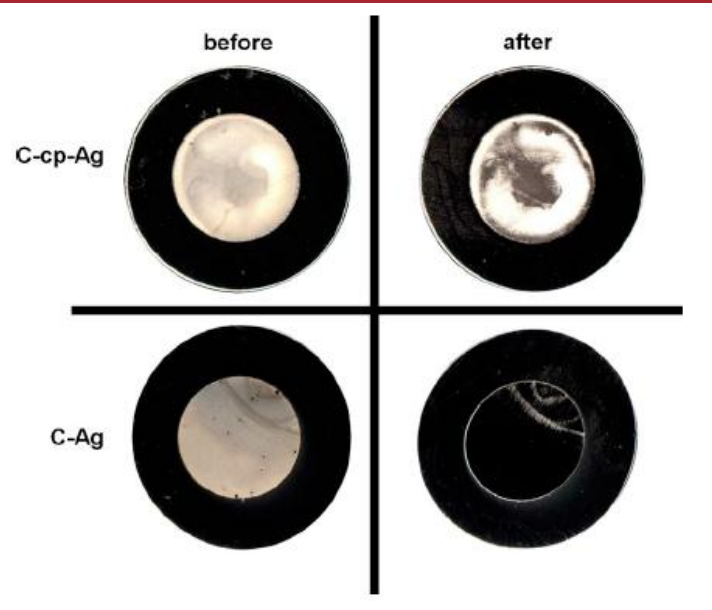
cp, then Ag
deposition



cp coating
mitigates
impact of
substrate

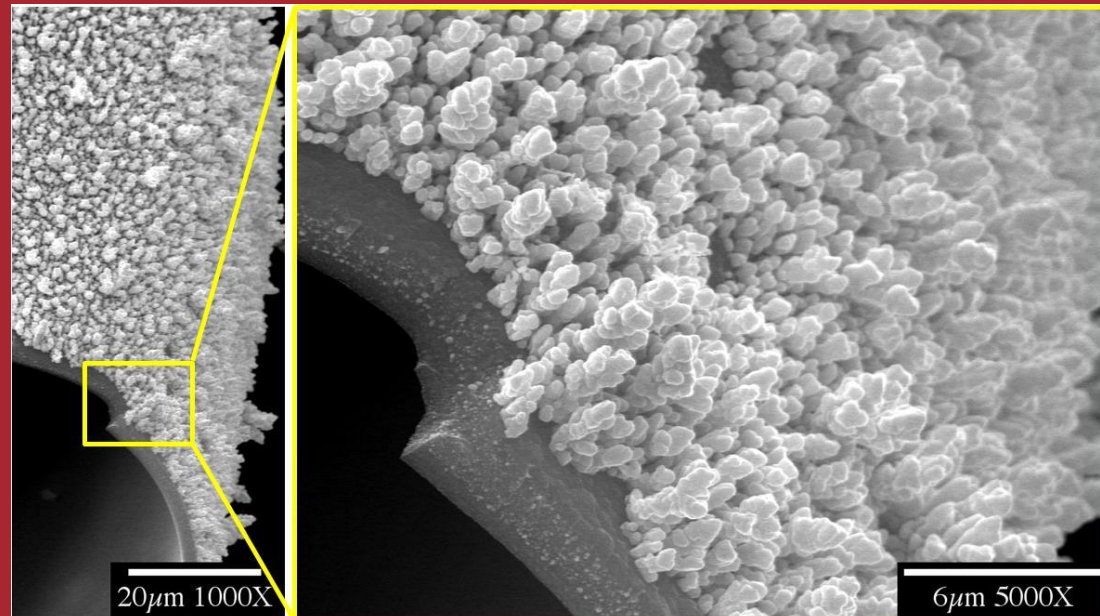


C-cp-Ag composites are robust

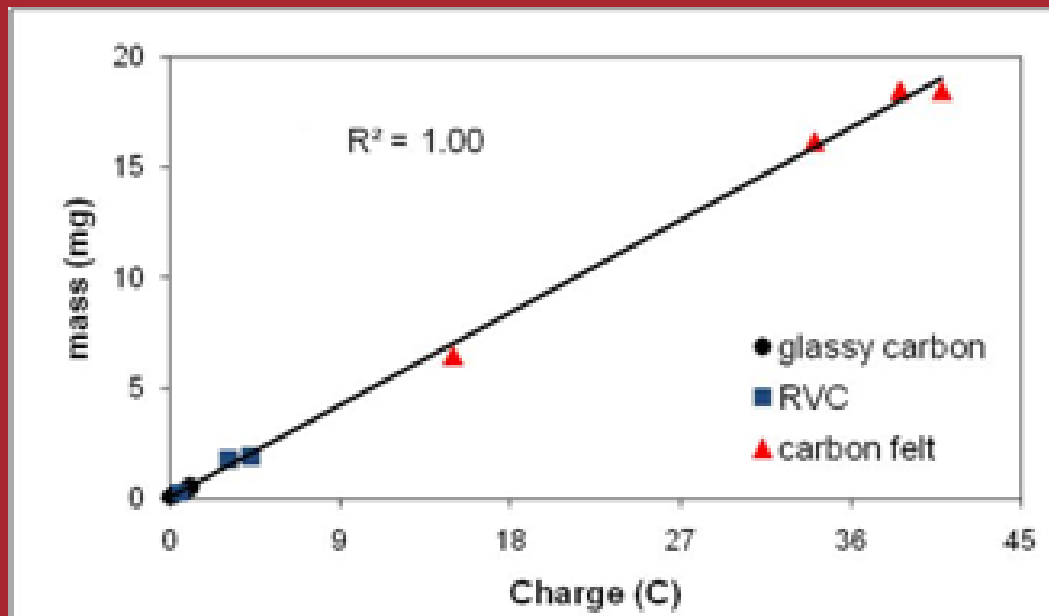


number	12
average	73%
median	72%
st. dev.	8.7%

demonstrated macroscopic and microscopic Ag (and activity) retention after physical stresses

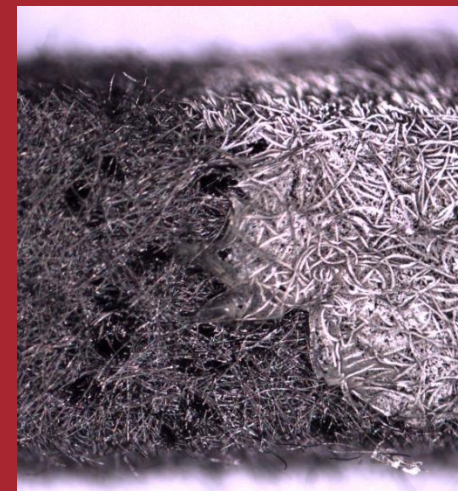


3D C-cp-Ag electrodes can be fabricated

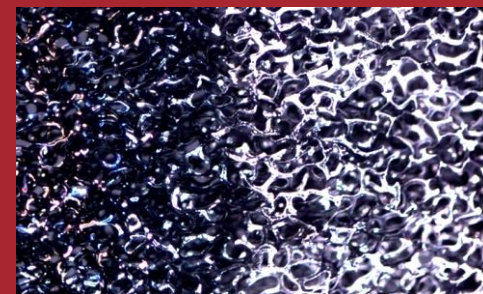


Achieved successful cp and Ag-cp deposition on non-planar (3D) substrates of varying geometry and porosity.

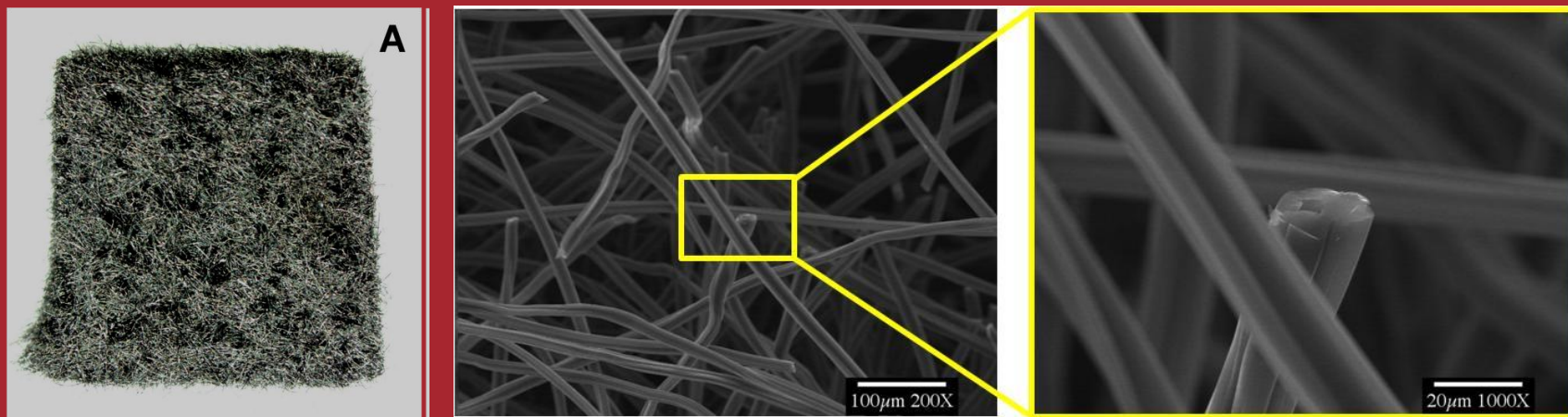
C-felt



RVC



3D C-cp-Ag electrodes can be fabricated



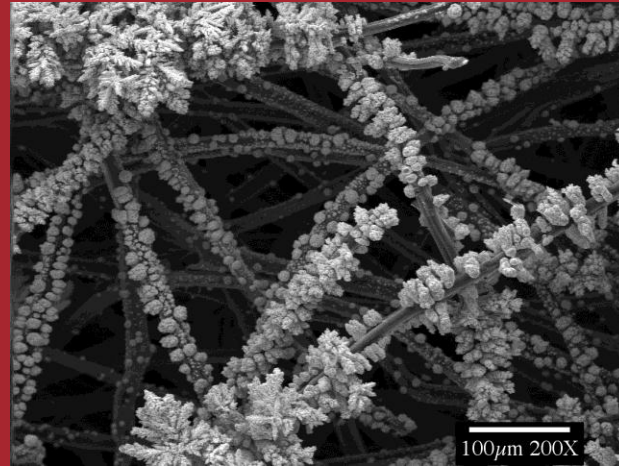
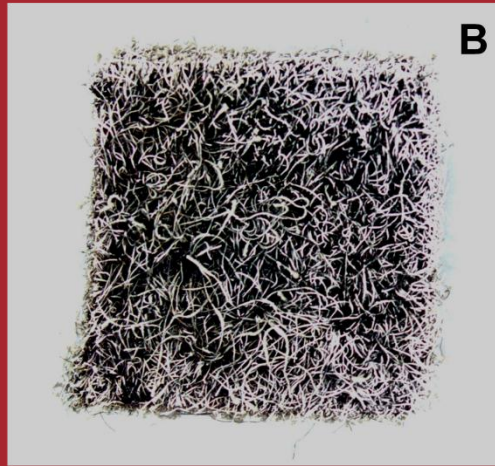
electrode	<u>electrode surface area (cm²)</u>			
	reported	planar	geometric	electrochemical
C	0.071	0.069	0.069	0.067
Cfelt	121	1.0	3.2	17

estimated cp thickness ~4X greater for C than for Cfelt

electrode	estimated cp thickness (μm)	<u>electrode surface area (cm²)</u>		
		planar	geometric	electrochemical
C-cp	3.5	0.076	0.076	0.053
Cfelt-cp	0.9	1.0	3.2	9.6

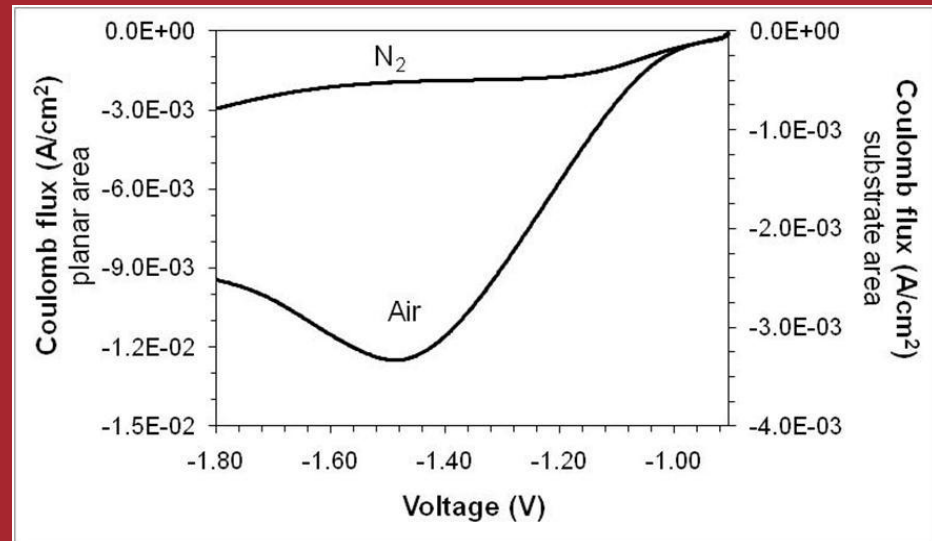
electrochemically active surface area reduced 20% for C, > 40% for Cfelt

3D C-cp-Ag composite electrodes

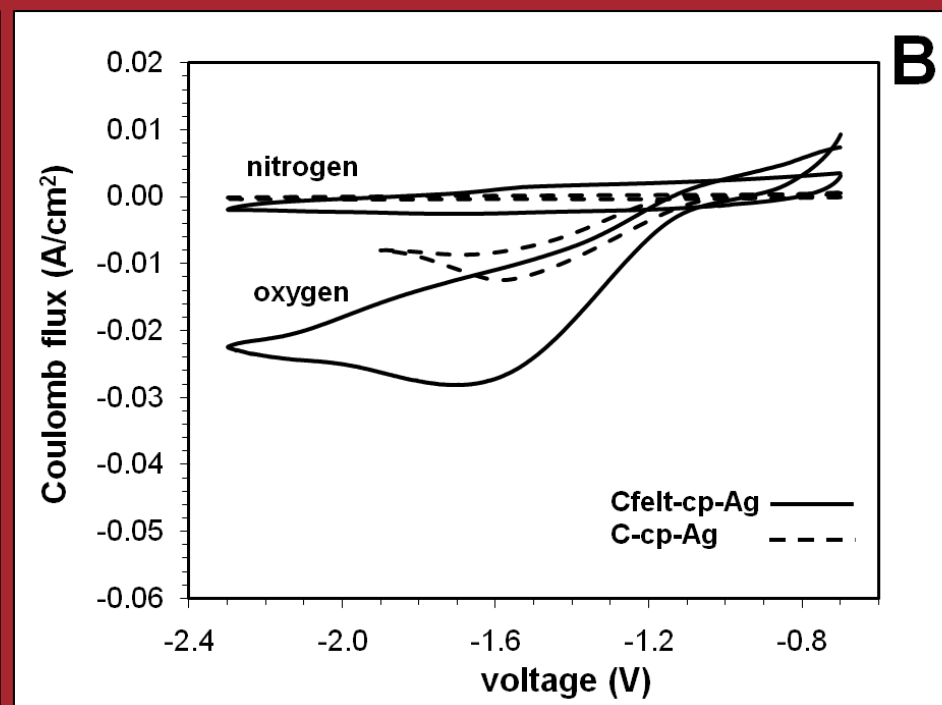
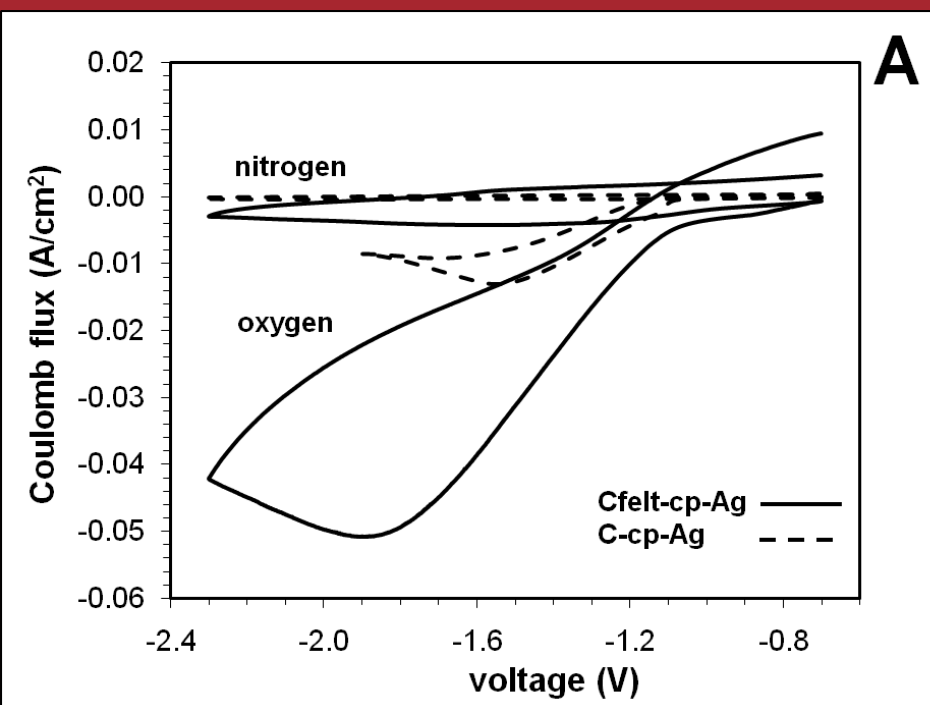


For C-cp-Ag composites, use of 3D substrates provided 4X improvement over 2D substrates based on planar area.

There is opportunity to further improve homogeneity of the 3D composite.



3D C-cp-Ag composite electrodes



Cycle 1 – 2 peak Coulomb flux was unchanged for the planar C-cp-Ag electrode, while the 3D Cfelt-cp-Ag composite showed a significant decrease.

Difference is consistent with reduction on the surface and interior during cycle 1, with surface only on cycle 2.

Publications

- 1) “Metal-air electrochemical cells: Silver-polymer-carbon composite air electrodes.” *Electrochem. S. S. Lett.* **2010**, 13(11), A162-A164.
- 2) “Electrodes for nonaqueous oxygen reduction based upon conductive polymer-silver composites.” *J. Electrochem. Society.* **2011**, 158(3), A223-A226.
- 3) “Oxygen reduction activity of carbon-conductive polymer-silver composite electrodes.” *ECS Transactions*, **2012**, 41(10), 9-13.
- 4) “Three dimensional carbon-conductive polymer-silver (C-cp Ag) composite electrodes for metal-air batteries.” *J. Composite Materials.* **in press.**
- 5) “Secondary Battery Science: At the Confluence of Electrochemistry and Materials Engineering.” *Electrochemistry.* **in press.** (invited highlight)
- 6) “Mechanistic investigation of the oxygen reduction reaction on carbon-conductive polymer-silver composites.” *in preparation.*
- 7) “Activation energy of oxygen reduction on carbon substrates in nonaqueous media.” *in preparation.*

Patent

“Electrodes for metal-air batteries and fuel cells.” US 2010-300719P, Feb 2, 2010; WO 2011097286, Aug. 11, 2011; WO 2011097286, Dec. 29, 2011.

Acknowledgement



Air Force Office of Scientific Research
AFOSR Program Officers: Dr. Joan Fuller, Dr. Ali Sayir
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