

Electrochemical Antifouling Technology for Replacement of Heavy Metal and Organic Biocides in Marine Hydrokinetic Energy Generation

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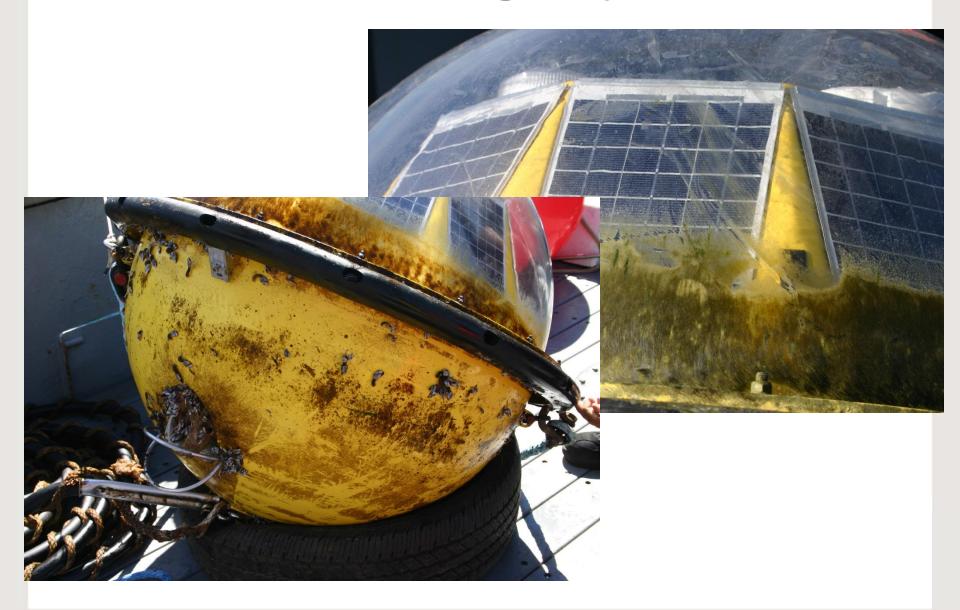
Wave Energy Converters (WECs)



Ocean Sentinel Instrumentation Buoy



Triaxis Wave Monitoring Buoy



In Practice



Commercial Technologies

Tributyl tin self polishing

Copper paints

- Work fairly well
- Hard epoxies or self polishing
- Sometimes booster biocides
- Environmental concerns
- ~4-5 years max

Foul release/slick paints

- No biocide release
- Longer life (~7 years)
- Soft/vulnerable coatings
- Need significant water velocity

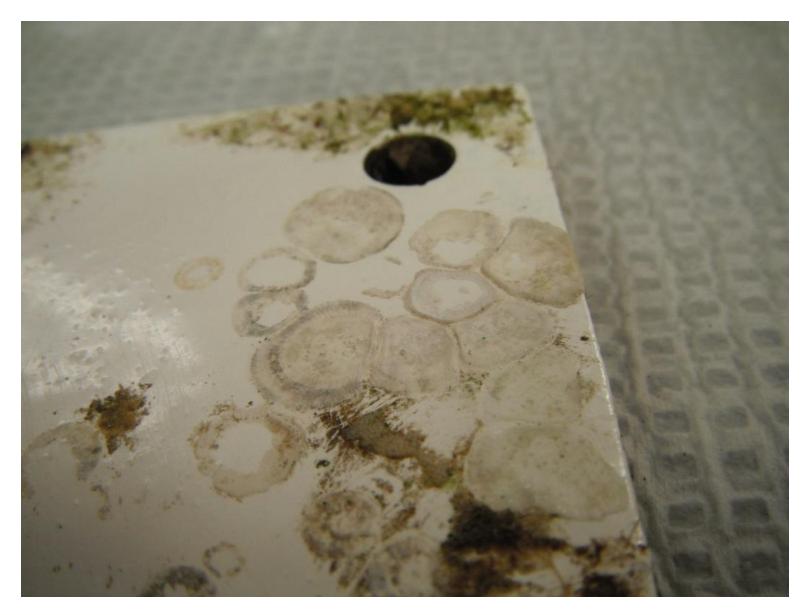








Problems



Longer Term Solution Needed

Dry docking works fine for ships

WECs

- Mooring lines
- Live power lines
- Neighboring devices
- Shape



We need better than what's on the market!

Design Requirements

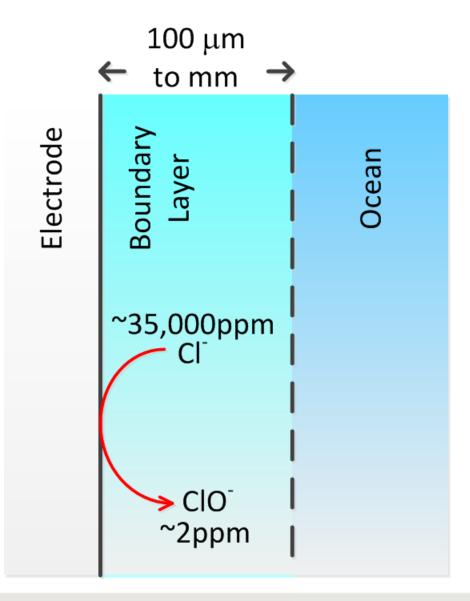
Long lasting (~20 years)

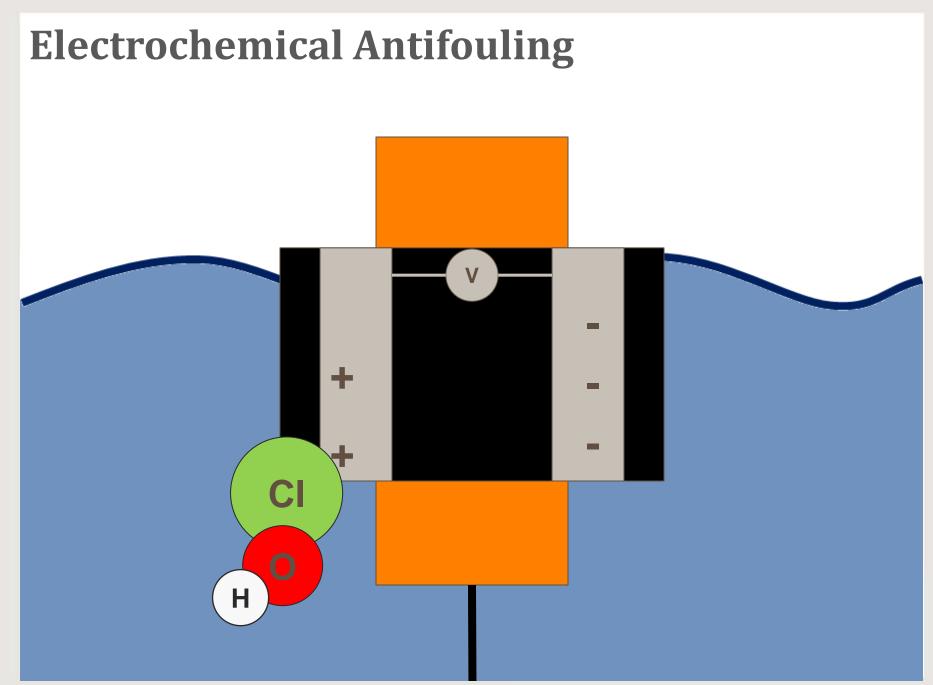
Applicable to large/complex surfaces

Inexpensive

Environmentally friendly

Electrochemical Antifouling





Chemical, Biological and Environmental Engineering

Electrochemical Antifouling Advantages

Utilizes chloride ubiquitous in seawater

- Generate as much or as little hypochlorite as desired : <u>adaptable</u>
- Does not deplete!

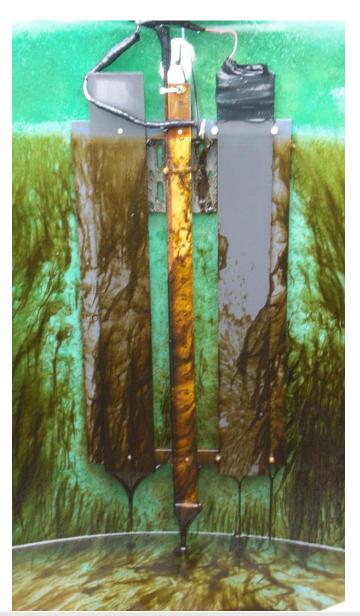
Power consumption < 1W/m²

Cheap materials

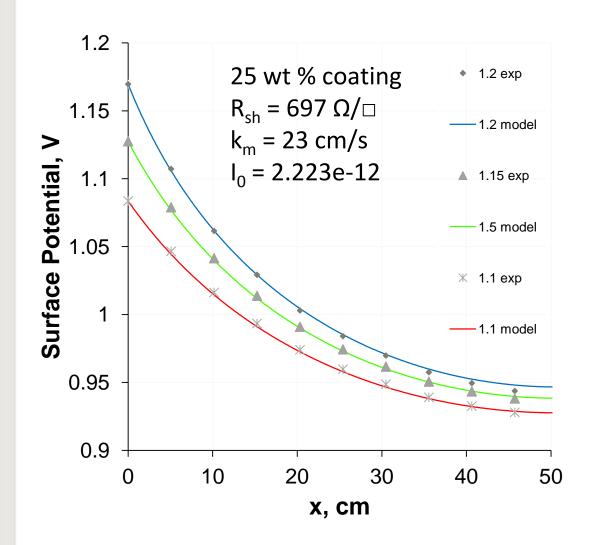
Easily applied (liquid system)

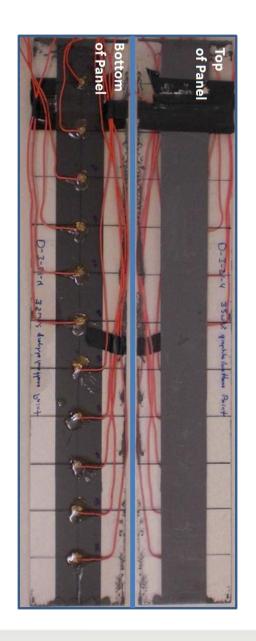
They Work!





Validating Model

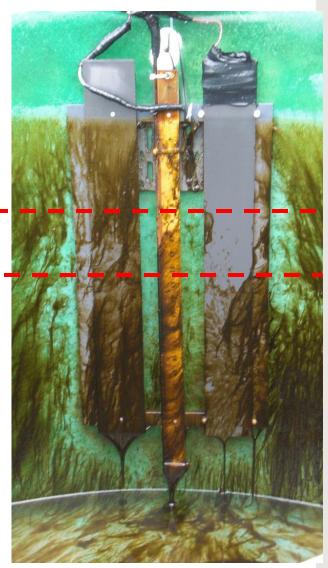




Required Potential

Maybe less?

~1.32V v NHE



Application of Nernst Equation

$$E = E^{0} - \frac{RT}{nF} \ln \frac{[Products]}{[Reactants]}$$

$$Cl^- + H_2O \leftrightarrow HClO + H^+ + 2e^-$$

рН	[CI-]	[HCIO]	Т	E vs NHE
0	1M	1M	25° C	-1.49V
8	3.5 wt% NaCl	5ppm	4.4° C 40° F	-1.17V

Minimum Potential



Governing Equations

Momentum conservation:

$$\frac{\Delta P}{\mu L} = \frac{\partial^2 u}{\partial y^2}$$

Mass conservation

$$u\frac{\partial C}{\partial x} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right)$$

Boundary Conditions

$$u = 0 @ y = \pm \frac{h}{2}$$

$$C_{red} = C_{red,in} for all x, y$$

$$C_{ox} = C_{ox,in} @ x = 0$$

$$C_{ox} = C_{ox,in} @ y = +\frac{h}{2}$$
$$\frac{dC_{ox}}{dy} = j_{rx} @ y = -\frac{h}{2}$$

Reaction Current

$$vReduced \leftrightarrow vOxidized + ne^{-}$$

$$i = i_0 e^{\frac{\alpha F}{RT}\Delta V}$$

$$\Delta V = E - E_{eq}$$

$$E_{eq} = E^{\emptyset} - \frac{RT}{nF} \ln Q$$

$$Q = \frac{\prod C_{oxidized}^{\nu}}{\prod C_{reduced}^{\nu}}$$

$$j_{rx} = \frac{i}{nF} i = i_0 e^{\frac{\alpha F}{RT}\Delta V}$$

$$j_{rx} = \frac{i_0}{nF} e^{\frac{\alpha F}{RT} \left(E - \left[E^{\emptyset} - \frac{RT}{nF} \ln \frac{\prod C_{oxidized}^{\nu}}{\prod C_{reduced}^{\nu}} \right] \right)}$$





Electrochemical Reaction Rates

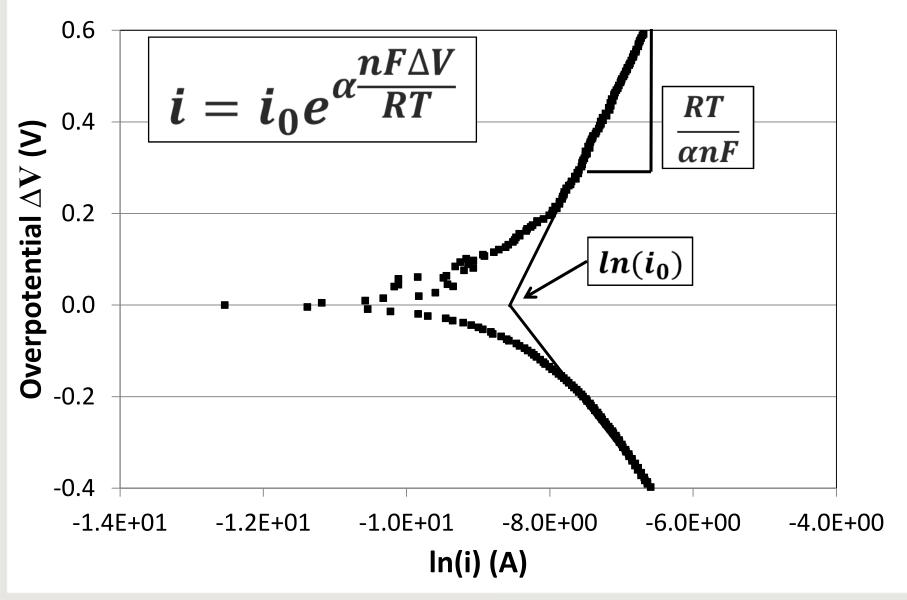
Electrochemical reaction kinetics governed by Tafel equation

$$i_{Rx} = i_0 e^{\alpha \frac{nF\Delta V}{RT}}$$

 i_0 = exchange current density

 α = charge transfer coefficient

Measuring Kinetic Parameters



Accelerated Aging

Hypotheses:

Reactions at graphite surface may cause loss of activity

Reactions are driven by current, so degradation will be proportional to current passed

Accelerated Aging

Strategy:

Operate 2 electrode system at high current density

Field operating condition is $\sim 20 \frac{\mu A}{cm^2}$

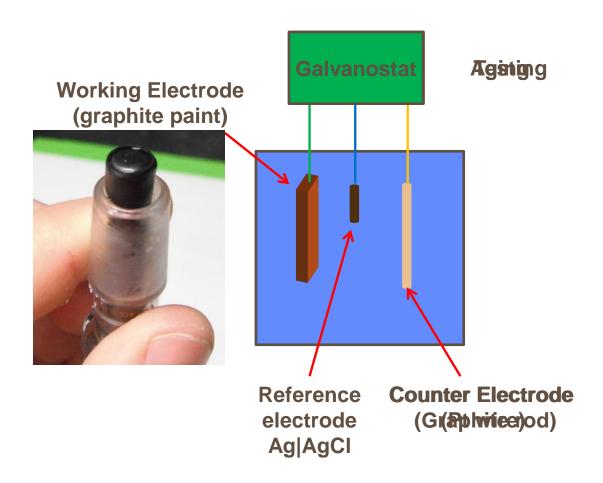
Acceleration factor = 158x

46 days simulates 20 years operation

Measure kinetic parameters

Plot parameters and fit an appropriate reaction mechanism

Experimental Setup



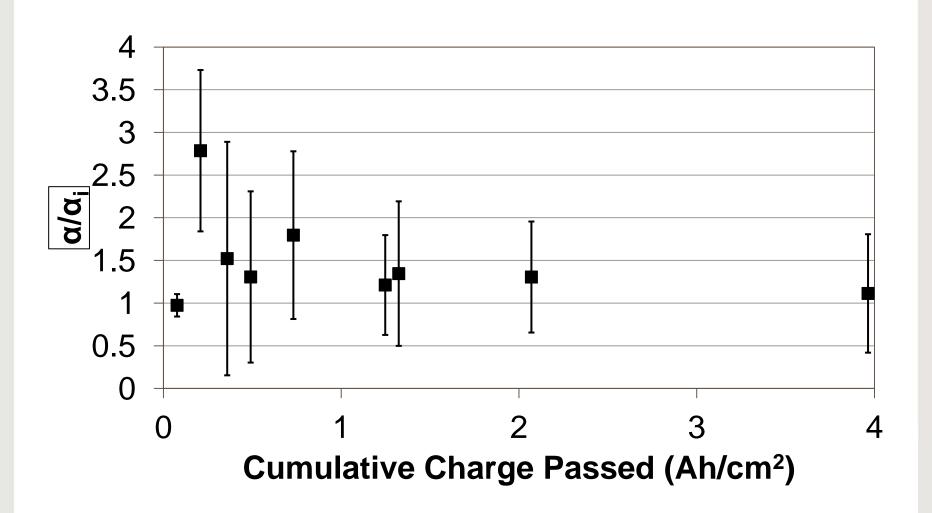


Results: Exchange Current Density

Significant correlation for all three trials (95% CI)

Positive trend indicates better performance developing over time

Results: Charge Transfer Coefficient



Results: Charge Transfer Coefficient

Appears to be a negative correlation

Indicative of degradation

Linear regression shows only 1 of 3 is statistically significant at 95% confidence interval

Worst case scenarios is ~50% reduction over 20 years Over-potential would have to double (0.16V \rightarrow 0.32V)

1.32V \rightarrow 1.48V NOT 1.32V \rightarrow 2.64V

Conclusions

Electrochemical methods have been shown to be effective at preventing biofouling in marine environment

Degradation is probably nothing to worry about in chloride oxidation at prescribed conditions

Model simulating flow channel electrochemical reactor has been developed

Once validated model can be extended to design applications

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