This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

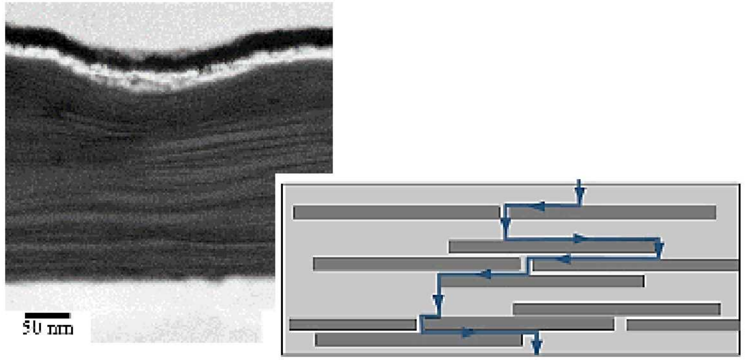
SAND2020-10067C

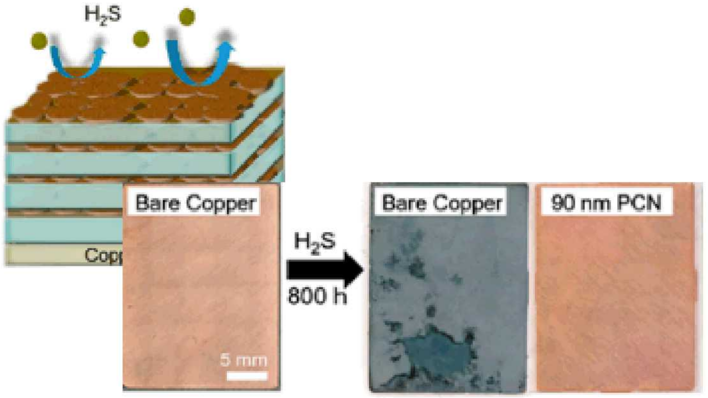
Ultrathin corrosion barrier films enabled by layer-by-layer polymer clay nanocomposites

Eric Schindelholz

Erik Spoerke[1], Jaime Grunlan[2], Michael Melia[1], Stephen Percival[1], Shuang Qin[2], Erin Barrick[3], Chris Alexander[4], Derek Nelson[1]

[1] Sandia National Labs, [2]Texas A&M University, [3]Lehigh University, [4]University of South Florida





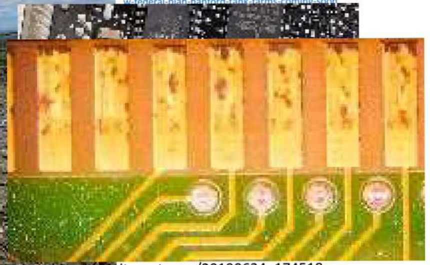
Sandia National Laboratories

THE OHIO STATE UNIVERSITY

This work was supported by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories. Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

The Continual Need for Anti-Corrosion Coatings

https://www.google.com/search?q=nuclear+waste+hanford+corrosion&tbm=ischhttps://www.nwnewsnetwork.org/post/new-federal-plan-hanford-tank-farms-coming-soon



https://ripitapart.com/20190624_174518

-https://www.zerustproducts.com/rust-prevention/zerust-boat-rust-prevention-keeps-corrosion-at-bay/and-control-ship-corrosion/

National Association for Corrosion Engineers (NACE) IMPACT study estimated 2013 ***global cost of corrosion to be US$ 2.5 trillion annually*** (3.4% of GDP)

Attributes of an Ideal Anti-Corrosion Coating

- Impermeable
- Actively protective
- Mechanically robust (scratch, wear, adhesive strength)
- Lightweight/low profile
- Cheap
- Easy application

Desired Functionality

Optical
Self-healing
Thermal Barrier
Hydrophilic/phobic
Self-cleaning
Low-friction
Fire resistance
Photoluminescence
Conductive/Insulating
Shielding
Electromagnetic

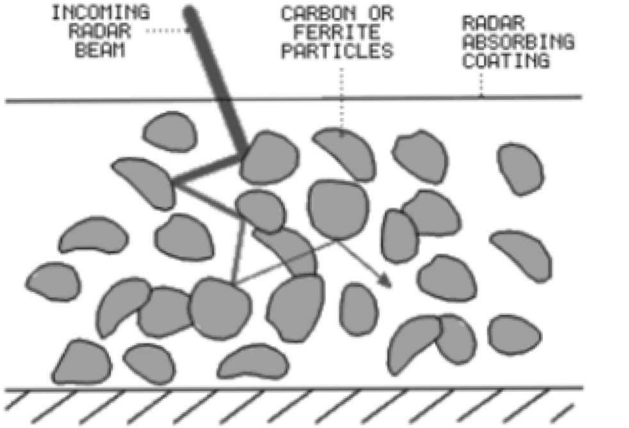


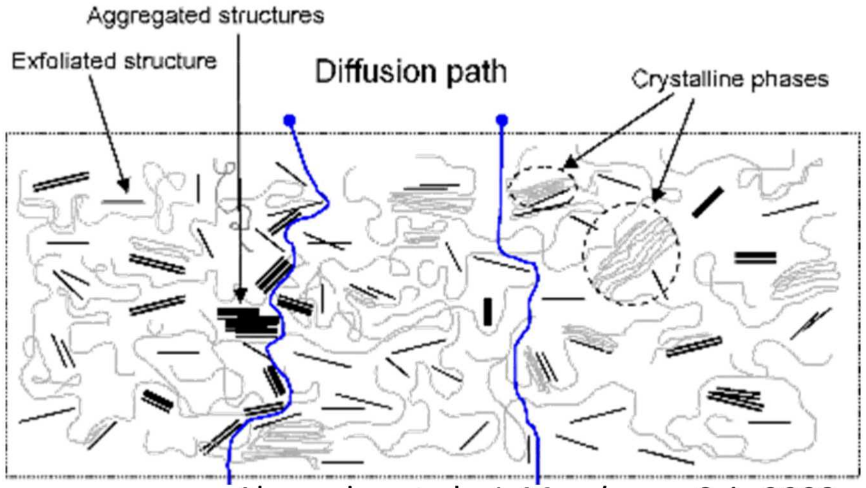
Figure 10: Incident Radar Beam Dissipated in RAM Coating

Jha, Int. J. Eng. Tech. Res., 2010

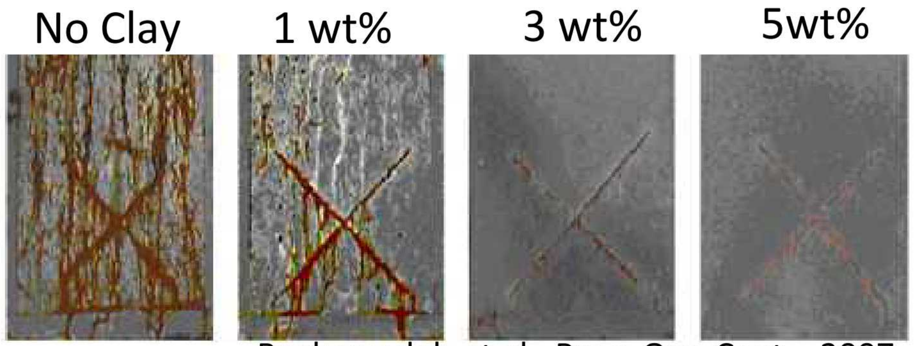
Polymeric-based Coating Improvements via Nanoparticle Additions

Ideal Characteristics

Impermeable
Actively protective
Mechanically robust
Lightweight/low profile
Cheap
Easy application



Alexandre et al., *J. Membrane Sci.*, 2009

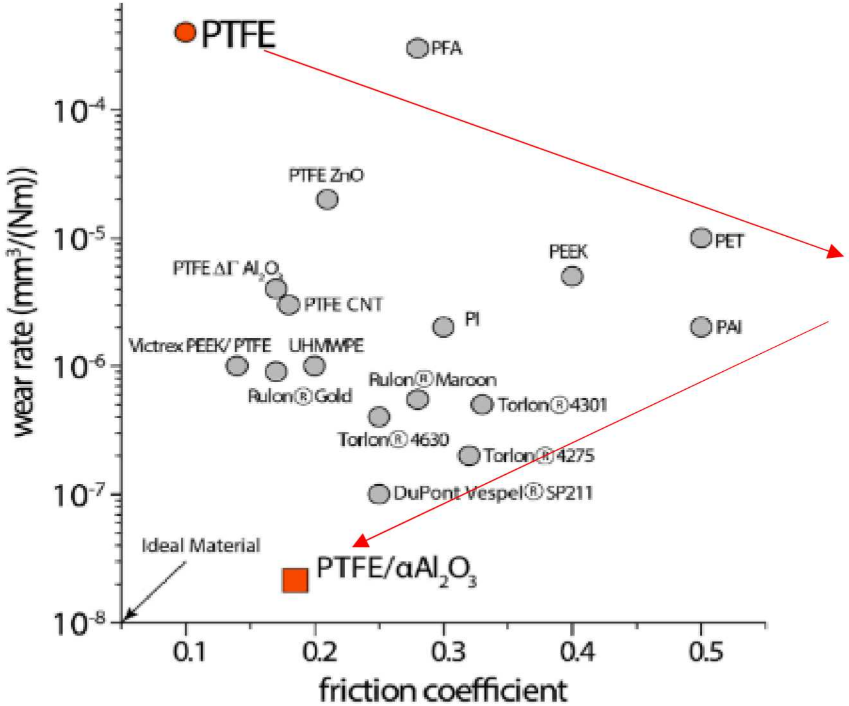


Bagherzadeh et al., Prog. Org. Coat., 2007

60 μm thick MMT in DGEBA Epoxy resin on carbon steel after 500 h in salt spray

Desired Functionality

Optical
Self-healing
Thermal Barrier
Hydrophilic/phobic
Self-cleaning
Low-friction
Fire resistance
Photoluminescence
Conductive/Insulating
Shielding
Electromagnetic



5 wt% nano-alumina addition to PTFE creates ultra-low-wearing material

Krick et al., Tribology Int., 2012

LBL nanocomposites as robust and agile anti-corrosion coatings

Ideal Characteristics

Impermeable
Actively protective
Mechanically robust
Lightweight/low profile
Cheap
Easy application

Desired Functionality

Optical
Self-healing
Thermal Barrier
Hydrophilic/phobic
Self-cleaning
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Fire resistance
Photoluminescence
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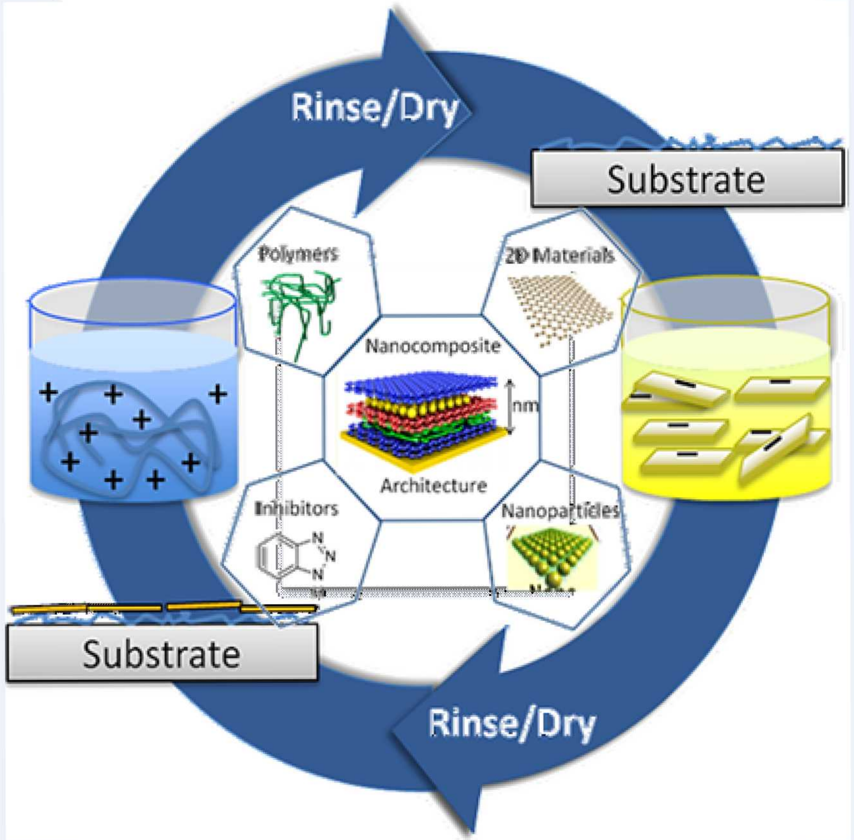
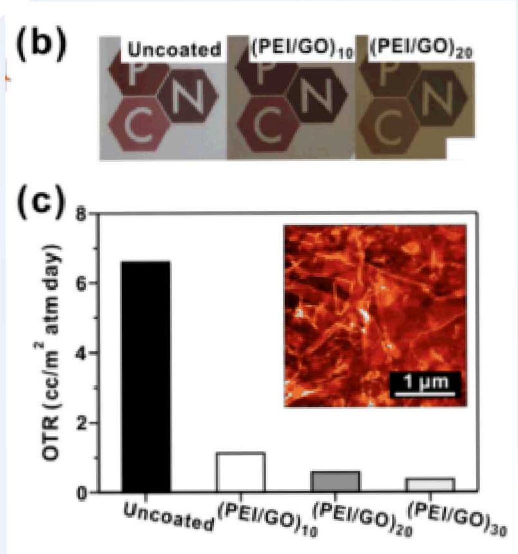
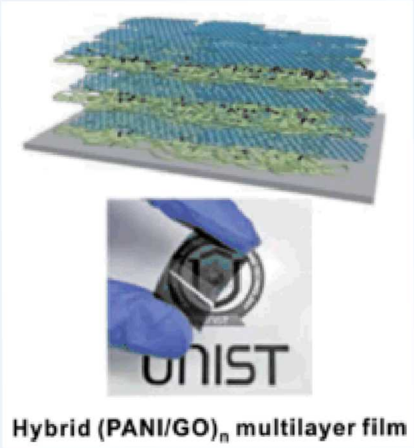
Shielding
Electromagnetic





Yang et al., Adv. Mat., 2013



Hybrid (PANI/GO)$_n$ multilayer film

Lee et al., Chem. Mater. 2015

High loading and highly aligned particles Improves Coating Permeability

Relative Permeability of a Composite Coating:

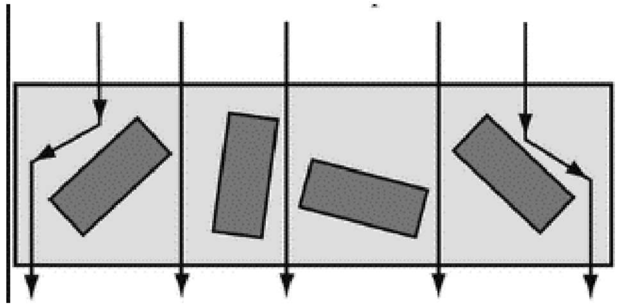
particle loading (vol. fraction)

$$\frac{P_s}{P_p} = \frac{1 - \phi_s}{1 + \frac{L}{2W}\phi_s\left(\frac{2}{3}\right)\left(S + \frac{1}{2}\right)}$$

particle aspect ratio

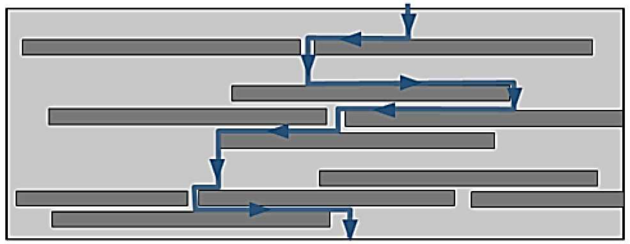
particle order ranging from 1/2 (long direction is perpendicular to substrate surface) to 1 (long direction is parallel to substrate surface).

Bulk Nanocomposite



Loading < 10 vol. %

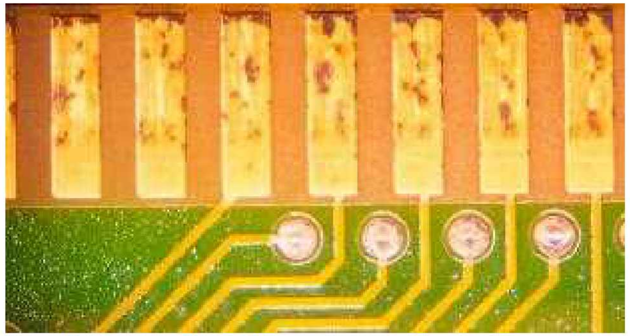
LBL Nanocomposite



Loading >> 10 vol. %

Bharadwhaj, Macromolec., 2001

Coating Design for Protection from Corrosive Gases



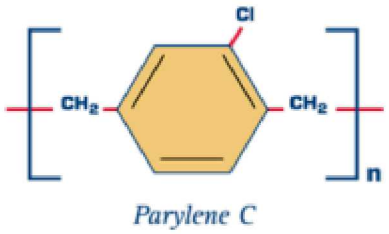
https://www.purafil.com/causes-corrosion-corrosion-monitoring/

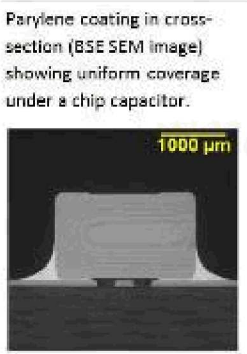
Copper sulfidation in microelectronics

Acetic acid corrosion of PV cell metallization/ribbon

<u>Desirable Coating Qualities</u>

Low permeability
(water, oxygen, H_2S, acetic acid)
Inhibiting
Low profile
Conformal
Tough and wear resistant
Optically transparent
Inexpensive (materials, processing)

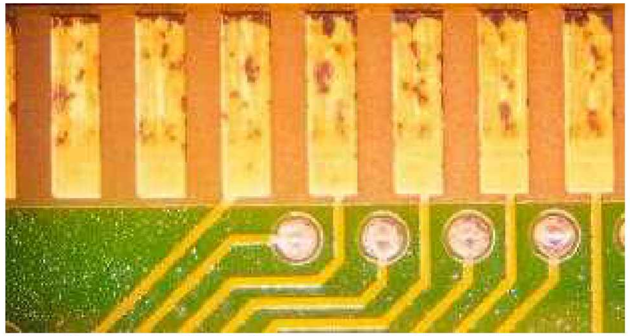




chemical vapor deposition Parylene coatings for corrosive environments

Limitations: high material and production costs (up to $5,000/kg, vacuum dep.), low wear resistance

LBL Polymer-Clay Nanocomposites Possess Desirable Qualities for Anti-Corrosion



https://www.purafil.com/causes-corrosion-corrosion-monitoring/

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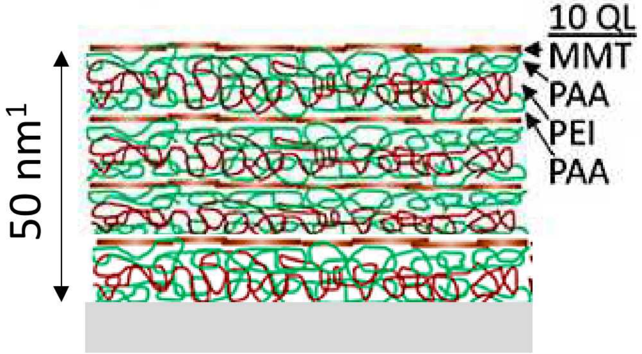


Quad layer LBL Gas Barrier

4 QL (50 nm)[1] : OTR ≤ 10^{-5} cc/m^2·day
Parylene (3 μm)[2]: OTR ~ 10^{-3} cc/m^2·day

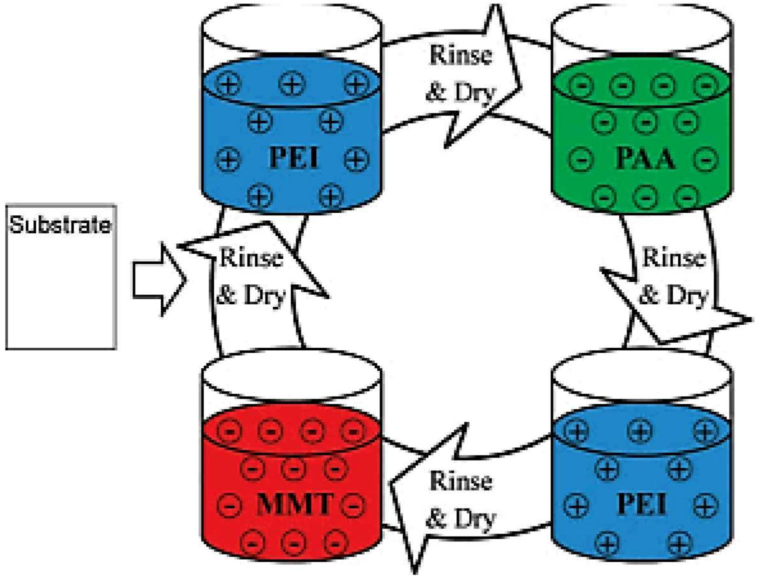
O_2 H_2S

d_ν = 3.5 Å d_ν = 3.6 Å

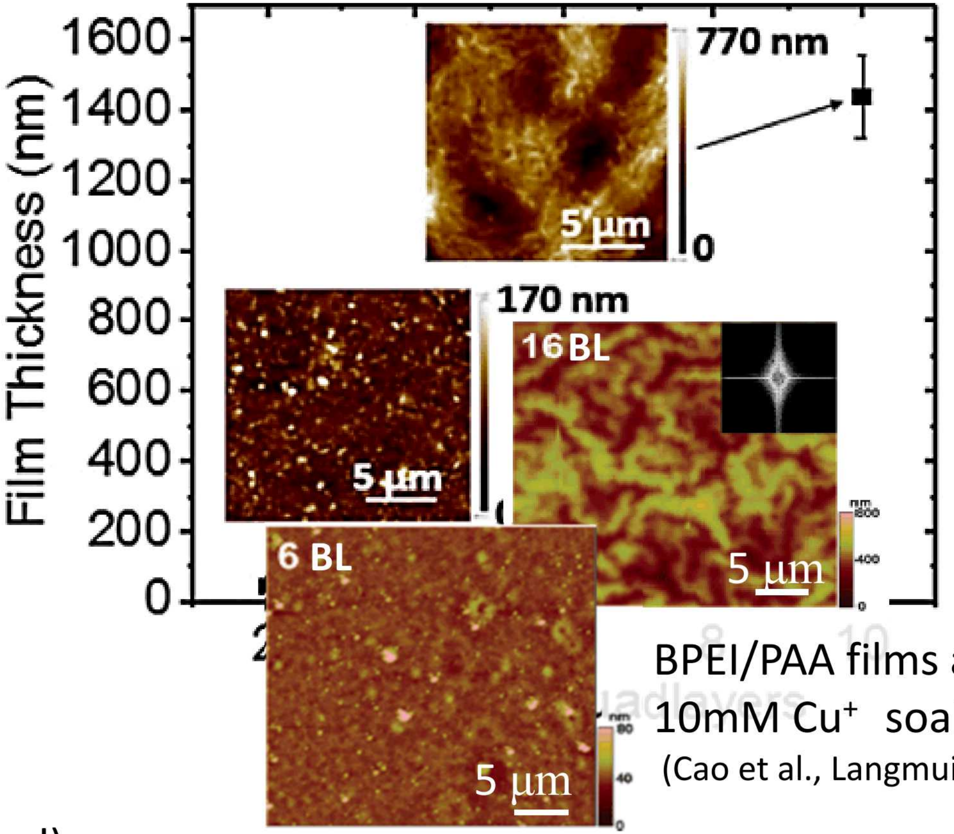
Commercial Montmorillonite: ~$0.50/kg
Commercial PEI: ~$1-10/kg
Commercial Parylene-C: $100-5000/kg

[1]Priolo et al, Adv. Mat., 2012; [2]McKeen, 2016

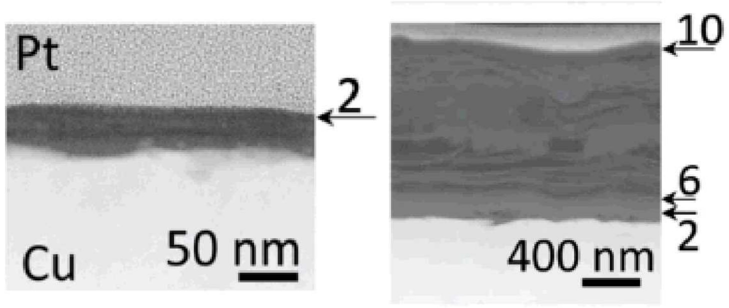
Successful Growth of Contiguous QL PCN Coatings on Copper Substrate

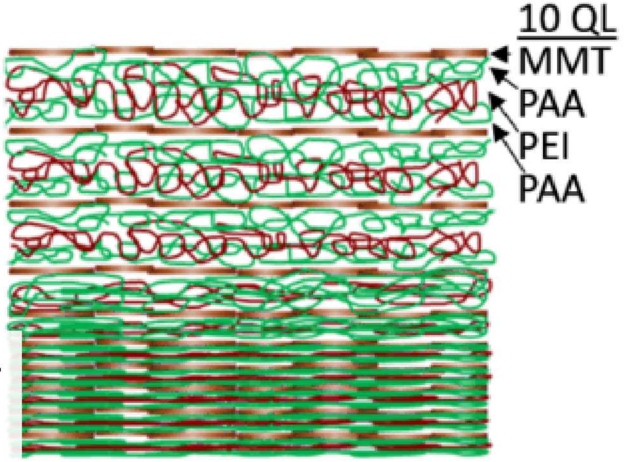


Priolo, 2010



BPEI/PAA films after
10mM Cu^{+} soak
(Cao et al., Langmuir, 2007)



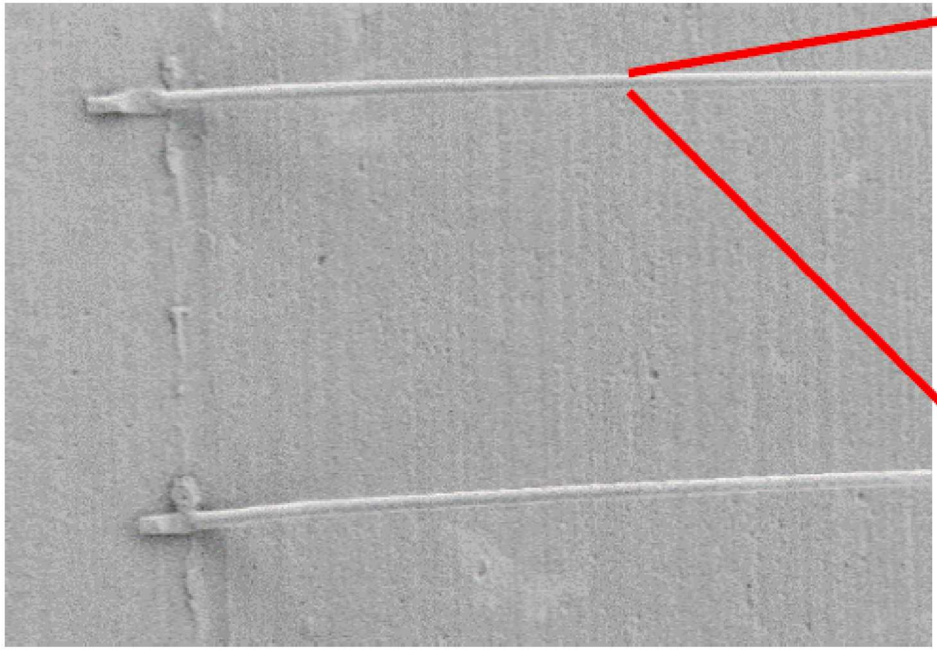


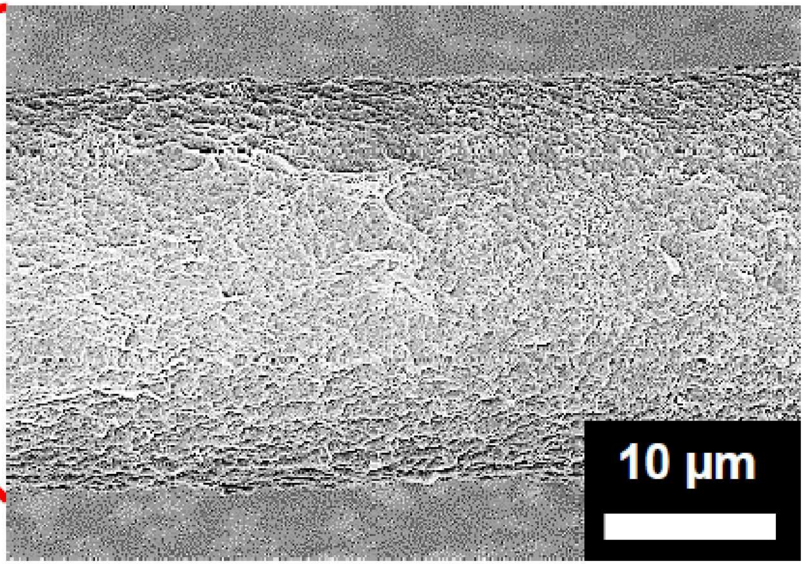
Experimental Details

Polished Cu (99.95% pure)
Branched PEI: 0.1 wt% (M_W~ 25,000 g/mol)
PAA: 0.2 wt% (M_w ~ 100,000 g/mol)
MMT: 1 wt%
Dip time: 1 min

Schindelholz et al., App. Mat. Int., 2018

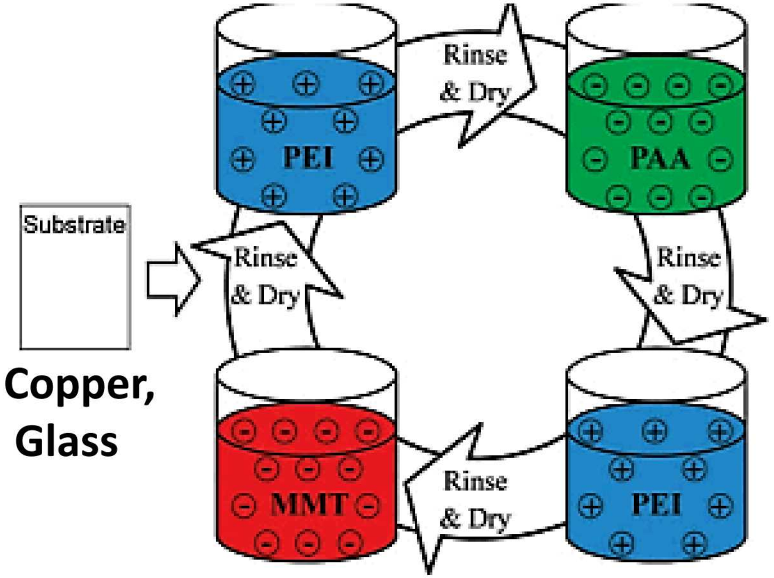
PCNs can be effectively and conformally grown on complex electronics geometries





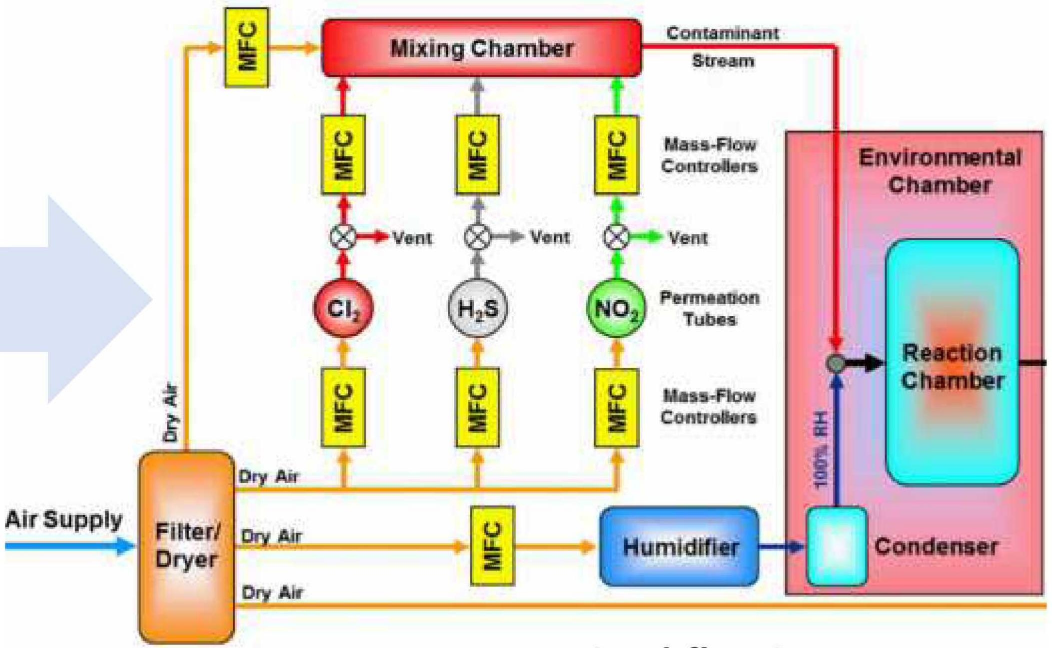
Conformal 6QL film on
metalic interrconnect

How Effective are PCN Gas Barriers as Anti-Corrosion Barriers?



Copper, Glass

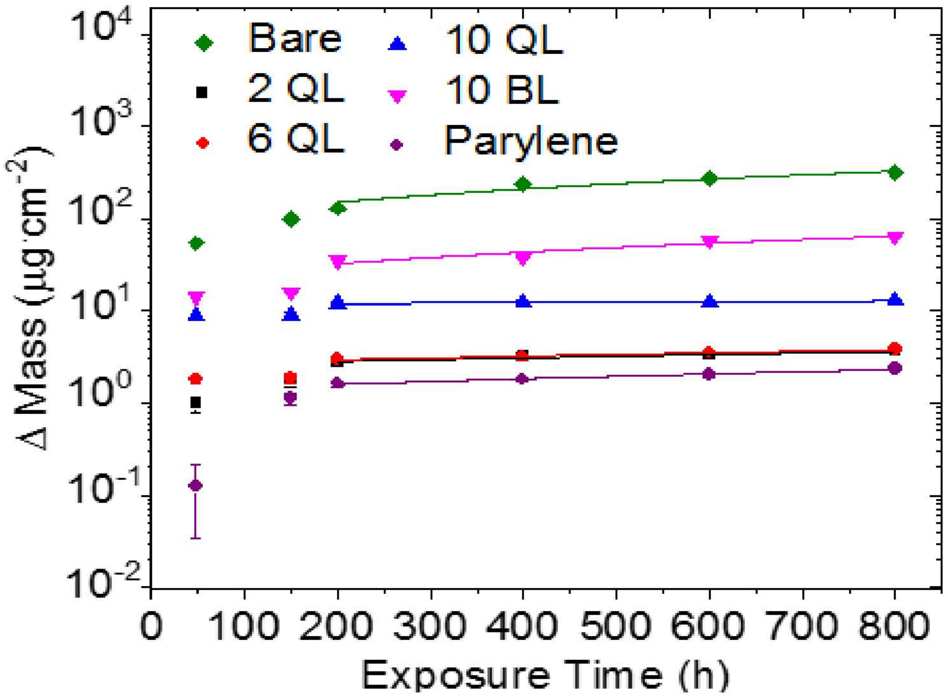
2,4,6,10 QL; 10 BL; bare
5 replicates each

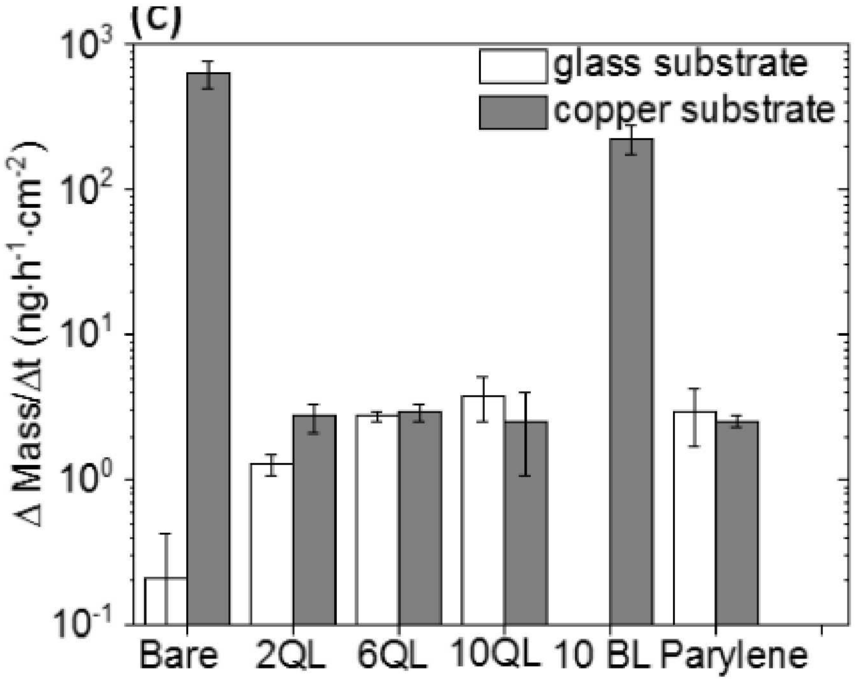


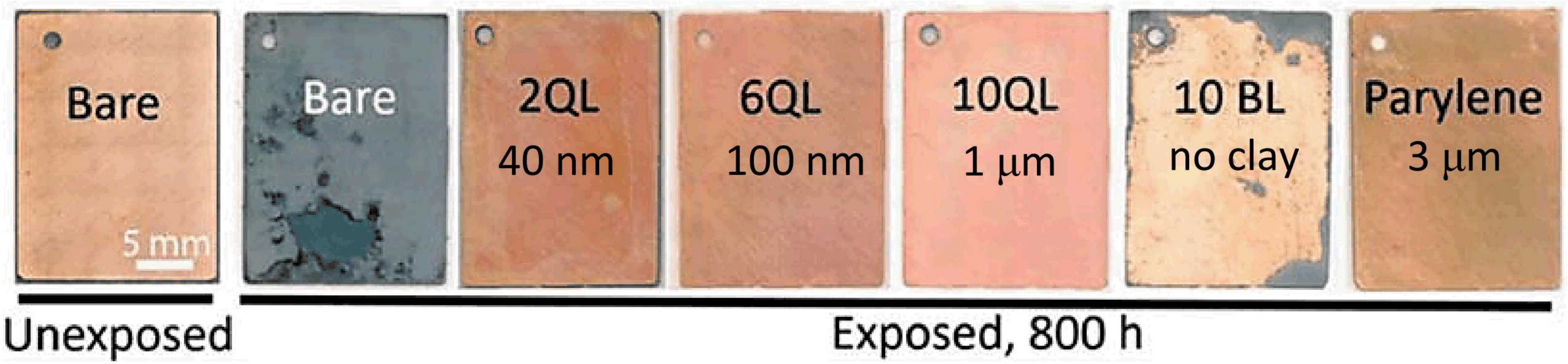
Exposure to mixed flowing gas chamber at 10 ppb H_2S, 70% RH, 30°C

Periodically weigh and measure reflectance

PCN Films as thin as 100 nm Inhibit Corrosion in 10 ppm H_2S by ≥ 1000x

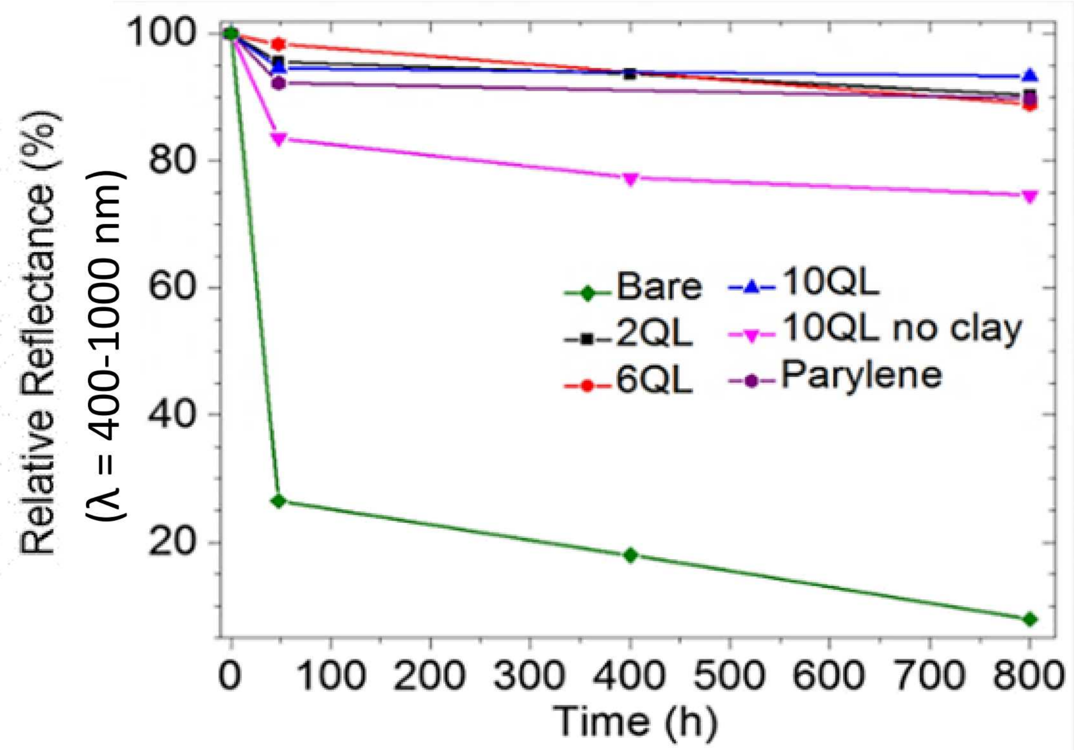


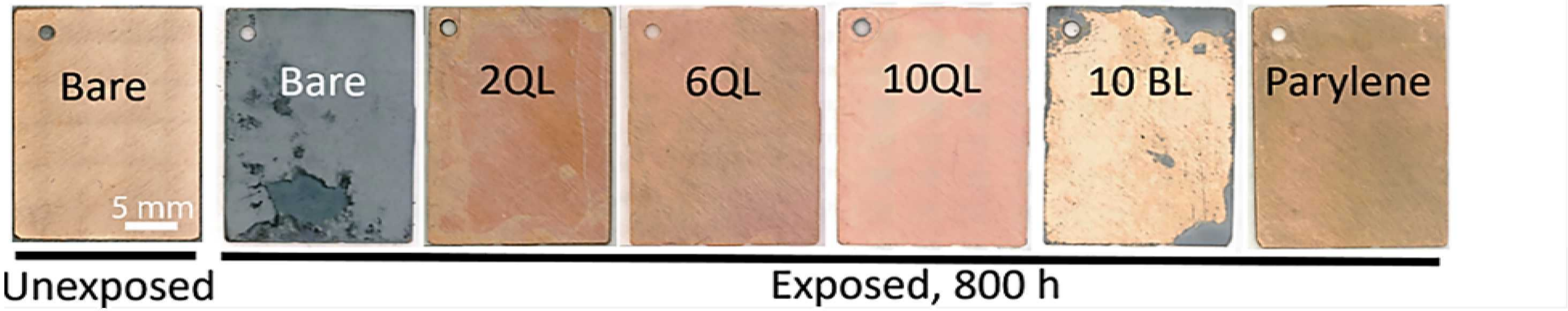




Schindelholz et al., App. Mat. Int., 2018

10 QL PCN Films Outperform "Gold Standard" Industrial Coating





Schindelholz et al., App. Mat. Int., 2018

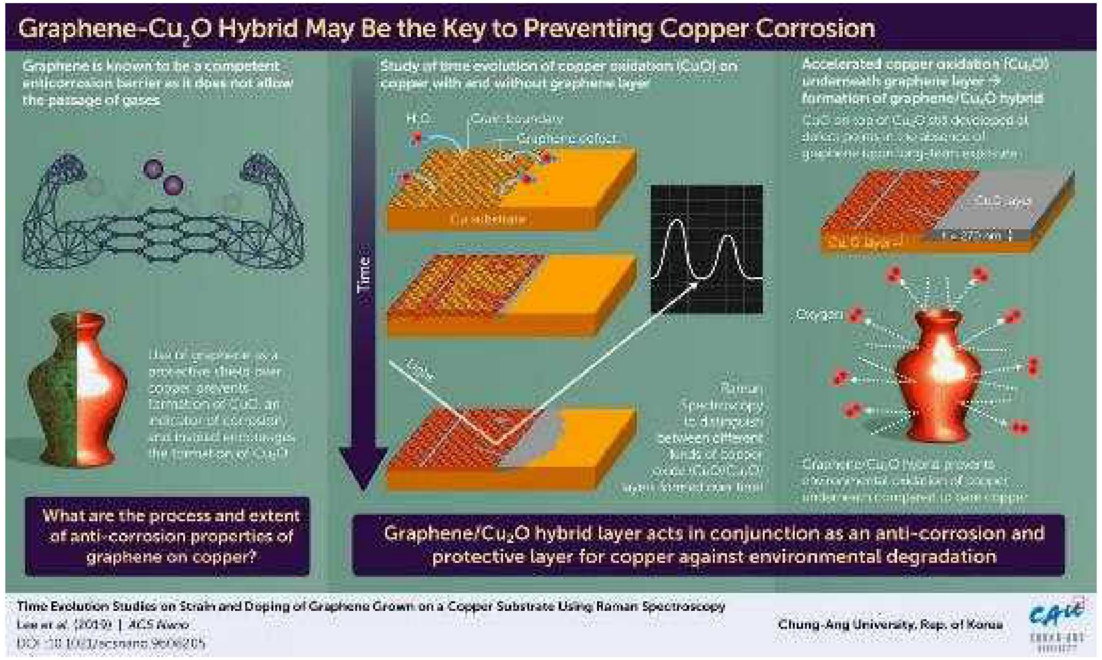
PCNs as Advantageous Alternative to Other Emergent Ultrathin Coatings

nature communications

Article | Open Access | Published: 16 November 2017

Oxidation behavior of graphene-coated copper at intrinsic graphene defects of different origins

Jinsung Kwak, Yongsu Jo, Soon-Dong Park, Na Yeon Kim, Se-Yang Kim, Hyung-Joon Shin, Zonghoon Lee, Sung Youb Kim & Soon-Yong Kwon



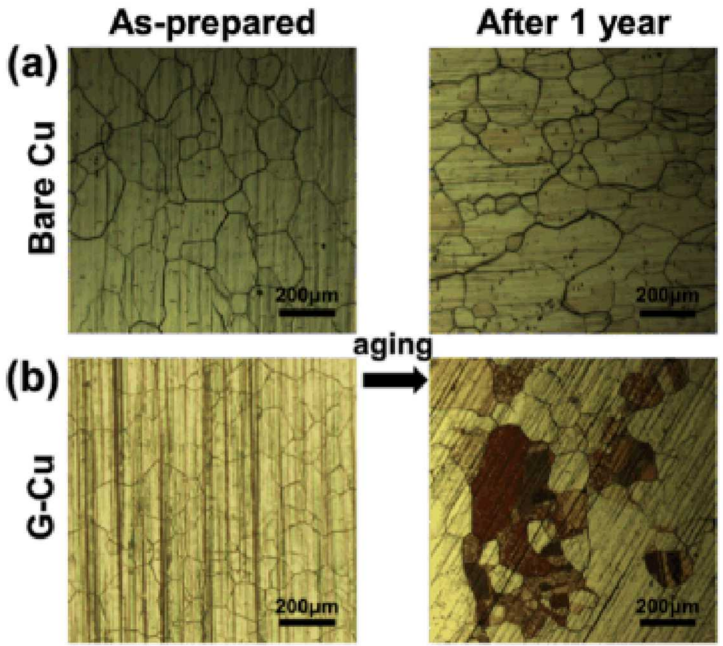
ELSEVIER

Carbon

Volume 116, May 2017, Pages 232-239

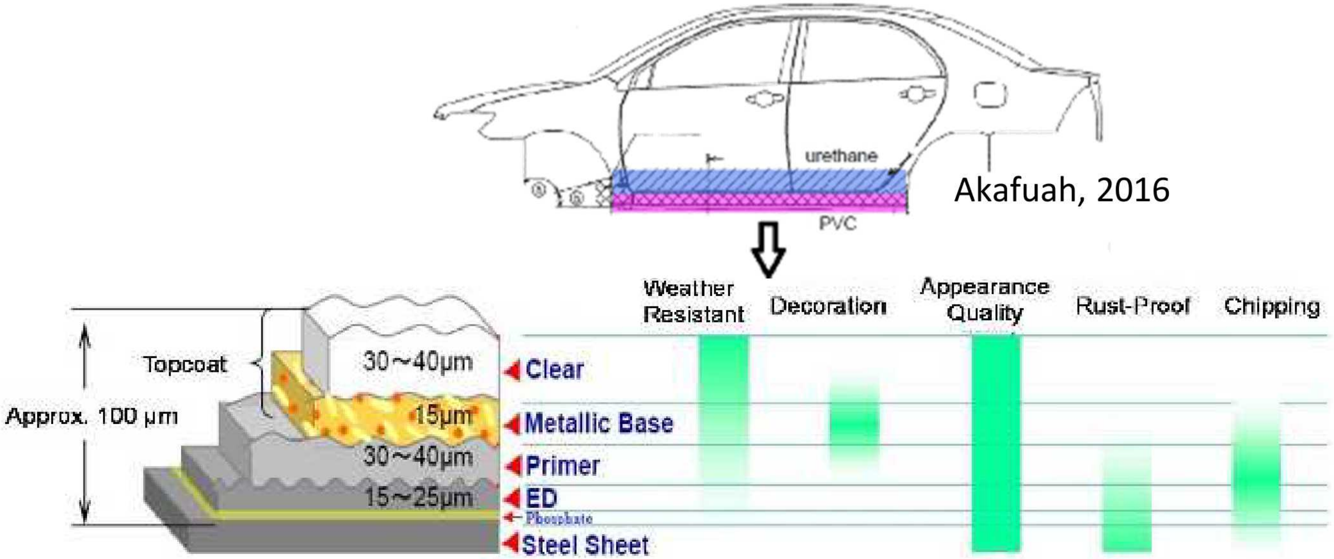
Graphene as a metal passivation layer: Corrosion-accelerator and inhibitor

Mankyu Jo [1], Hyo Chan Lee [1], Seung Goo Lee, Kilwon Cho



What Critical Characteristics of LBL PCNs Inhibit Aqueous Corrosion of Structural Alloys?

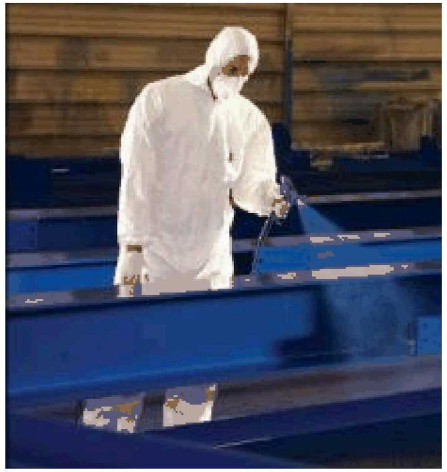
https://www.safinah-group.com/offshore-windfarms-presentation/



Desirable Coating Qualities for Structural Alloys

Light weight (e.g., transportation applications)
Low permeability (water, oxygen, ions)
Conformal
Tough and wear resistant
Inexpensive (materials, processing)
Health and Environmentally Friendly

https://www.durr.com/en/products/paint-shop-application-technology/pretreatment-and-electrocoating/



https://www.steelconstruction.info/Standard_corrosion_protection_systems_for_buildings

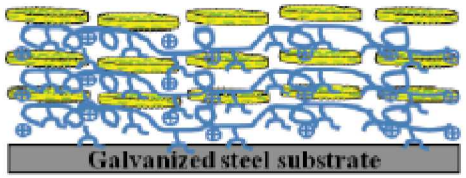
Initial Studies Show Promise for Protection of Steel and Aluminum Alloys

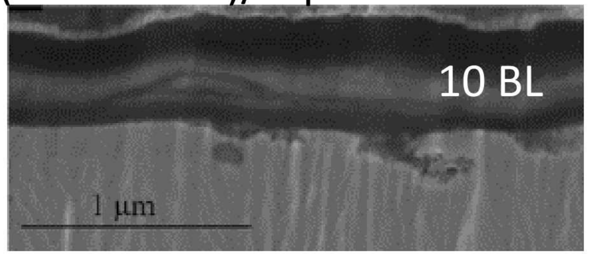
2011

Clay and DOPA Containing Polyelectrolyte Multilayer Film for Imparting Anticorrosion Properties to Galvanized Steel

Emilie Faure,[†] Emilie Halusiak,[†] Fabrice Farina,[†] Nicoletta Giamblanco,[§] Cécile Motte,[‖]

P(mDOPA)-coP(DMAEMA+)/Laponite





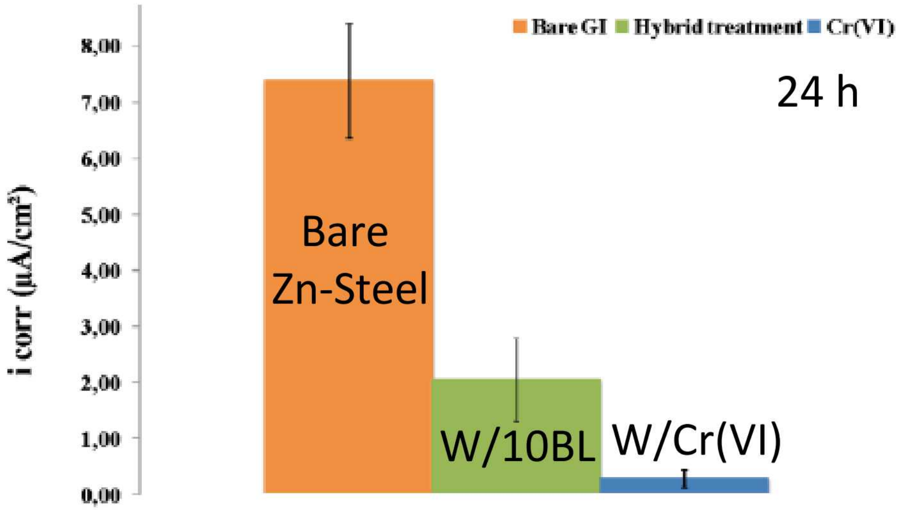


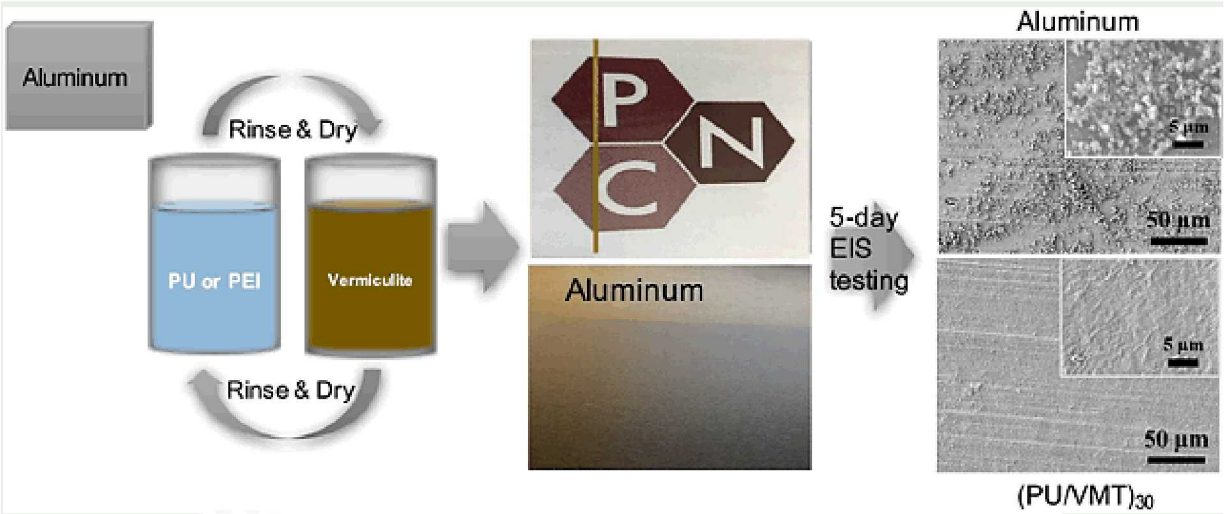
Figure 6. Estimated corrosion current values for bare and treated HDG samples in aerated 0.1 M NaCl.

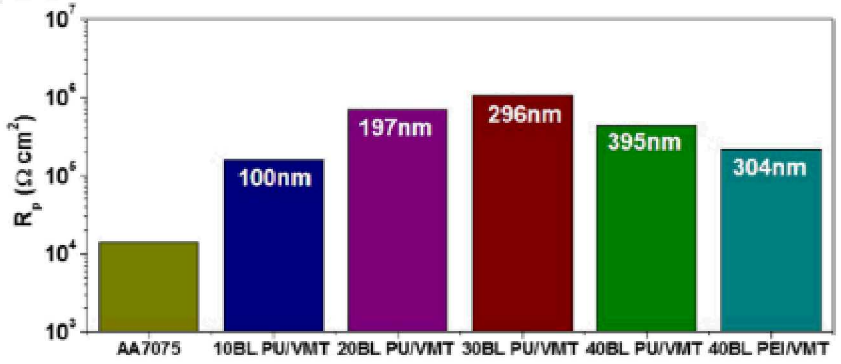
2018

Ultrathin Transparent Nanobrick Wall Anticorrosion Coatings

Shuang Qin,[†] Yenny Cubides,[†] Simone Lazar,[‡] Ramatou Ly,[†] Yixuan Song,[†] Joseph Gerringer,[†] Homero Castaneda,[†] and Jaime C. Grunlan*[†,‡,§]

PU/VMT, PEI/VMT





What are critical component and architectural factors governing barrier performance?

Water Permeability Model for PCN:

permeant solubility factor

particle loading (vol. fraction)

$$\frac{P_n}{P_m} = \frac{1-\beta\phi_i}{\xi_{(\phi)}(1+\phi_i((1+(\alpha'_{(\phi)}/3))(V_m/V_i)-1))}\left[\frac{(1-X_C^n)}{(1-X_C^0)}\right]^2\left[\frac{\gamma'_n}{\gamma'_m}\right]^{\varepsilon}$$

polymer chain immobility factor

particle aspect ratio

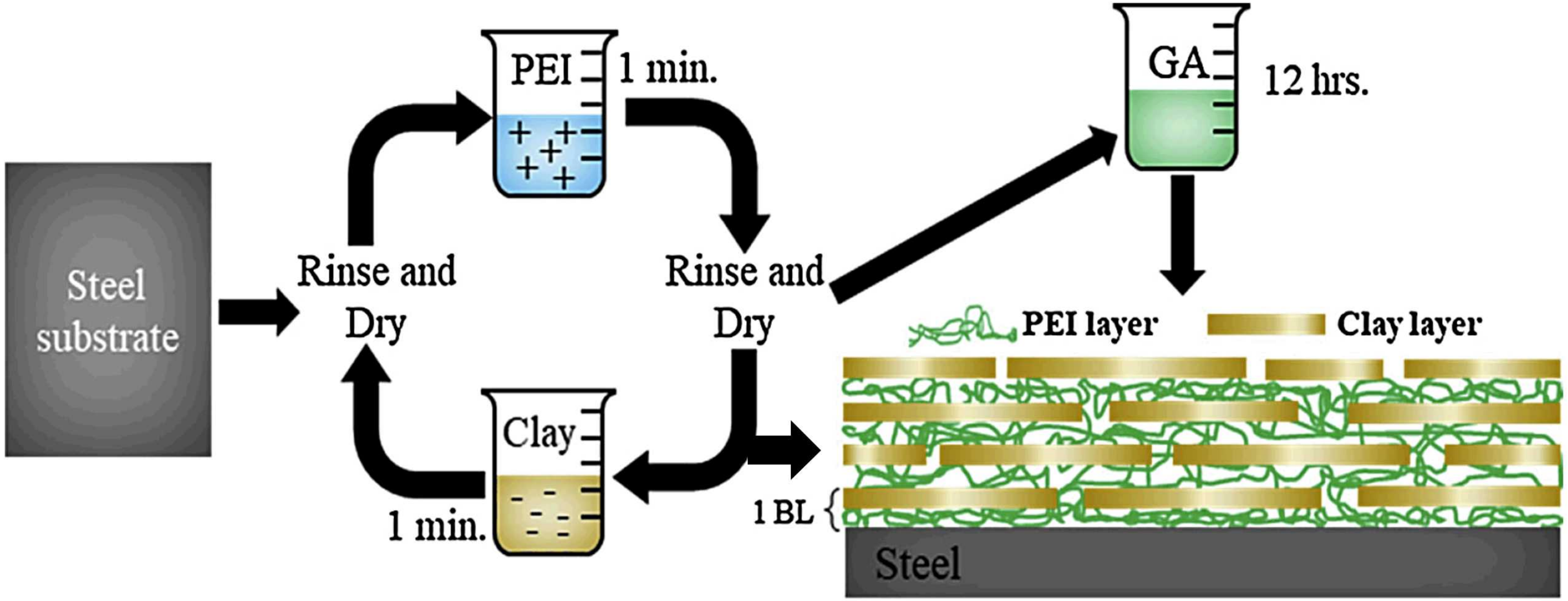
relative permeant velocity factor

relative crystallinity of filled and unfilled polymer

relative plasticization factor

Alexandre et al., J. Memb. Sci. 2009

Can we grow a "defect-free" coating on plain steel? What coating characteristics are critical for performance ?



Experimental Details

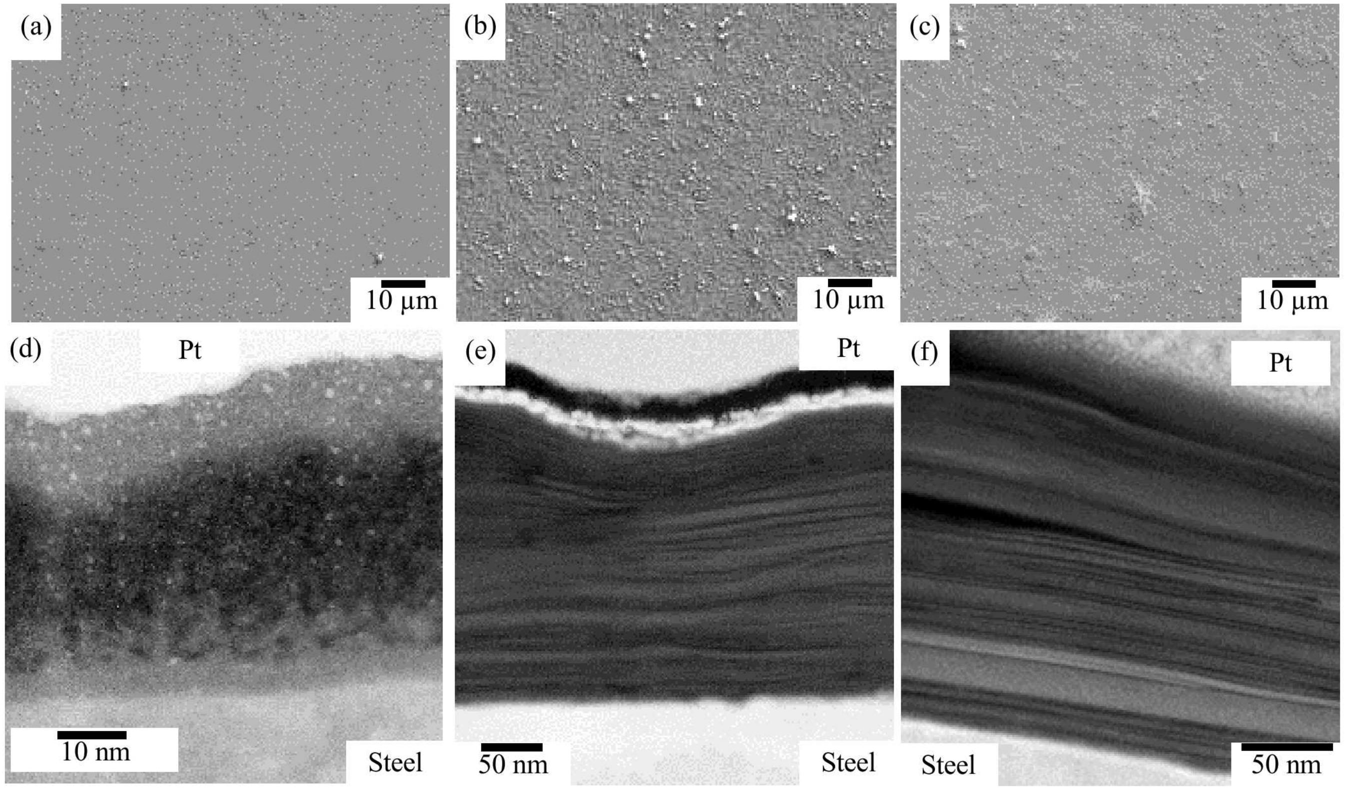
1018 steel, 180 grit finish, alkaline passivation

Branched PEI: 0.1 wt% (~ 25,000 g/mol)
Clay: 1 wt%
GA: 25 wt%

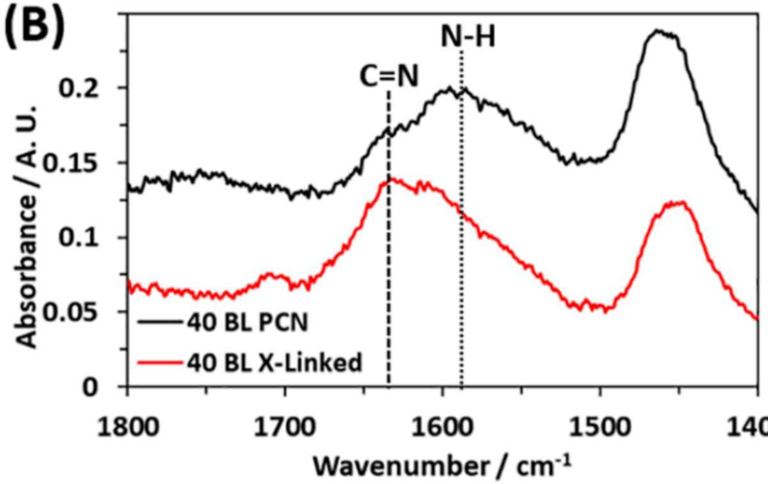
Clay	Diameter (nm)	Loading (wt%)*
LAP	30	83
MMT	400	83
VMT	2000	92

*determined from previous studies : Li et al., 2009; Priolo et al., 2012

LBL Coatings on Steel Exhibit Highly Aligned Exfoliated Clay Layers with no observable through-defects



$(PEI/LAP)_{20}$ $(PEI/MMT)_{20}$ $(PEI/VMT)_{20}$

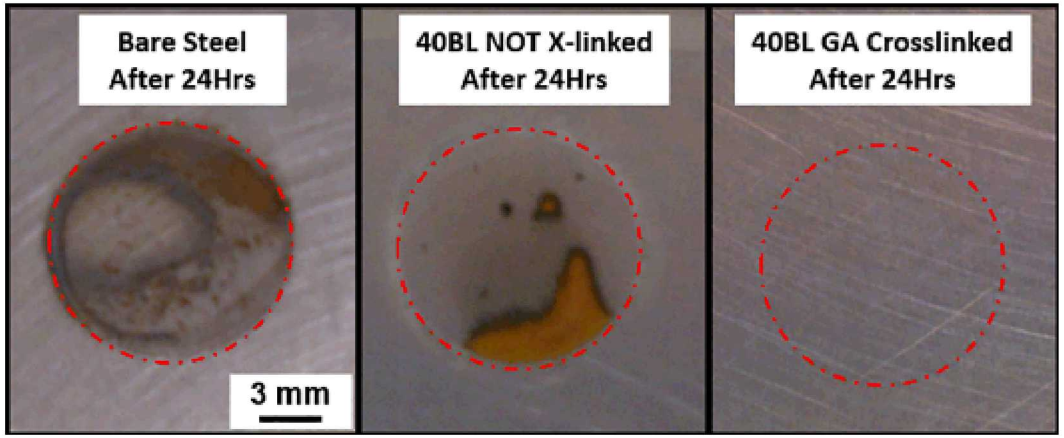


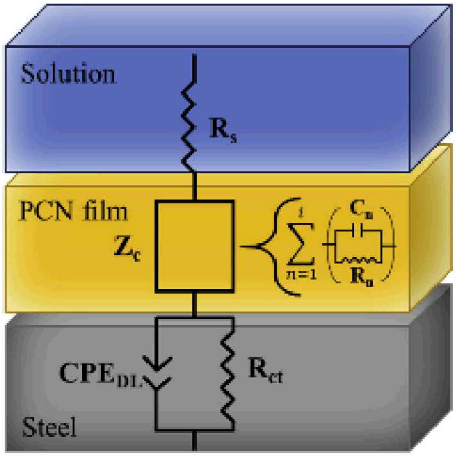
GA crosslinks films by reacting with PEI primary amines

Percival et al., Surf. Coat and Tech, 2020
Melia et al., Prog. Org. Coat., 2020

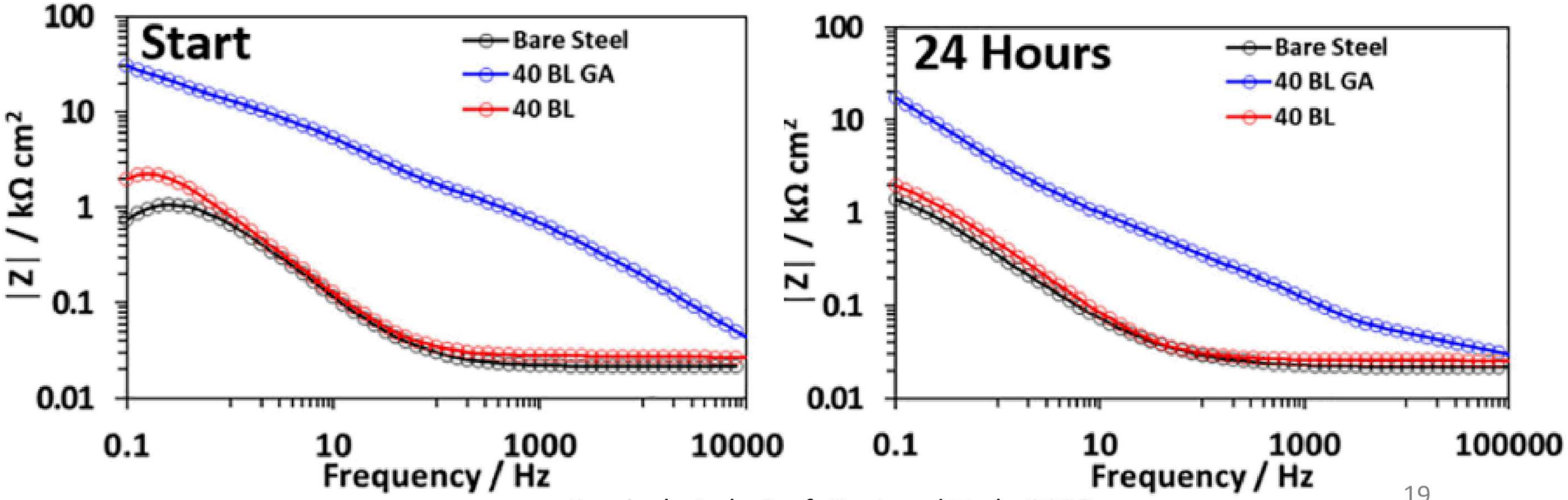
GA Cross-Linking Was Necessary for Creating Protective Coatings

- Bare and coated steel was immersed in 0.6 M NaCl (seawater analog) for up to 7 days.
- Electrochemical impedance of coated steel used to track coating integrity and steel corrosion rate



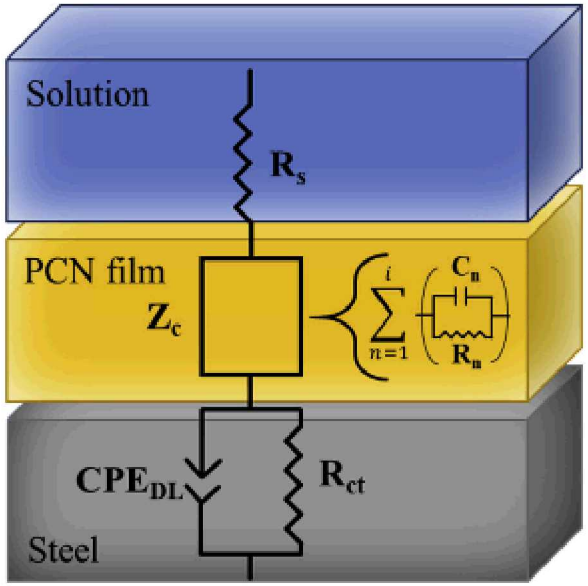


electrochemical impedance model for coated steel

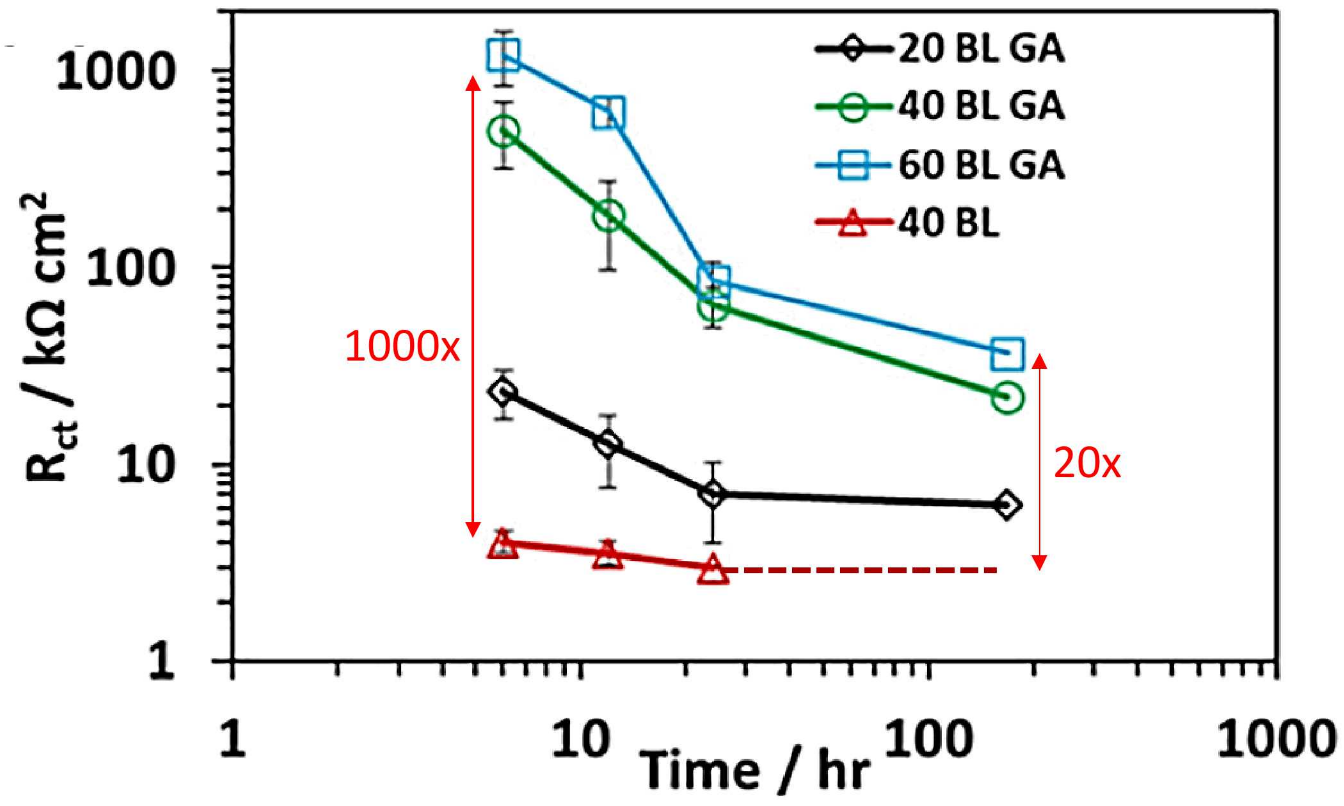


Percival et al., Surf. Coat and Tech, 2020

Coating Protection Could be Further Improved by Increasing Number of Layers

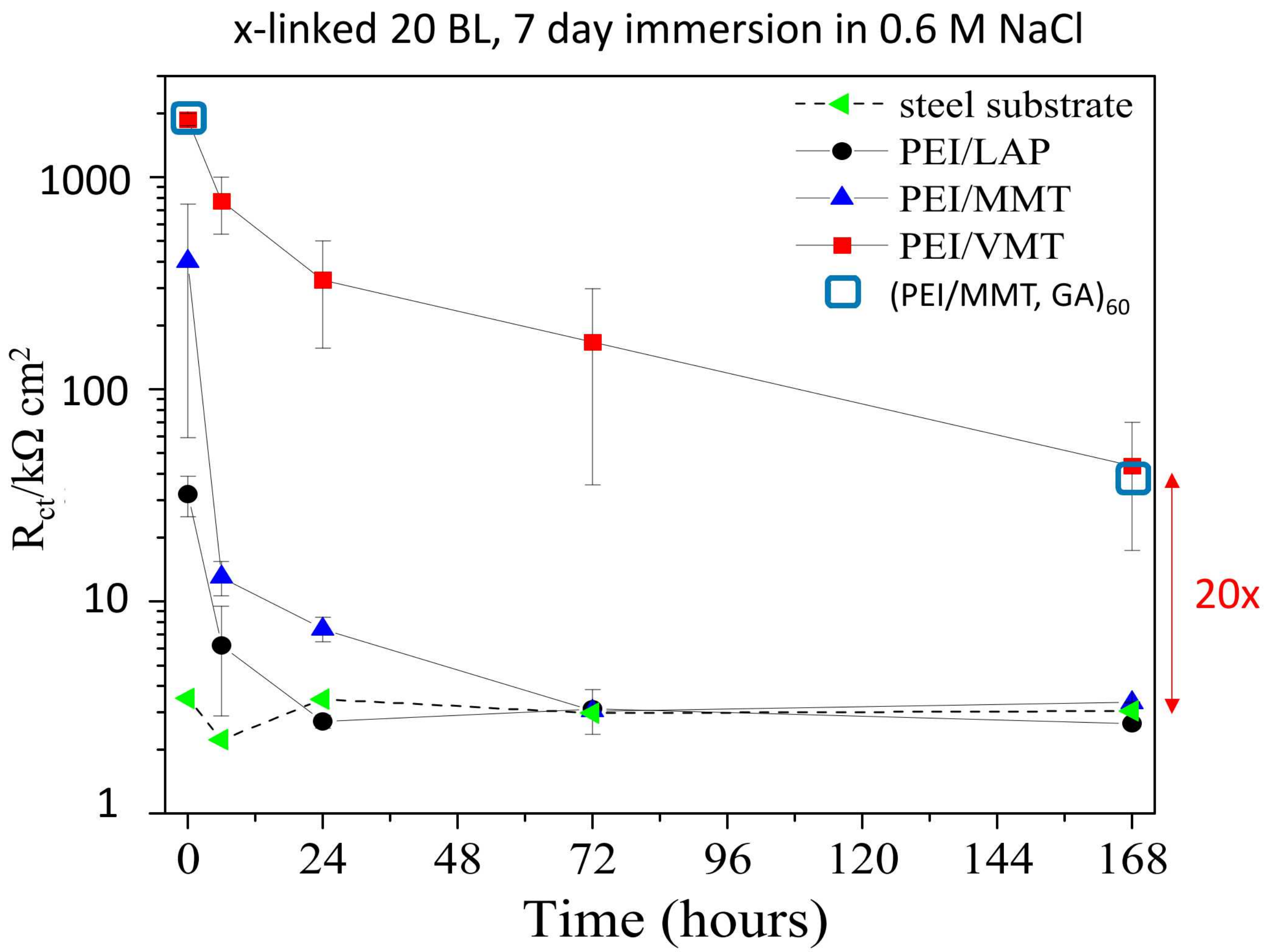


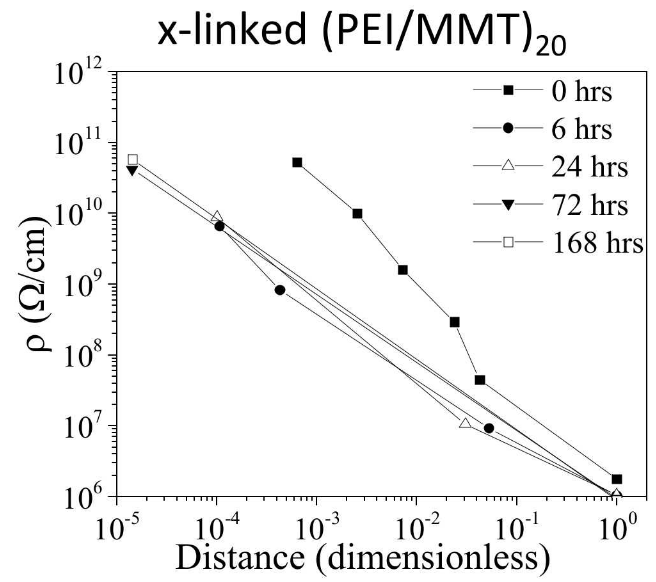
7 day immersion in 0.6 M NaCl

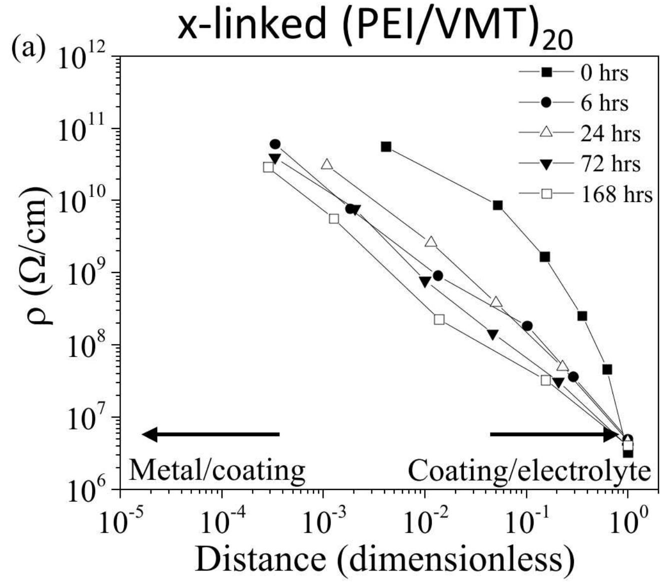


Percival et al., Surf. Coat and Tech, 2020

Protection and Permeability Improved With Increasing Particle Aspect Ratio



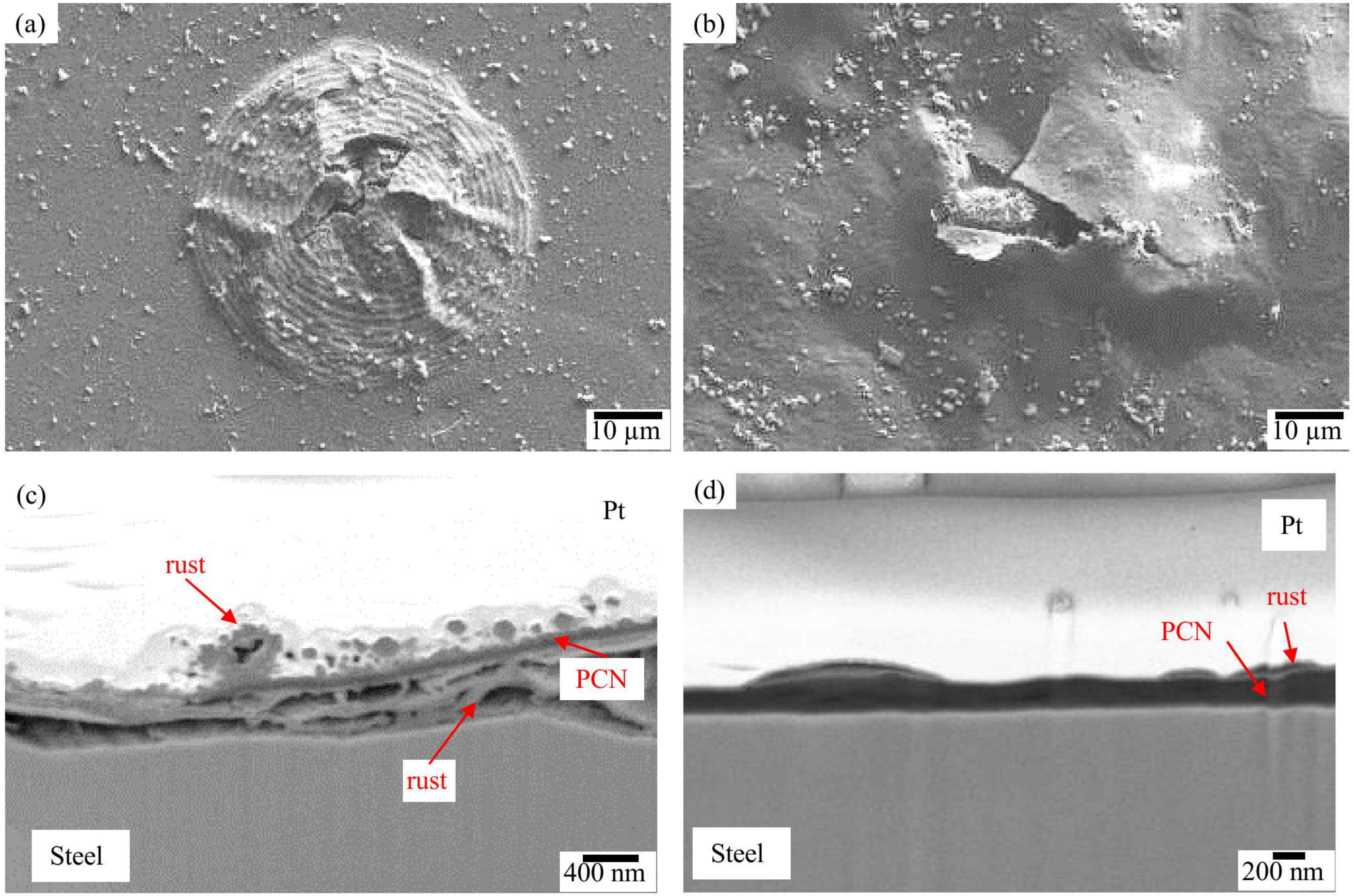




Melia et al., Prog. Org. Coat., 2020

Film Debonding Was a Primary Coating Failure Mode for All Films

Film Damage After 7 day Immersion in 0.6 M NaCl



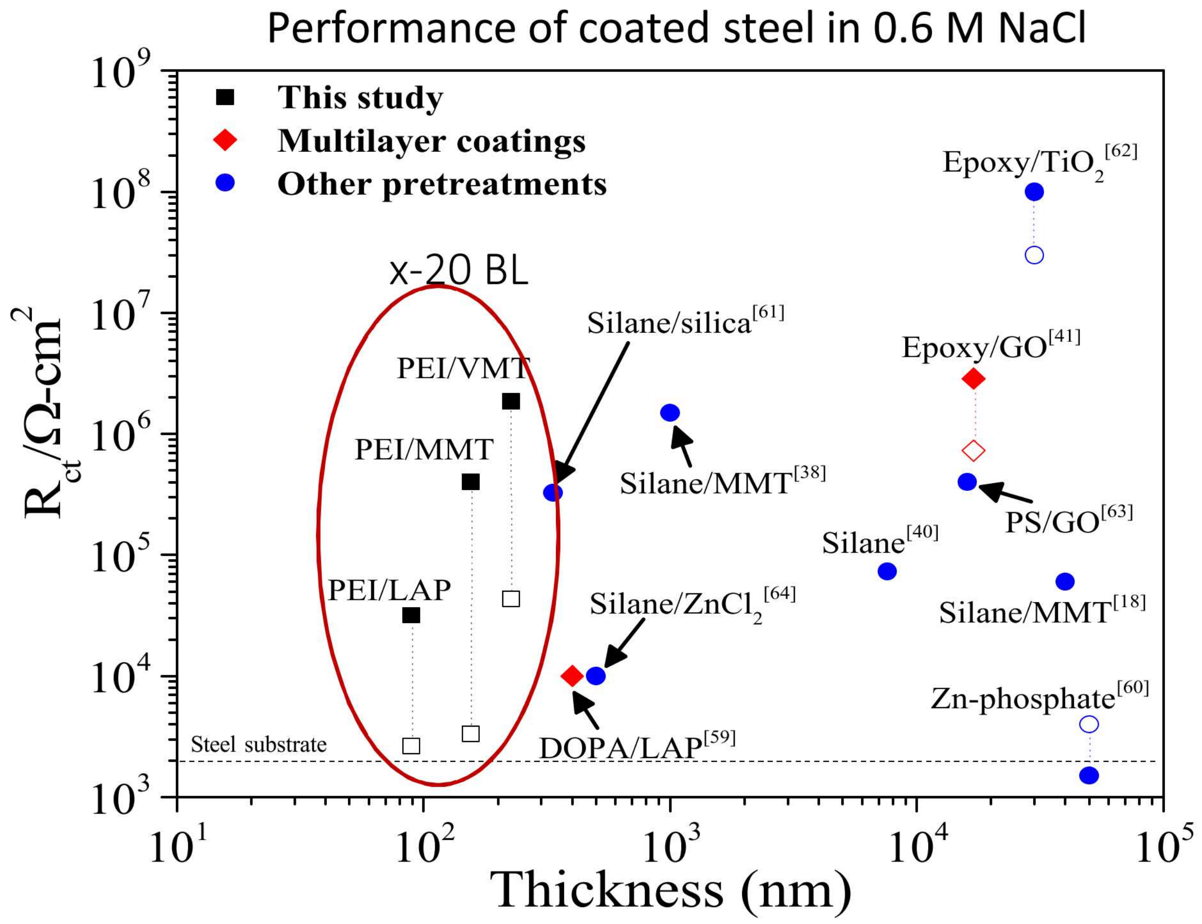
x-linked 20BL PEI/LAP

x-linked 20BL PEI/VMT

Debonding Likely Played a Minor Role in the Performance Differences Observed Between LAP, MMT and VMT films

Melia et al., Prog. Org. Coat., 2020

PEI/VMT Films Had Highest Reported R_{CT} Values Per Coating Thickness



Melia et al., Prog. Org. Coat., 2020

Conclusions

Layer-by-layer PCN films are a promising, low-cost solution for protection of metals against corrosive gases and saline aqueous environments.

Films as thin as 90 nm, can reduce copper corrosion rates by >1000× in highly corrosive H_2S atmosphere.

Contiguous PEI/Clay LBL films were successfully grown on carbon steel, providing exceptional protection (20x in aggressive chloride salt environments).

Increasing clay aspect ratio and cross-linking can critically improve the corrosion barrier performance of LbL PCN films.

Film debonding with the steel was common coating failure mode in immersed environments → Pathway to further improving LBL PCN coatings.

Ideal Characteristics

- Impermeable
- Actively protective
- Mechanically robust
- Lightweight/low profile
- Cheap
- Easy application