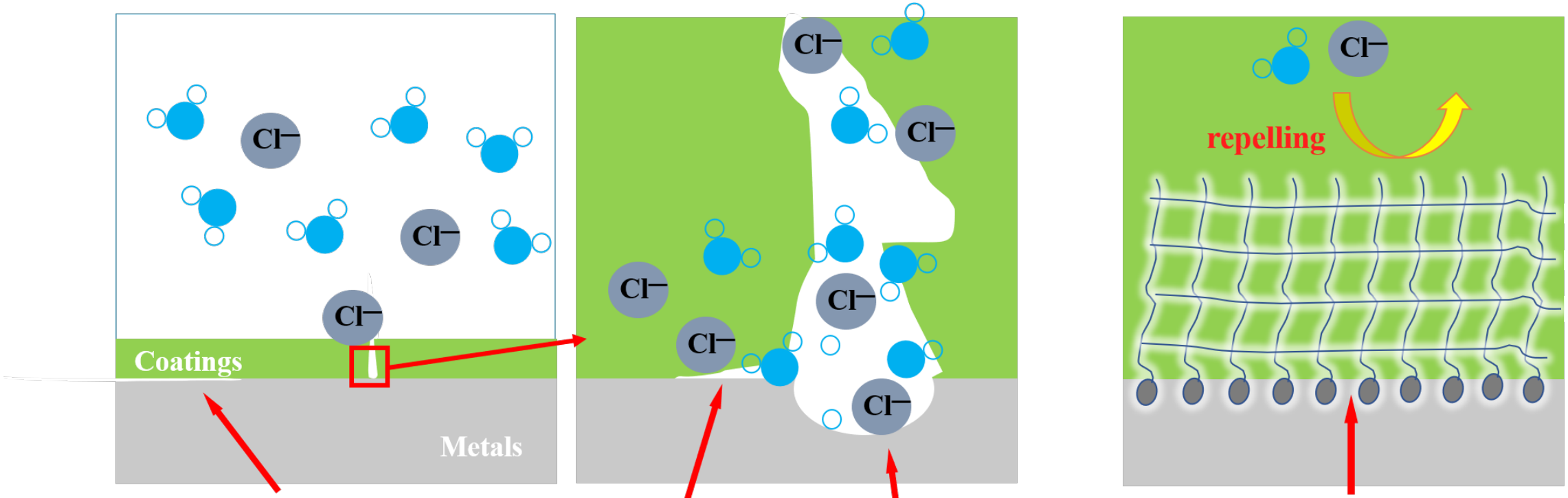
天津大学
Tianjin University

Covalent Surface Modification of 2024 Aluminum Alloy Surface by Self-assembly Dodecyl phosphate Film towards Corrosion Protection

Cheng-cheng Pan

Tianjin Key Laboratory of Composite and Functional Materials
School of Materials Science and Engineering
Tianjin University

Practical Questions About Corrosion Protection for Aluminum Alloy



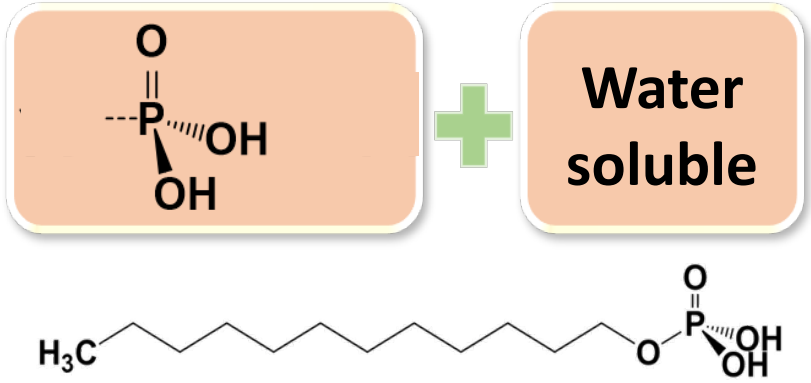
① Weak surface adhesion

② Adhesion failure induced by the intrusive particles

③ Chloride ions adsorption and breaking the passive film

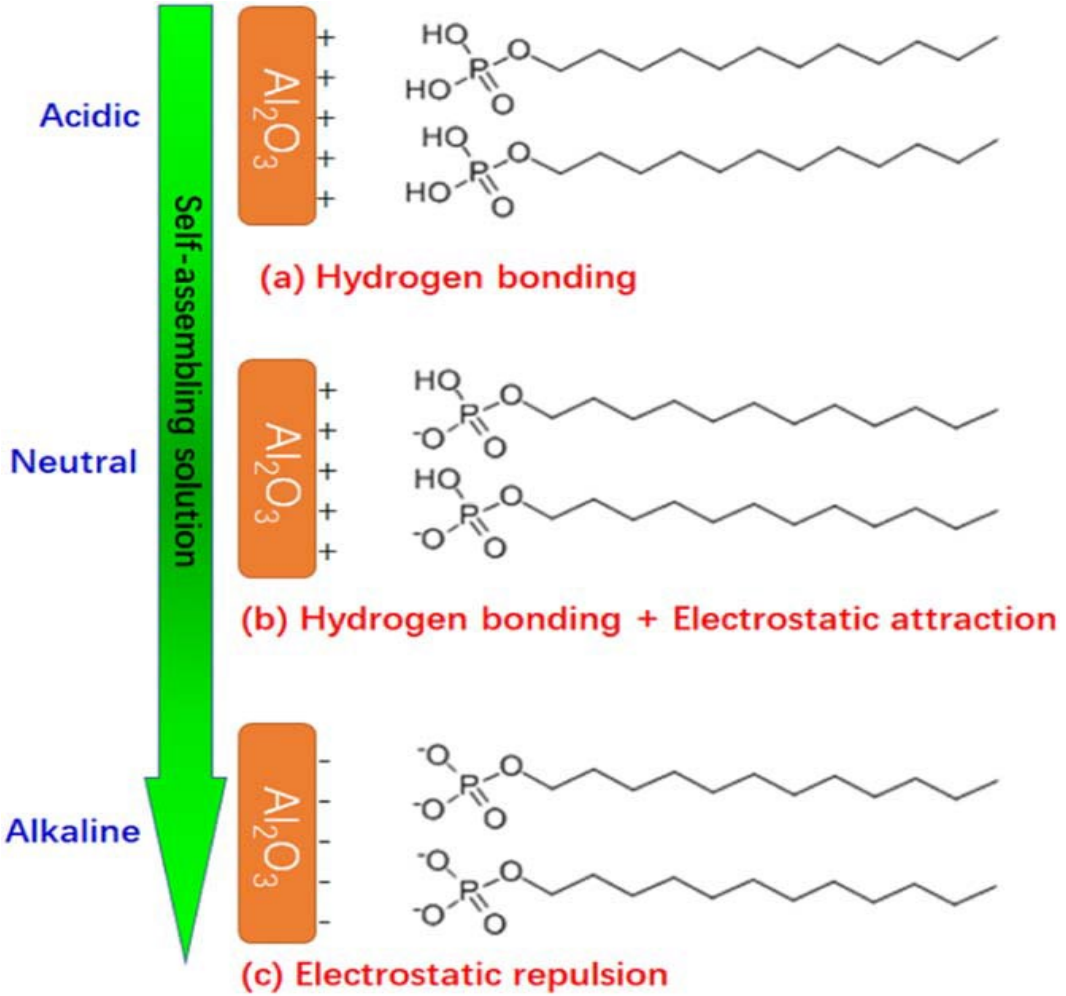
The Ideal Strategy:
Enhancing the interface adhesion between coatings and metals

Dodecyl phosphate (DDPO4)



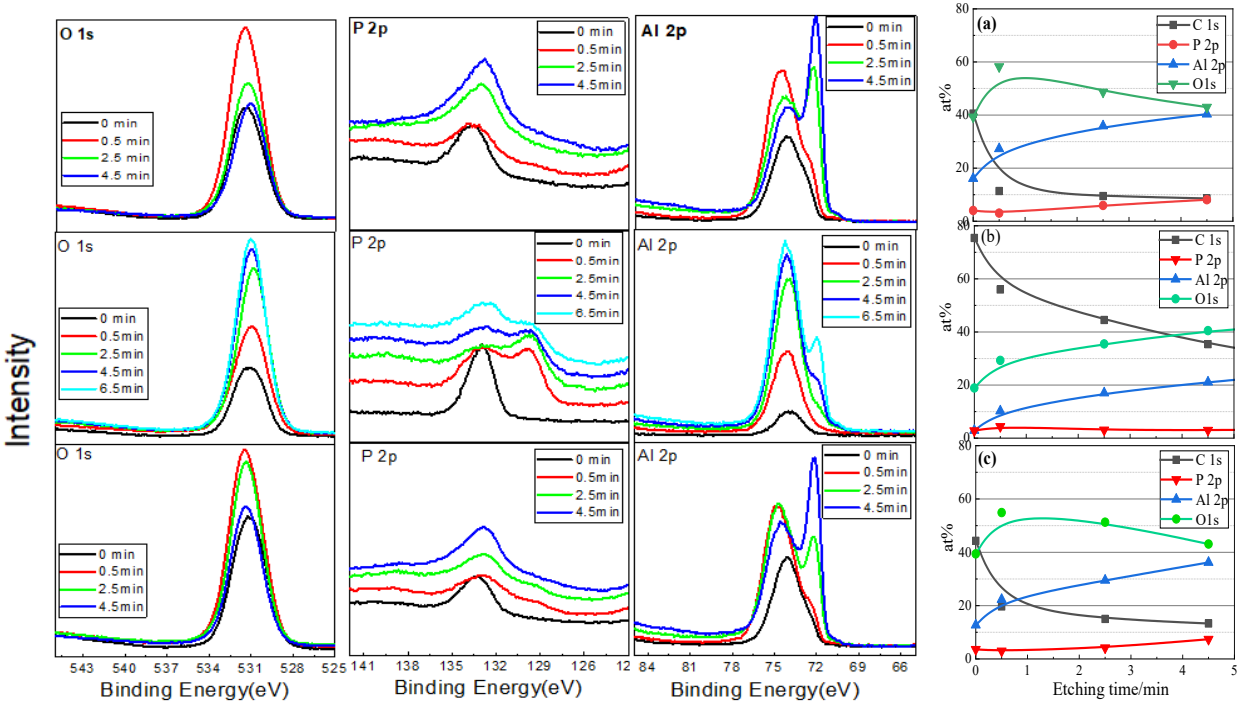
The adsorption processes will be influenc -ed by:

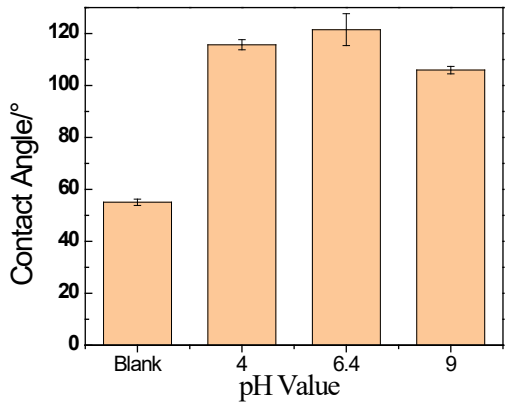
1. The water solubility of DDPO4 molecular (temperature);
2. molecular structure: the number of P-OH bond (which main influenced by pH);
3. Chemical states for aluminum alloy surface (pH and temperature);

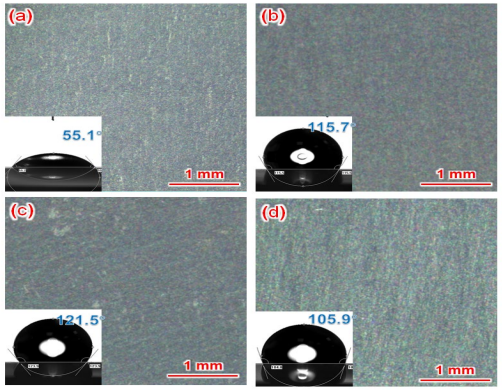


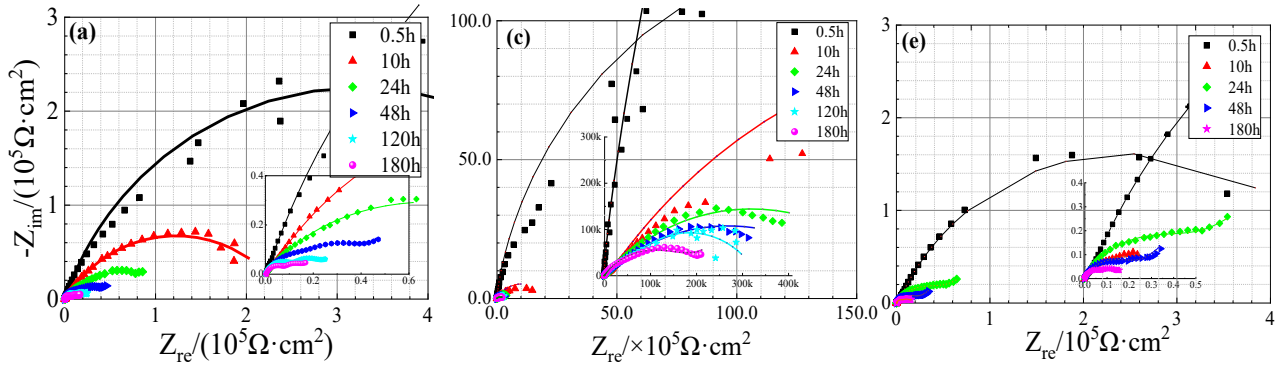
How pH influences the adsorption process?

1. Chemical state of Aluminum alloy surface changes with the pH of modification solution;
2. DDPO4 molecular structure changes with the modification solution;
3. Interaction between DDPO4 molecules and aluminum alloy surface;





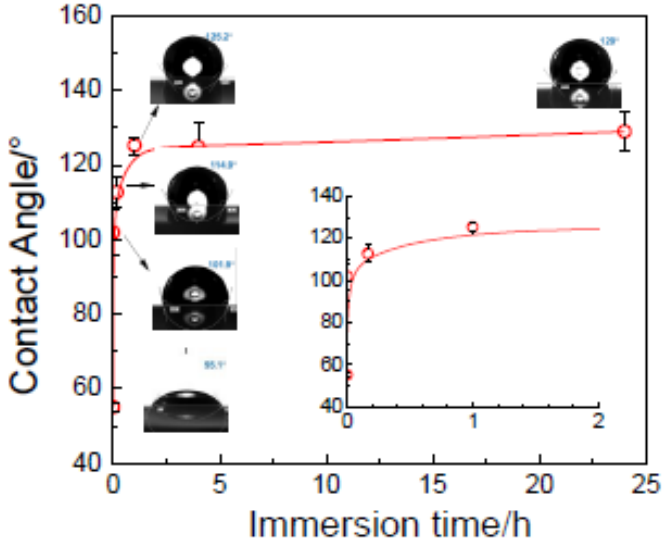


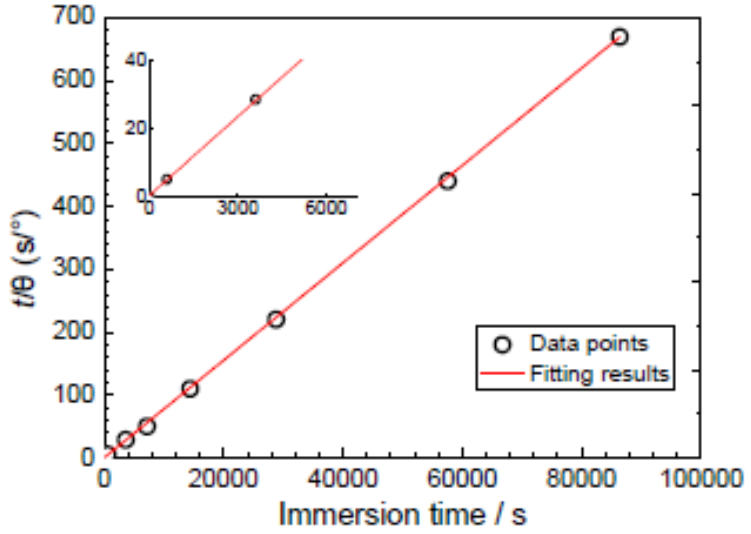


Adsorption Kinetics —— pseudo-second-order model

Two stages for adsorption process:

Adsorption stage and stable stage.



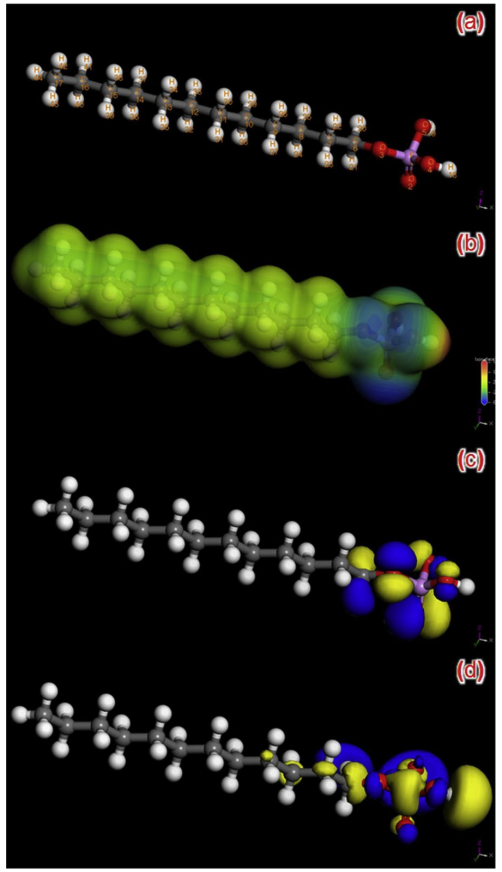


$$\frac{t}{\theta} = 0.00775t + 0.479 \qquad R^2 \approx 1.$$

Molecular Dynamic Simulation

Fukui function indices:

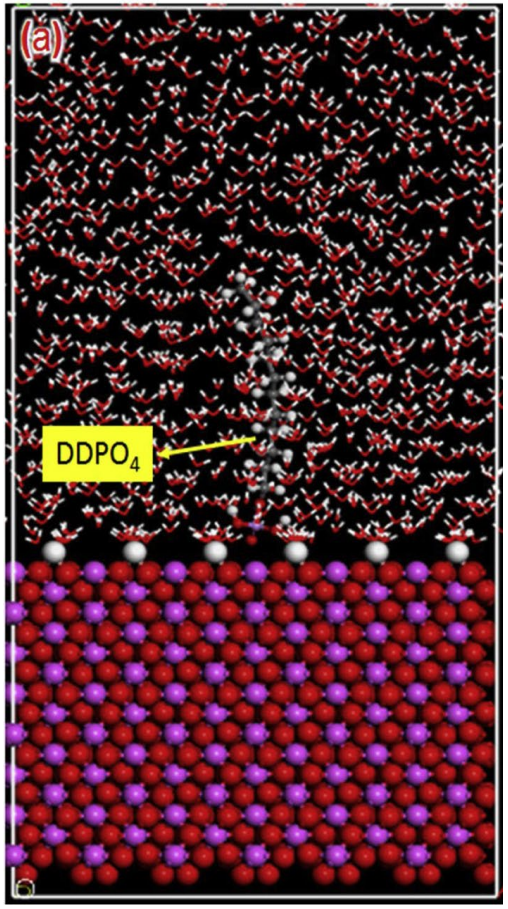
Atom	f_K^+	f_K^-
C17	0	−0.292
C16	0	−0.211
C15	0	−0.192
C14	0	−0.193
C13	0	−0.195
C12	0	−0.195
C11	0	−0.195
C10	−0.001	−0.195
C9	0	−0.195
C8	−0.004	−0.207
C7	−0.009	−0.213
C6	0.042	0.038
O5	−0.066	−0.577
O4	−0.068	−0.562
O3	−0.016	−0.588
O2	0.011	−0.708
P1	0.217	1.417



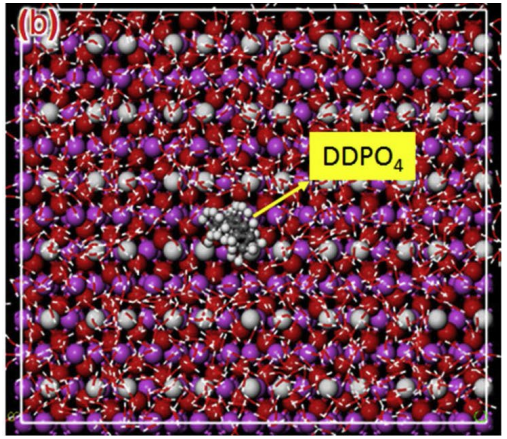
Quantum parameters for DDPO4: optimized structure with the number of condensed atoms (a), molecular electrostatic potential map (b), HOMO (c) and LUMO (d) energy distributions.

Adsorption processes:

1. due to the negative charge of the O in P=O bond, it can adsorb on the positively charged Al_2O_3 surface, to form a monolayers.

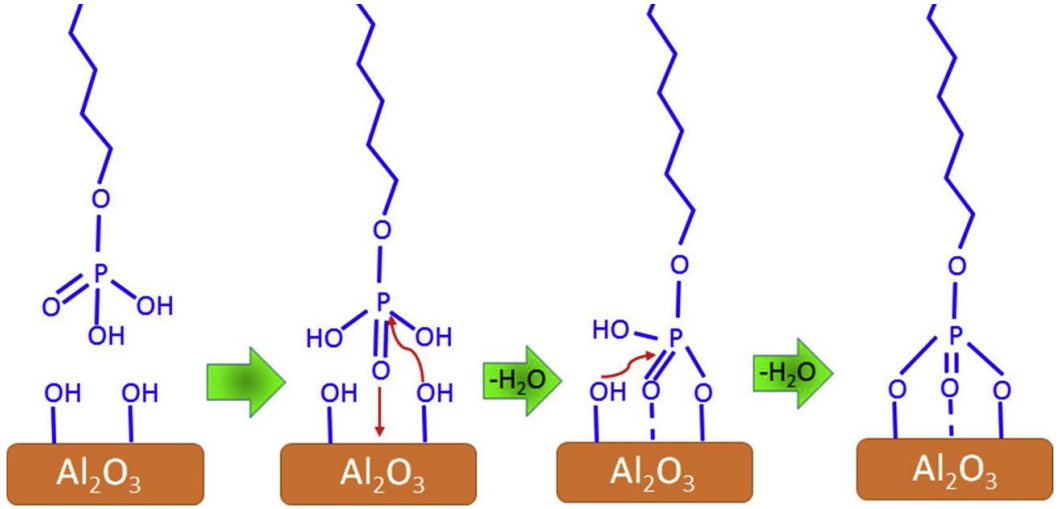


2. A “tail-up” orientation and a tilt angle of the hydrocarbon chains of about 30° with respect to the surface normal.



Bonding method

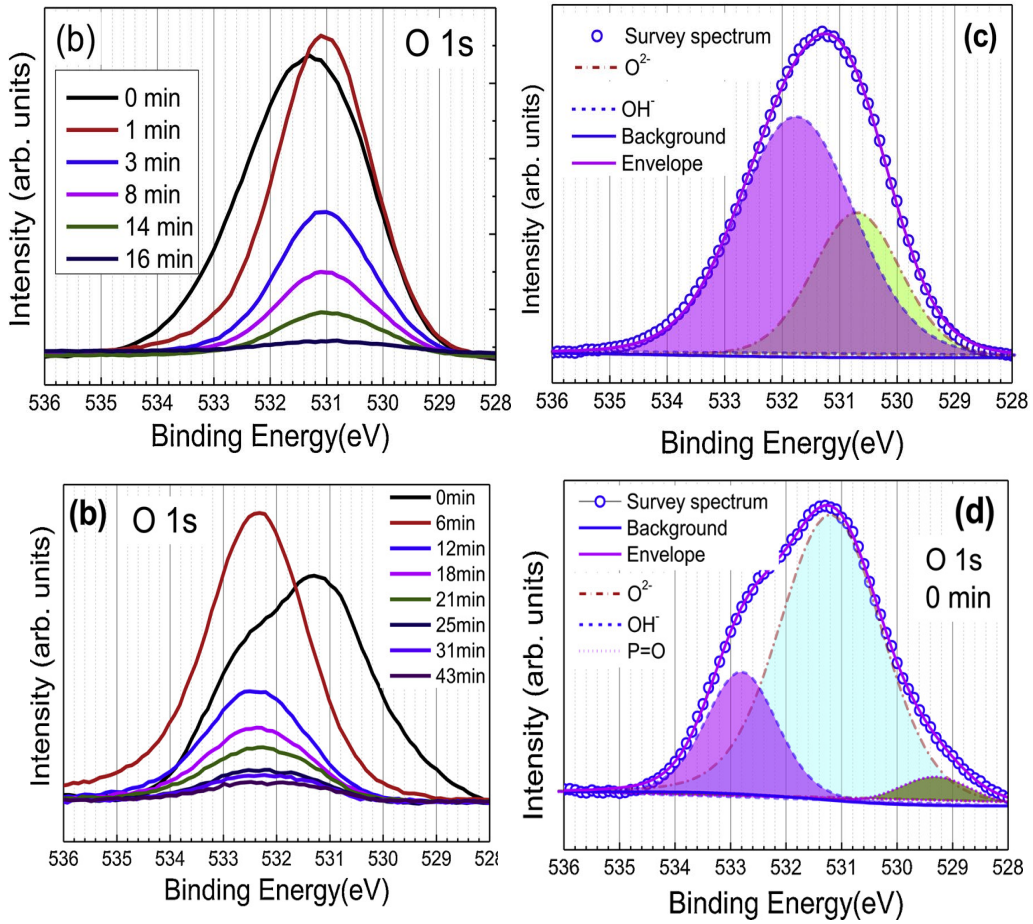
Surface bonding mode:



Step 1: Phosphate groups point to the Aluminum alloy surface under hydrogen bonding interaction.

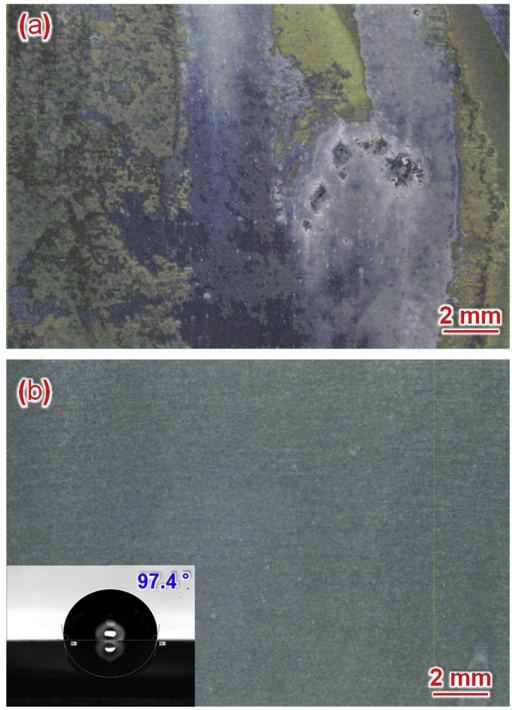
Step 2: The P=O bond in the DDPO4 adsorbs on oxide surface.

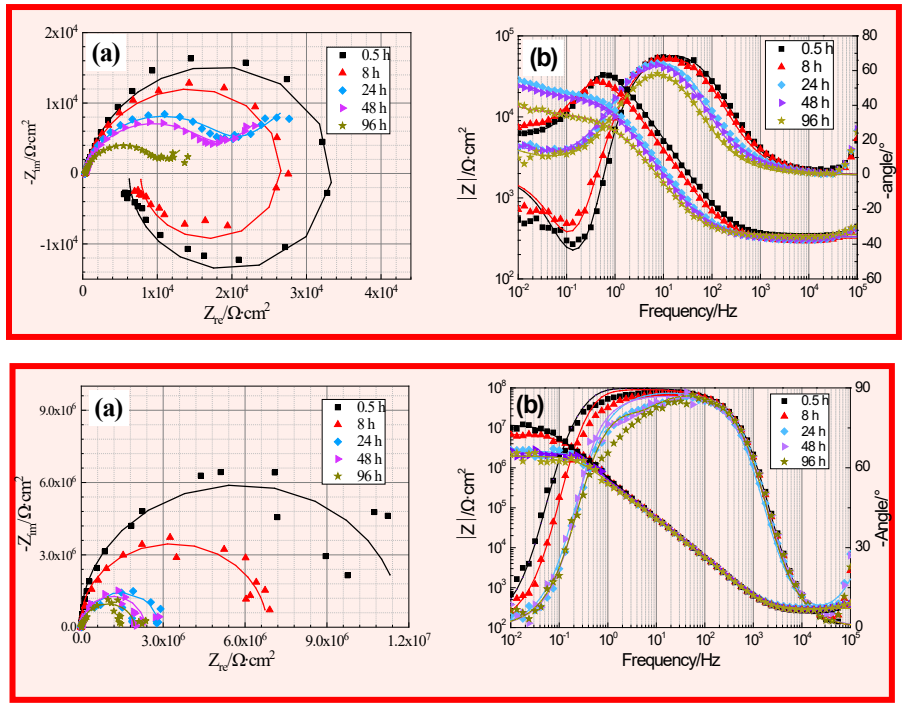
Step 3: Water discharging from the condensation of Hydrogen bond to form P-O-Al bond.



Corrosion Resistance

Laboratory simulation:

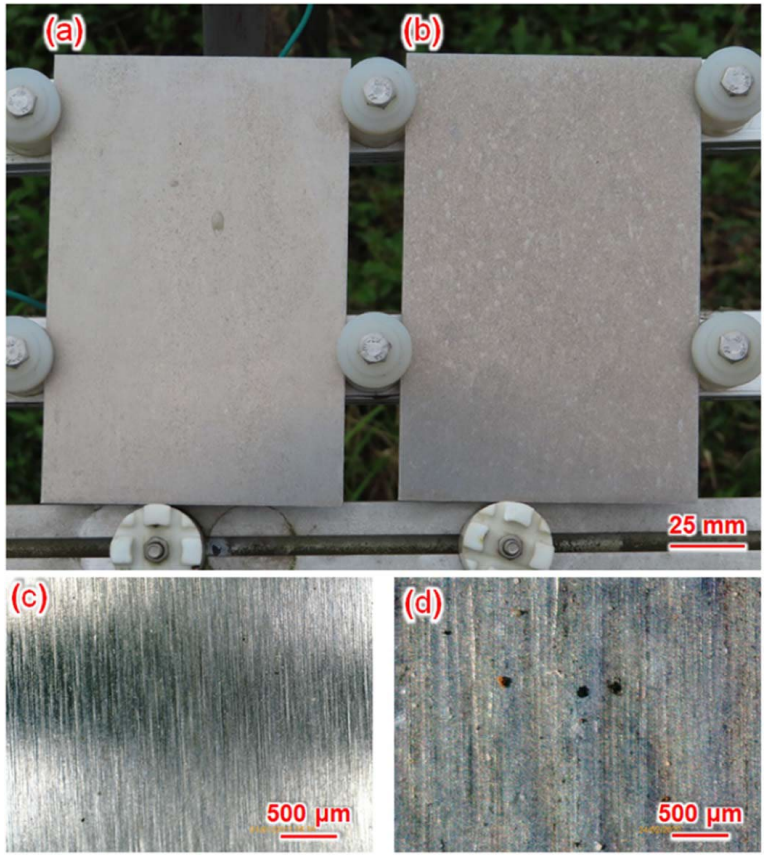




1. Corrosion morphology after exposed to 0.01M Cl^- +0.01M SO_4^{2-} for 96 h. (a) blank 2024AA, (b) 2024AA covered by DDPO4 film. (Left)

2. The charge transfer resistance of the DDPO4 covered aluminum alloy was ~100 times larger than that of the blank aluminum alloy. (Right)

Marine atmosphere:



Conclusion

1. The structure of DDPO4 and surface state of 2024AA surface changes with the pH value of modification solution, and after that, the adsorption process will be changed;
2. The adsorption kinetics of the molecule conforms to the pseudo-second-order model;
3. DDPO4 molecules binds to aluminum alloy surface with chemical bond form;
4. The corrosion resistance have been improved by ~100 times.

Thanks !