Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting information

Molecular structure effects on the mechanisms of corrosion protection of model epoxy coatings on metals

Yosra Kotb[1], Christopher M. Serfass[1], Alain Cagnard[2], Katelyn R. Houston[2], Saad A. Khan[1], Lilian C. Hsiao[1], and Orlin D. Velev[1*]

[1] *Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 26795, USA*

[2] *Eastman Chemical Company, Kingsport, TN 37660, USA*

Confocal imaging

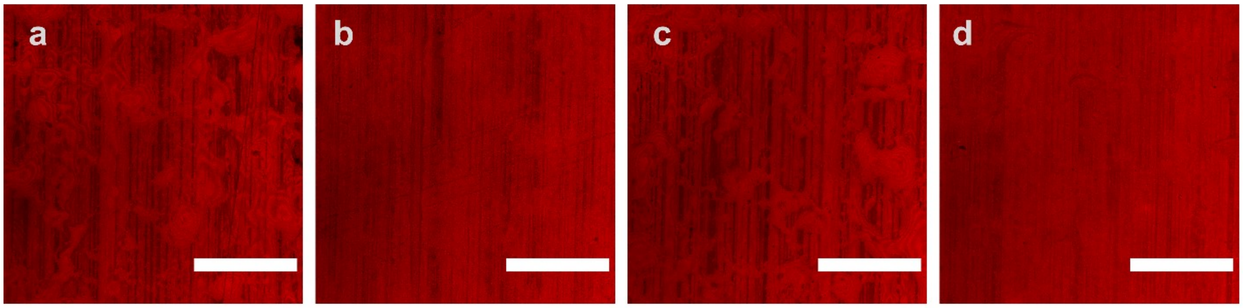

Fig. S1. Confocal xy projections of type 9 coatings on (a) T23 and (b) TFS, and type 7 coatings on (c) T23 and (d) TFS after 1 hr of degradation showing no obvious defect sites across the coating surface.

EDX analysis

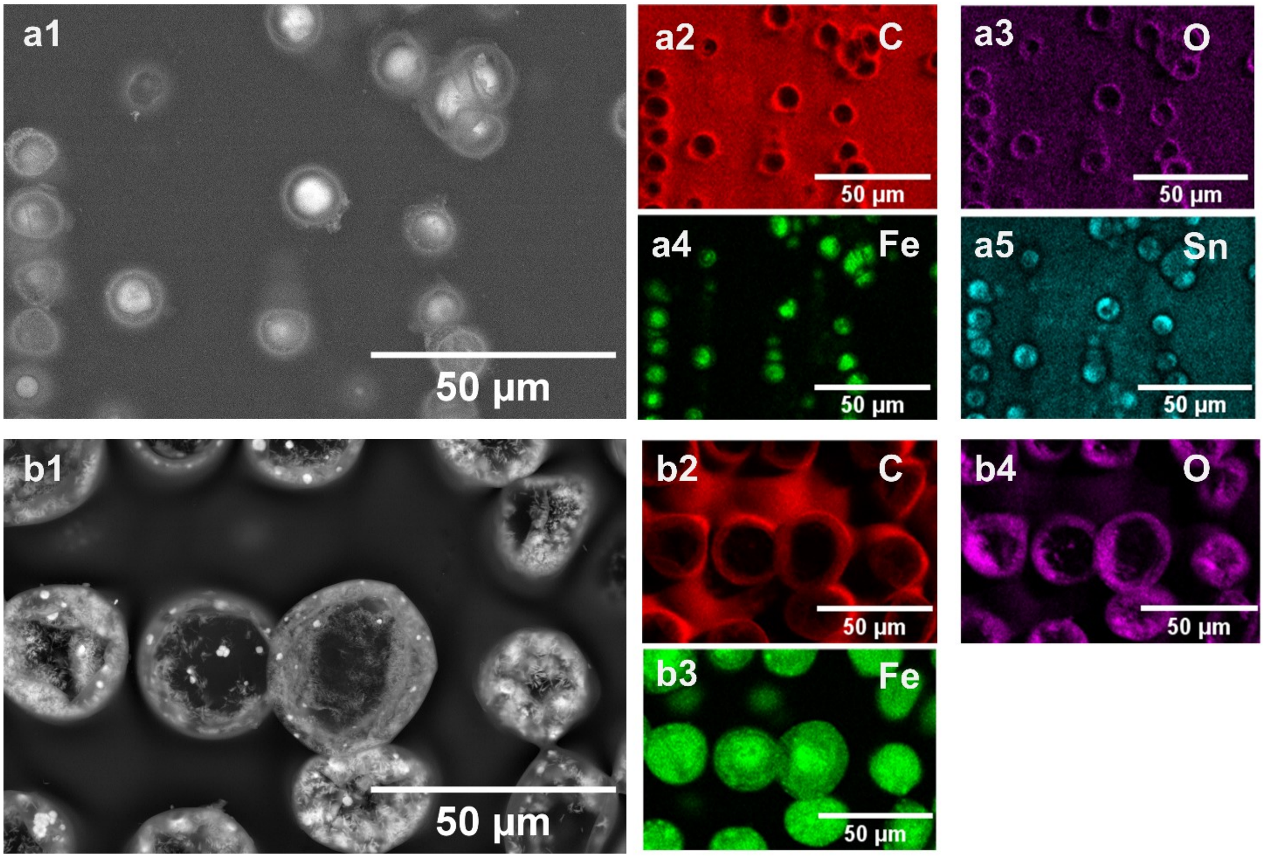

Fig. S2. Backscattered SEM micrographs and corresponding elemental mapping of type 7 coatings after 24 hrs of immersion on (a1-a5) T23 and (b1-b4) TFS.

XPS analysis

Chemical analysis of the bare substrates was done using a SPECS X-ray photoelectron spectroscopy (XPS) system with a PHOIBOS 150 analyzer. Spectra were generated using an Al Ka X- ray source operated at 400 W. The deconvolution of the Cr 2p peak showed four components: metallic Cr at 574.3 eV, Cr_2O_3 at 576.5 eV, $Cr(OH)_3$ at 577.3 eV, and CrO_3 at 578.9 eV. For all analyses, data reduction and fitting were carried out using CasaXPS software.

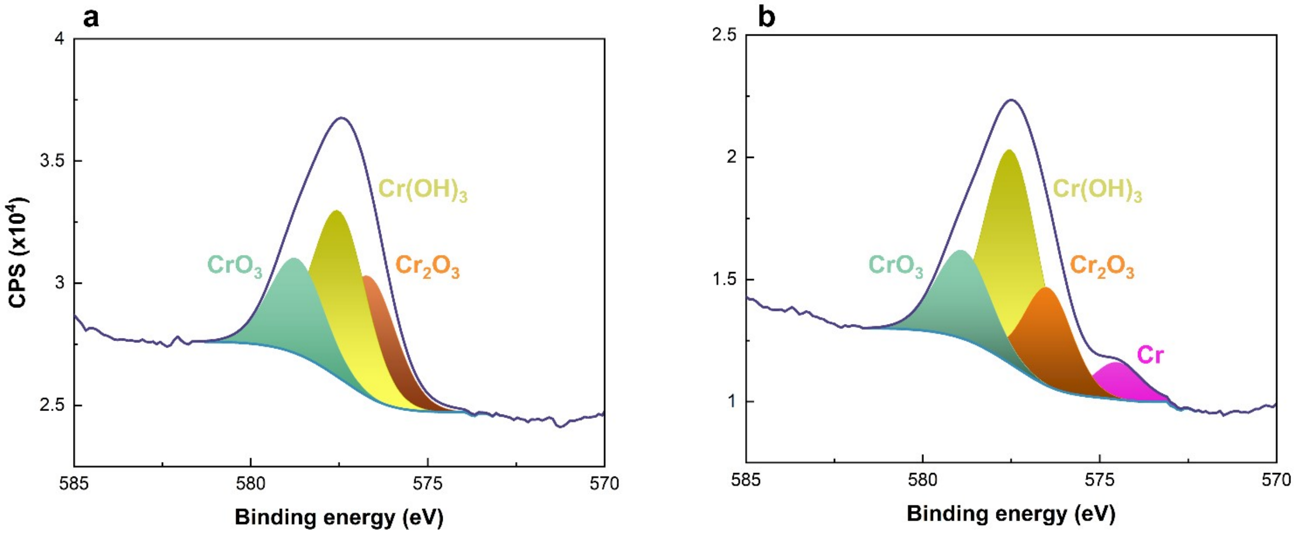

Fig. S3. High resolution deconvoluted XPS spectra of the Cr 2p peak on bare (a) T23 and (b)TFS.

Electrochemical impedance spectroscopy

Estimation of electrolyte uptake of coatings

The electrolyte uptake of the coatings throughout the exposure time was estimated using the Brasher-Kingsbury relationship (eq. S1) to analyze the barrier properties differences between the coatings.

$$\chi_v = \frac{100 * \log_{10} \frac{C(t)}{C(t=0)}}{\log \varepsilon_w} \qquad \text{eq. S1}$$

where χ_v is the water volume fraction, C(t) and C(t=0) are the coating capacitances at time t and time 0 respectively, and ε_w is the water permittivity (69.3 at 65°C). Coating capacitance C in parallel with coating resistance is computed from the CPE elements (Y0 & n) as follows: C=

$$\frac{(Y_0 * R)^{n^{-1}}}{R}$$

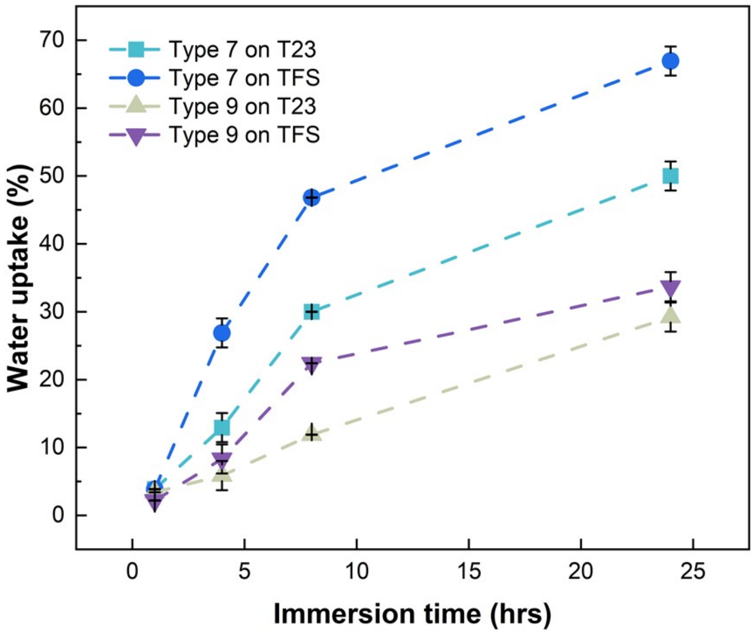

Fig. S4. Volumetric water uptake for types 7 and 9 coatings on T23 and TFS throughout the immersion time using the Brasher Kingsbury relationship.

EIS spectra of bare T23 and TFS

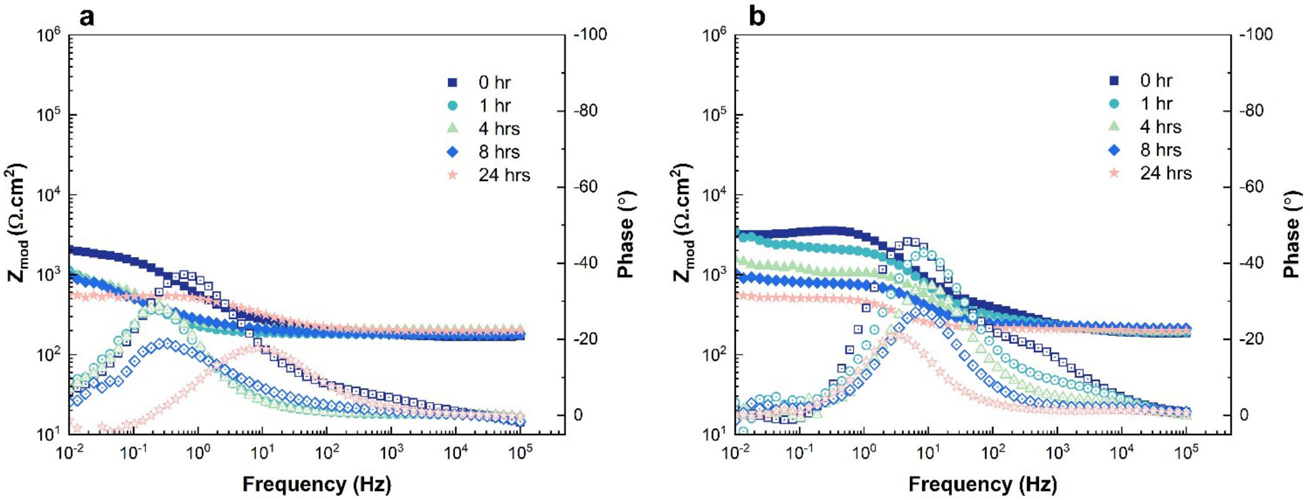

Fig. S5. EIS spectra at different times of degradation of bare (a) T23 and (b) TFS.

Table S1. EIS fitting results of type 7 coatings on T23 and TFS during exposure to 5% acetic acid

			T23 **TFS**			
Time (hr)	**R_{coat} ($\Omega.cm^2$)**	**CPE_{coat}, Y0 ($S.s^n.cm^{-2}$)**	**CPE_{coat}, n**	**CPE_{dl}, Y0 ($S.s^n.cm^{-2}$)**	**CPE_{dl}, n**	**R_{pol} ($\Omega.cm^2$)**
0	2.17E+08	1.102E-09	0.9759	-	-	-
	2.29E+08	8.41E-10	0.9849			
1	1.81E+07	8.72E-10	0.9821	-	-	-
	1.54E+07	1.04E-09	0.9687			
4	2.99E+05	9.82E-10	0.9762	2.26E-07	0.8205	4.85E+06
	9.14E+05	1.22E-09	0.9763	2.24E-07	0.7633	1.26E+06
8	2.70E+05	1.14E-09	0.9675	3.12E-07	0.7745	1.64E+06
	1.01E+05	1.68E-08	0.9128	7.80E-06	0.7824	5.95E+05
24	4.60E+03	1.44E-08	0.8217	1.85E-06	0.8442	1.04E+05
	1.38E+03	1.57E-05	0.3897	1.03E-04	0.7829	3.92E+03

Table S2. EIS fitting results of type 9 coatings on T23 and TFS during exposure to 5% acetic acid

			T23 **TFS**			
Time (hr)	**R_{coat} ($\Omega.cm^2$)**	**CPE_{coat}, Y0 ($S.s^n.cm^{-2}$)**	**CPE_{coat}, n**	**CPE_{dl}, Y0 ($S.s^n.cm^{-2}$)**	**CPE_{dl}, n**	**R_{pol} ($\Omega.cm^2$)**
0	2.33E+09	6.73E-10	0.9775	-	-	-
	5.51E+08	2.85E-10	0.9876			
1	5.21E+08	7.66E-10	0.9719	-	-	-
	2.11E+08	3.88E-10	0.9726			
4	4.20E+07	7.99E-10	0.9731	5.29E-09	0.5576	2.39E+08
	2.04E+07	3.635E-10	0.982	8.209E-10	0.8044	4.60E+07
8	3.67E+06	8.21E-10	0.9695	3.36E-08	0.5698	2.65E+07
	1.17E+06	3.81E-10	0.9782	1.13E-08	0.8267	7.30E+06
24	8.22E+04	4.15E-09	0.8838	1.66E-06	0.4734	3.55E+05
	9.99E+04	8.58E-10	0.9329	4.95E-07	0.7414	2.14E+05

Rubber elasticity theory for calculating crosslink density:

According to this theory, the storage modulus (E') in the rubbery region (Tg+40°C) will change with crosslink density (υ_e) as follows:

$$\upsilon_e = \frac{E'}{3RT} \qquad \text{eq. S2}$$

where R is the universal gas constant, T is the absolute temperature in K, and v_e is the crosslink density in mol.m^{-3}

Toughness modulus calculation

$$U_T = \int_0^{\varepsilon_f} \sigma d\varepsilon \qquad \text{eq. S3}$$

where σ is the tensile strength and ε is the tensile strain.