Polyelectrolyte-modified Layered double hydroxide nanocontainers as vehicles for combined inhibitors

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Electronic Supplementary Information

Experimental Section:

Synthesis of Layered double hydroxides. The synthesis of LDH-NO_3, LDH-MBT and LDH-Mod (LDH-MBT modified with polyelectrolytes and cerium (III) nitrate compounds) was reported in the main text. Herein, the surface modification with polyelectrolytes, in the absence of cerium (III) nitrate, is presented.

The modification of LDH-NO_3 and LDH-MBT with polyelectrolytes is done using the same conditions reported in the main text, except for the step of incorporation of cerium.

An aqueous LDH slurry was added to 0.5 wt. % of PSS solution in deionized water. Then, the slurry was dispersed with magnetic stirring (10 min) and ultrasound treatment (10 min), and left under magnetic stirring for 20 min. Finally, LDHs were recovered by centrifugation, followed by 3 consecutive washing/centrifugation stages.

In the second step LDH platelets were re-dispersed in a 0.1 M sodium nitrate solution and left for one day under stirring at room temperature. The LDHs were recovered by centrifugation, and washed/centrifuged 3 times with distilled water. A second layer of PSS was deposited after treatment with sodium solution, following the same procedure used in the first deposition. The final layer of PAH was applied using similar conditions of concentration and time applied for PSS. The modified LDH was kept as a water-based slurry in a sealed container.

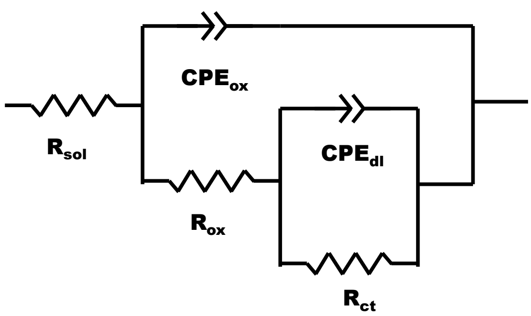
Characterization methods. The impedance plots were fitted using different equivalent circuits with the Gamry Echem Analyst software version 5.1. The equivalent circuits used were based on RC circuits (instead of pure capacitances constant phase elements were used), and the goodness of fittings evaluated by the values of χ^2.

Results and discussion:

The impedance data were fitted using the two equivalent circuits depicted in Figure S1. The first circuit was used for systems were the corrosion activity is still low and the relaxation time constant associated with the native aluminium oxide layer is visible. However, an additional time constant ascribed to the electrochemical corrosion processes can be already detected at low frequencies.

The second circuit was used for systems were corrosion processes are in more advanced stages. The response of the native oxide film is no longer detected, and only activity associated with corrosion processes (double layer response) and, in more severe cases, mass transport-controlled processes are already visible. Table S1 summarizes the main results obtained for the LDHs in solution, after 4 h of immersion in NaCl (Figure 7, main text).

Circuit 1



Circuit 2

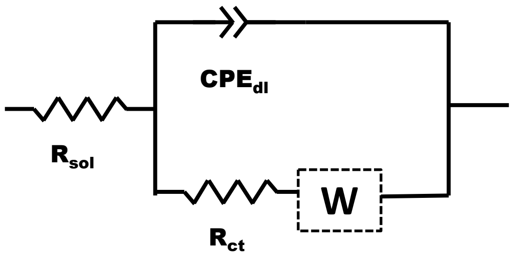


Figure S1: Equivalent circuits used to fit EIS data (Figure 7, main text), summarized in table S1.

Table S1: Results obtained from the fitting of EIS spectra depicted in Figure 7 of the main text.

System	Circuit n. (χ^2)	$Y(CPE_{ox})$ Ss^ncm^{-2}	R_{ox} Ωcm^2	$Y(CPE_{dl})$ Ss^ncm^{-2}	R_{ct} Ωcm^2
Reference	2 ($9.95x10^{-4}$)	-	-	$5.58x10^{-5}$ (n=0.879)	$3.44x10^{3}$
LDH-NO_3	2 ($1.21x10^{-3}$)	-	-	$3.58x10^{-5}$ (n=0.897)	$7.71x10^{3}$
LDH-NO_3-LbL	2 ($1.91x10^{-3}$)	-	-	$1.47x10^{-5}$ (n=0.882)	$3.81x10^{4}$
LDH-NO_3-Mod	2 ($8.48x10^{-4}$)	-	-	$8.79x10^{-6}$ (n=0.885)	$1.77x10^{4}$
LDH-MBT	2 ($7.76x10^{-4}$)	-	-	$1.11x10^{-5}$ (n=0.944)	$9.28x10^{3}$
LDH-MBT-LbL	1 ($8.77x10^{-4}$)	$5.47x10^{-6}$ (n=0.907)	$1.08x10^{5}$	$7.99x10^{-5}$ (n=0.972)	$9.69x10^{4}$
LDH-MBT-Mod	1 ($8.21x10^{-4}$)	$4.58x10^{-6}$ (n=0.915)	$2.46x10^{5}$	$1.06x10^{-4}$ (n=0.990)	$8.63x10^{4}$