

## Supporting Information

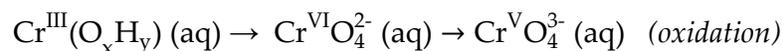
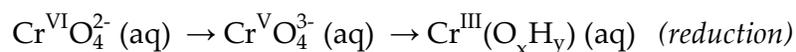
### Controlled synthesis of chromium oxide based protective layers on Pt: Influence of layer thickness on selectivity

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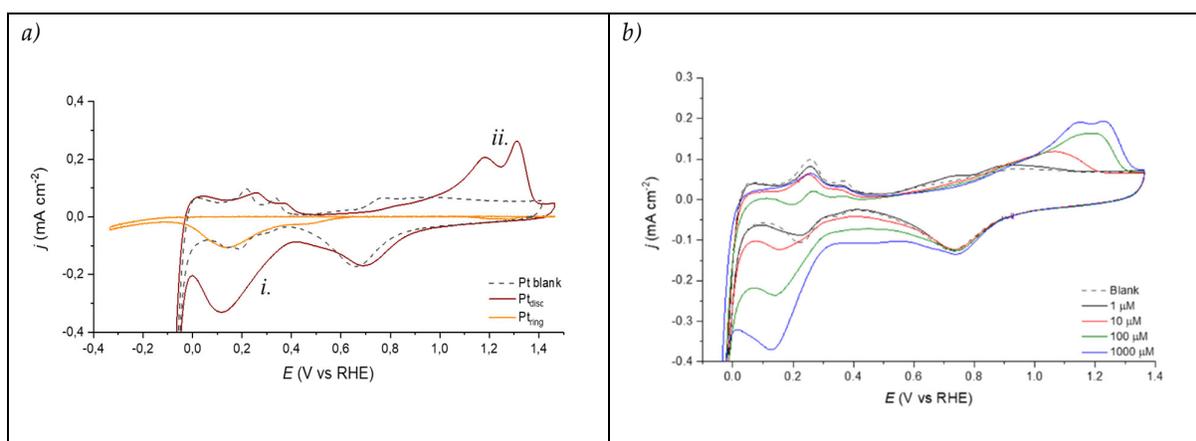
#### Chromate electrochemistry and eQCM measurements

Experiments were undertaken to explore the deposition of Cr-based oxide and/or oxyhydroxide coatings onto Pt rotating disc electrodes (RDEs). Figure S1a (dashed line) shows the typical CV obtained for a blank Pt disc in a N<sub>2</sub>-saturated 0.1M NaOH (aq) solution. These cycles were run at 50 mV s<sup>-1</sup>, 2000 rpm from open circuit (E<sub>oc</sub>) cathodically to -0.2 V and then up to 1.5 V vs RHE before returning to E<sub>oc</sub>. In basic solutions the dichromate converts to the single Cr<sup>VI</sup>O<sub>4</sub><sup>2-</sup> species, but here the concentrations are given in terms of the original Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> concentration added.

After addition of chromate anions (CrO<sub>4</sub><sup>2-</sup>) to the electrolyte several additional peaks appear on the Pt CV (Figure S1a, red line). Using similar scan parameters as the blank, the CrO<sub>4</sub><sup>2-</sup> reduction produces a single broad peak with maximum current density around 0.1V vs RHE (indicated by *i.* in the Figure). The HER starts before the reduction of the chromate ends which indicates that there is a region in which these occur simultaneously. As the scan moves anodically the chromate oxidation onset begins around 1V and continues to around 1.4 V vs RHE with two distinctive peaks (*ii.* in the Figure). The overall charge for these reduction and oxidation peaks was estimated to be 1.40 and 0.95 mC cm<sup>-2</sup> respectively. More reduction is occurring relative to oxidation of a surface coating suggesting the formation of an intermediate. This is supported by the data obtained on the ring (Figure S1a, orange line) on the RRDE where oxidation occurs in parallel to the reduction peak showing the presence of a soluble species, but of lower overall charge (0.45 mC cm<sup>-2</sup>). The expected reactions via the intermediate route are as follows:



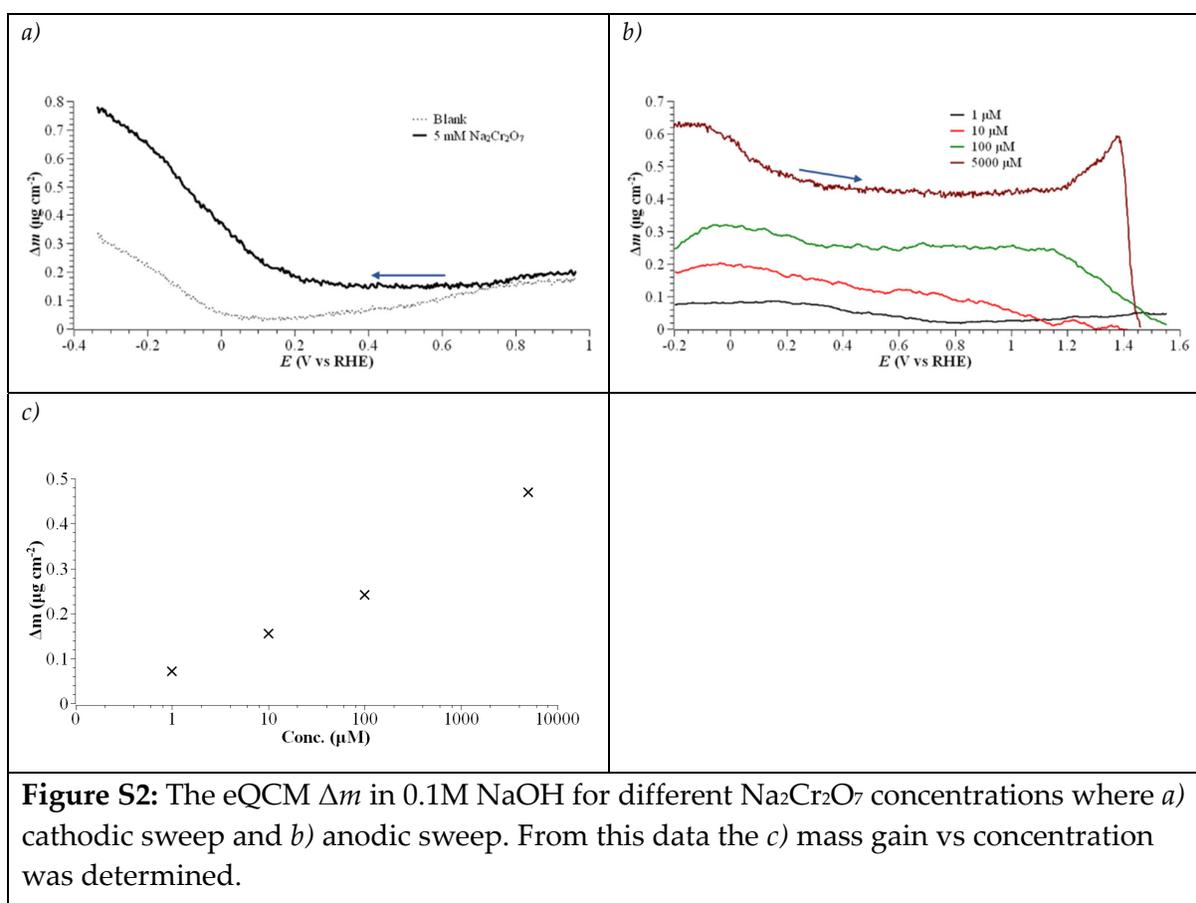
These findings are in line with previous studies (as referred to in the Introduction and throughout the main paper). Concentrations of  $\text{Na}_2\text{Cr}_2\text{O}_7$  ranging from 1  $\mu\text{M}$  up to 5 mM were investigated during the course of experimentation, for which a selection of the most used are shown in Figure S1b.



**Figure S1:** Cyclic voltammograms on Pt RRDE (both Pt working electrode and ring) in *a*) 0.1M NaOH for the disc only, 5mM  $\text{Na}_2\text{Cr}_2\text{O}_7$  / 0.1M NaOH for the disc and ring, where  $E_{\text{ring}} = +1.4$  vs RHE (ring  $j$  has been inverted and corrected for collection efficiency (26%) for clarity) and *b*) CVs of the different concentrations of the  $\text{Na}_2\text{Cr}_2\text{O}_7$  in 0.1M NaOH.

To further quantify the deposition of the chromate coatings on Pt eQCM measurements were used (Figure S2). Without the presence of  $\text{Na}_2\text{Cr}_2\text{O}_7$  only small changes of 0.2  $\mu\text{g cm}^{-2}$  are observed on the Pt QCM crystal and are likely related to bubble formation and Pt oxidation. After the addition of 5 mM chromate to the electrolyte there is a much greater change associated with the reduction of the chromate indicating the deposition of material on the surface with an overall mass increase of 0.48  $\mu\text{g cm}^{-2}$ . During oxidation a mass loss is observed of 0.51  $\mu\text{g cm}^{-2}$ , almost equal to the deposition process indicating

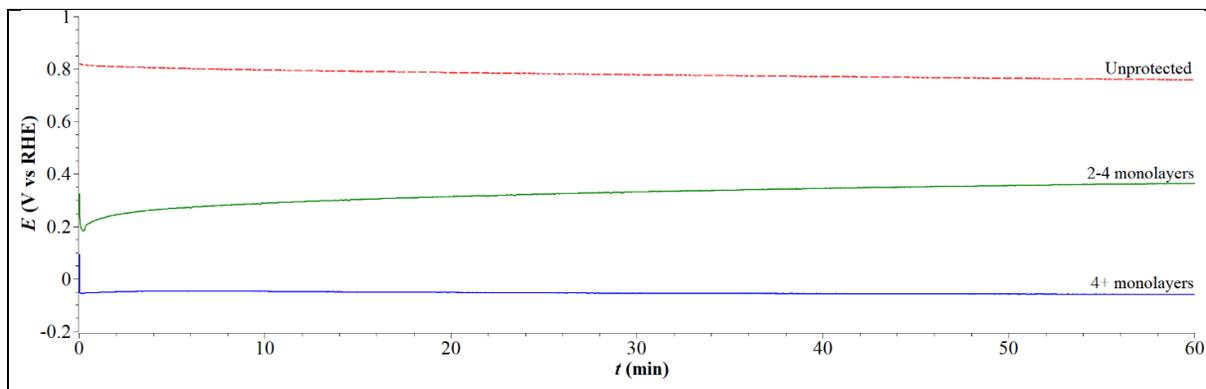
complete removal of the coating. Lowering the concentration results in a corresponding reduction in mass and Figure S2c shows the estimated thickness versus the concentration for all QCM data obtained and shows that there is an exponential increase in growth as the concentration increases.



### Stability testing

The stability of different thicknesses of the  $\text{Cr}_x\text{O}_y\text{H}_z$  coatings for the suppression of the ORR was measured using chronopotentiometry. The results for  $\text{H}_2$  production on unprotected,

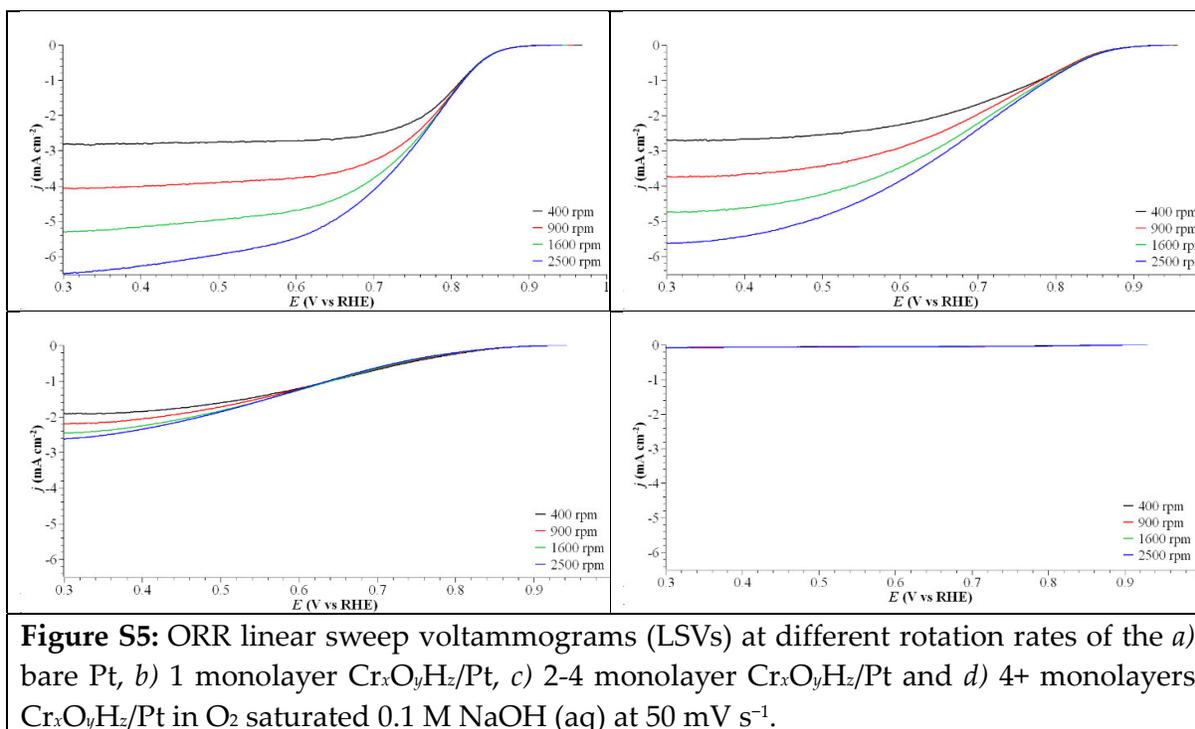
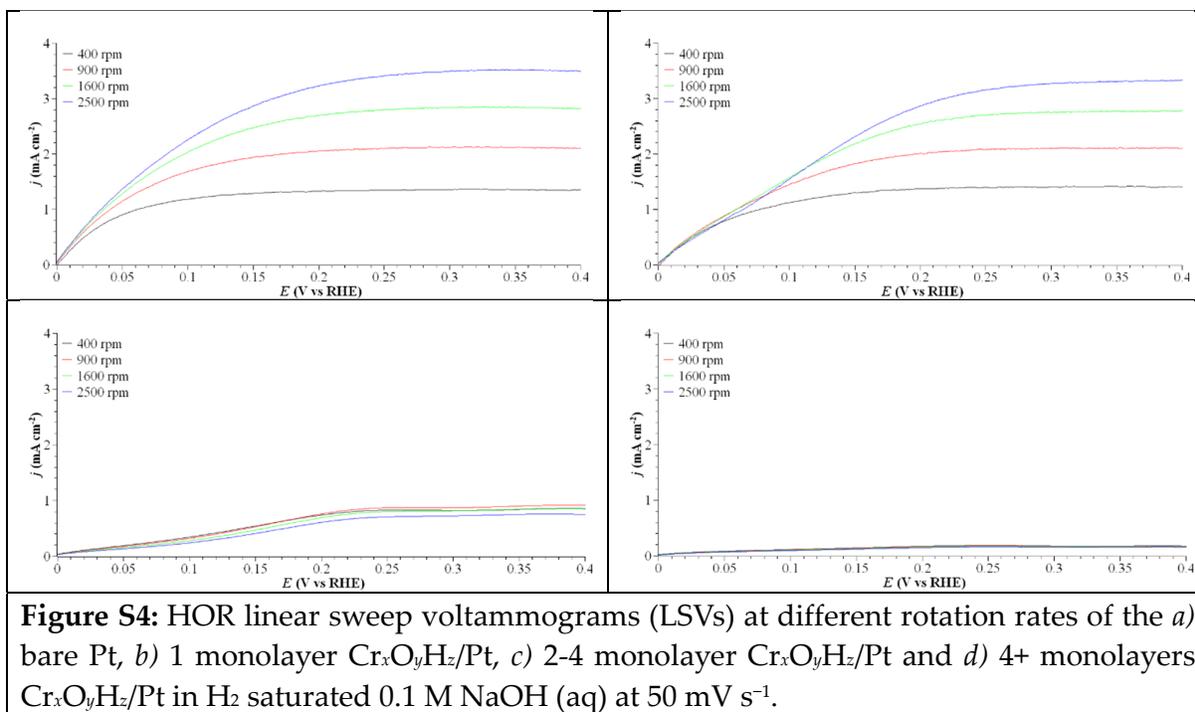
partially and fully protected coatings are given in Figure S3. These results suggest that the coating remains stable over time at H<sub>2</sub> evolution potentials (as indicated in the Figure), in particular for the full protection of 4+ monolayers. Partial protection takes a little bit of time to reach a stable level.

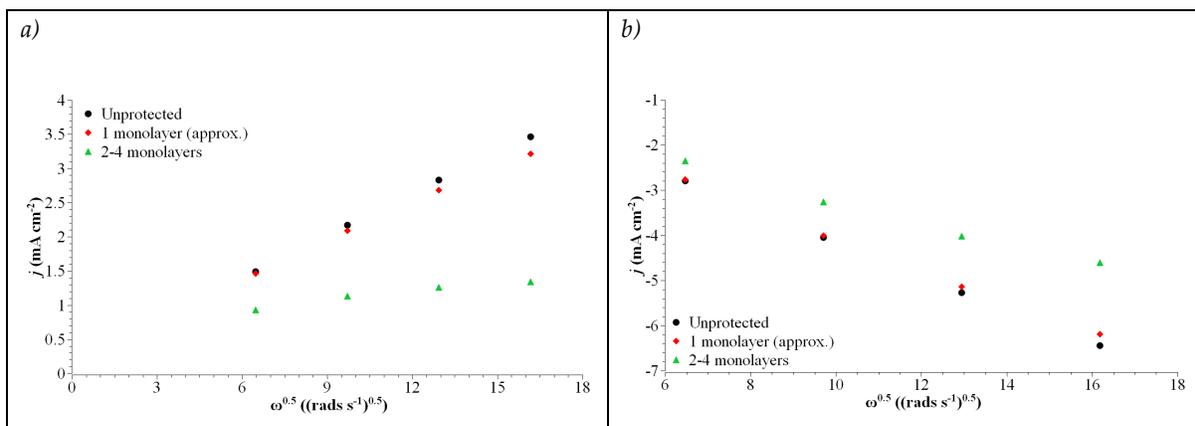


**Figure S3:** Chronopotentiometry (CP) at  $-0.2$  mA ( $-1.02$  mA cm<sup>-2</sup>), 900 rpm in O<sub>2</sub> saturated 0.1 M NaOH (aq) for 3 different levels of coating showing unprotected, partial (2-4 monolayers) and full protection (4+ monolayers).

### Levich analysis

A typical Levich analysis was undertaken for the HOR and ORR as described in the main paper. Using a Pt RDE at different rotation rates LSVs were measured for each of the Cr<sub>x</sub>O<sub>y</sub>H<sub>z</sub> coating levels of interest in H<sub>2</sub> (Figure S4) and O<sub>2</sub> (Figure S5) saturated 0.1M NaOH (aq) electrolyte. From these the limiting current was taken at 0.4 V vs RHE and 0.3 V vs RHE respectively and used to construct the Levich plots given in Figure S6.

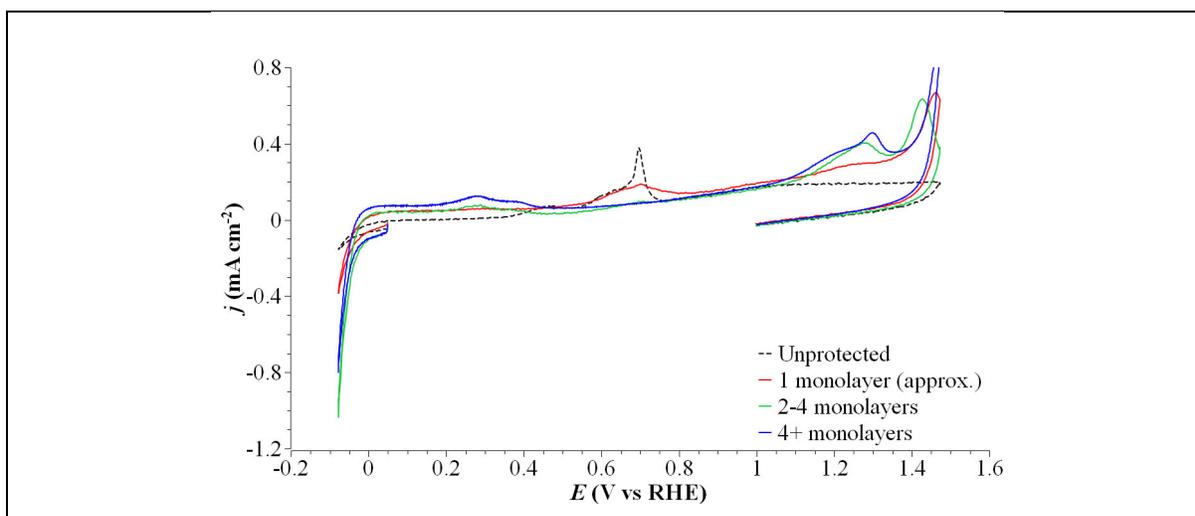




**Figure S6:** Levich plots of the *a*) HOR (H<sub>2</sub> saturated) and *b*) ORR (O<sub>2</sub> saturated) with different levels of Cr<sub>x</sub>O<sub>y</sub>H<sub>z</sub> coverage, both in 0.1 M NaOH (aq) at 50 mV s<sup>-1</sup>.

### CO stripping

CO stripping was undertaken in either N<sub>2</sub> saturated 0.1M NaOH (aq) electrolyte for the different levels of Cr<sub>x</sub>O<sub>y</sub>H<sub>z</sub> coating, including bare Pt for comparison. The voltammograms for these are given in Figures S7. The proportion of active sites was determined by integration of the CO stripping peak for each coating, obtaining charge per cm<sup>2</sup>, with unprotected Pt taken to represent 100% CO coverage.



**Figure S7:** CO stripping sweeps for the different coatings after poisoning for 15 min at 20% CO/N<sub>2</sub>,  $E = 0.05$  V vs RHE, followed by N<sub>2</sub> flush for another 15 min at same  $E$ , all at 900 rpm.