

Supporting Information

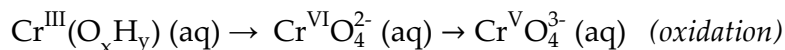
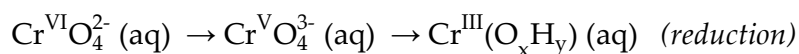
Controlled synthesis of chromium oxide based protective layers on Pt: Influence of layer thickness on selectivity

Myles Worsley, Vera Smulders, Bastian Mei

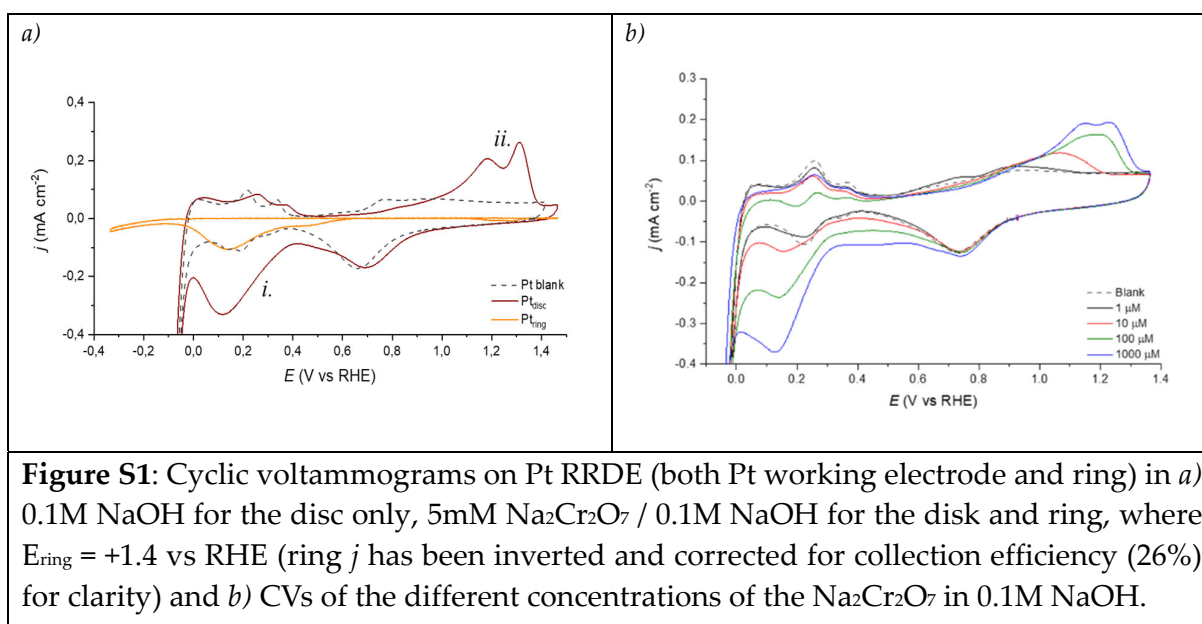
Chromate electrochemistry and eQCM measurements

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 N₂-saturated 0.1M NaOH (aq) solution. These cycles were run at 50 mV s⁻¹, 2000 rpm from open circuit (E_{oc}) cathodically to -0.2 V and then up to 1.5 V vs RHE before returning to E_{oc} . In basic solutions the dichromate converts to the single $Cr^{VI}O_4^{2-}$ species, but here the concentrations are given in terms of the original Na₂Cr₂O₇ concentration added.

After addition of chromate anions (CrO_4^{2-}) to the electrolyte several additional peaks appear on the Pt CV (Figure S1a, red line). Using similar scan parameters as the blank, the CrO_4^{2-} 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⁻² 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⁻²). The expected reactions via the intermediate route are as follows:

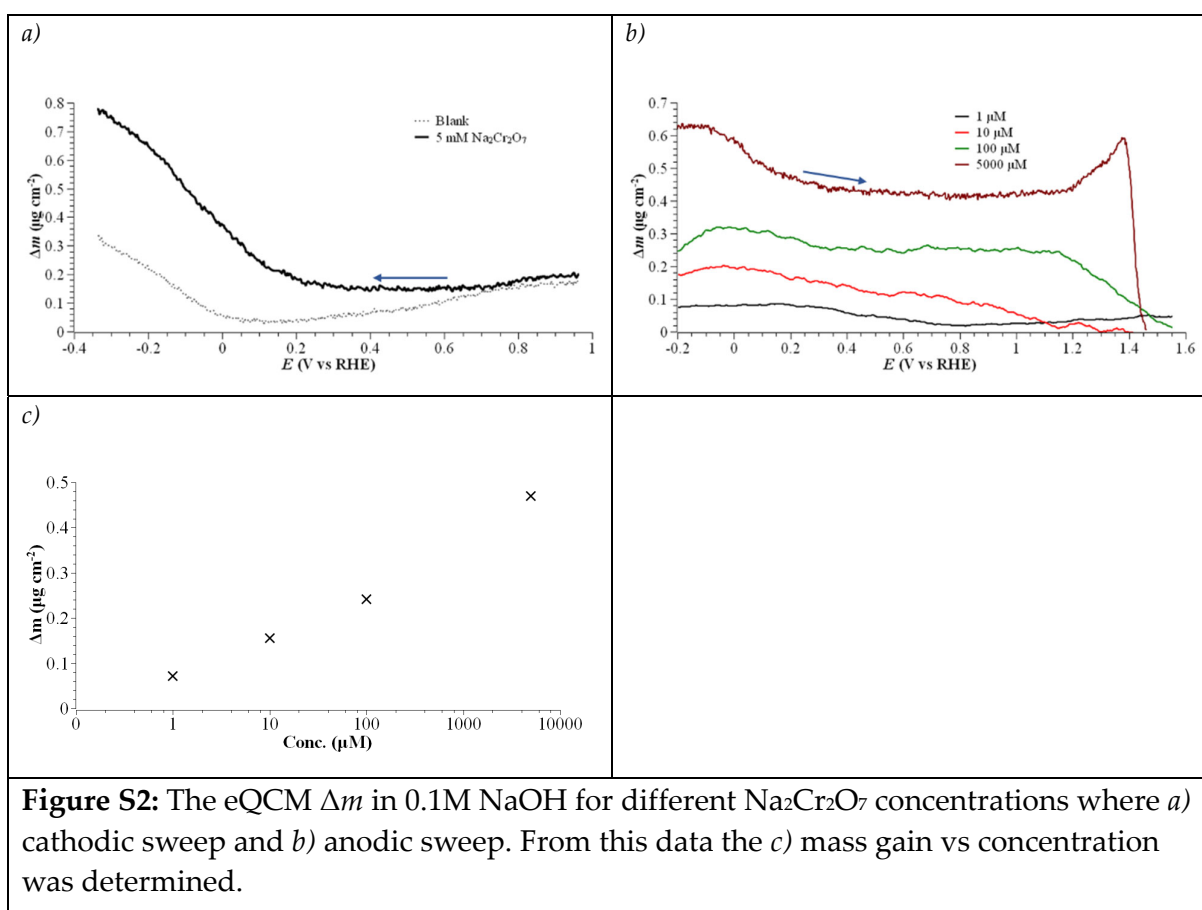


These findings are in line with previous studies (as referred to in the Introduction and throughout the main paper). Concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ ranging from 1 μM up to 5 mM were investigated during the course of experimentation, for which a selection of the most used are shown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



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 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 H₂ 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.

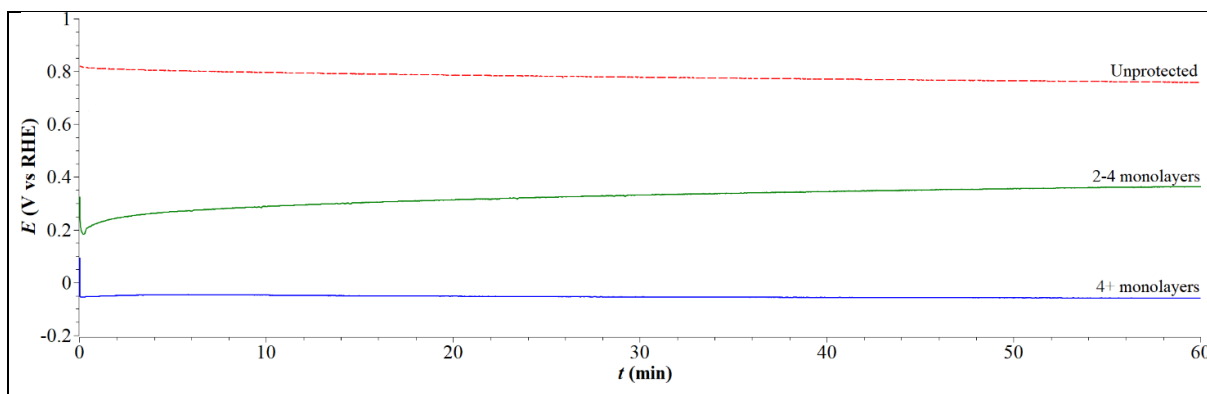


Figure S3: Chronopotentiometry (CP) at -0.2 mA (-1.02 mA cm⁻²), 900 rpm in O₂ saturated 0.1 M NaOH (aq) for 3 different levels of coating showing unprotected, partial (2-4 monolayers) and full protection (4+ monolayers).

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_xO_yH_z coating levels of interest in H₂ (Figure S4) and O₂ (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.

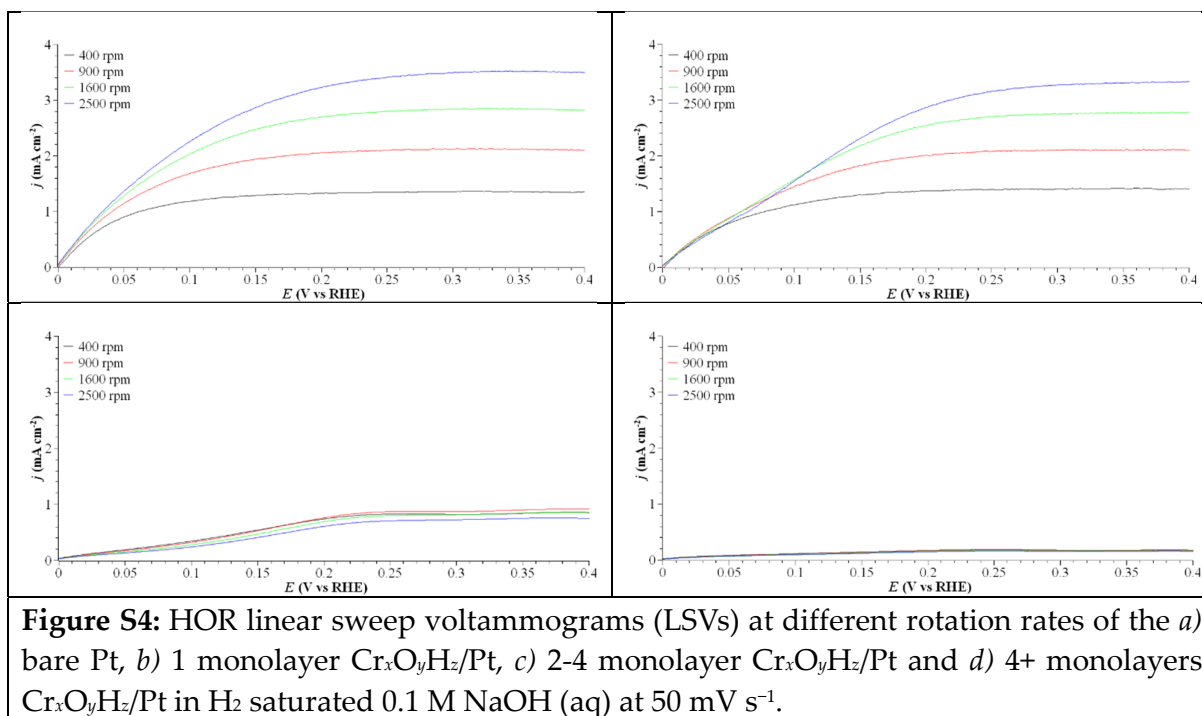


Figure S4: HOR linear sweep voltammograms (LSVs) at different rotation rates of the *a)* bare Pt, *b)* 1 monolayer $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$, *c)* 2-4 monolayer $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$ and *d)* 4+ monolayers $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$ in H_2 saturated 0.1 M NaOH (aq) at 50 mV s^{-1} .

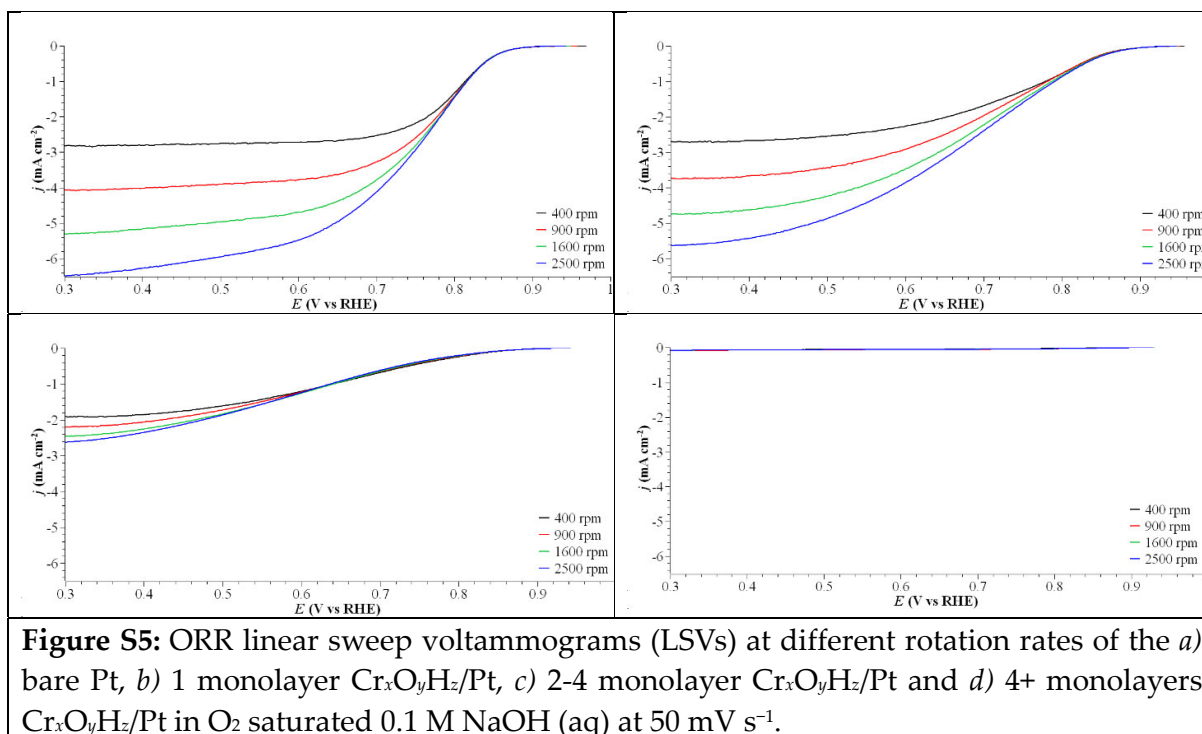
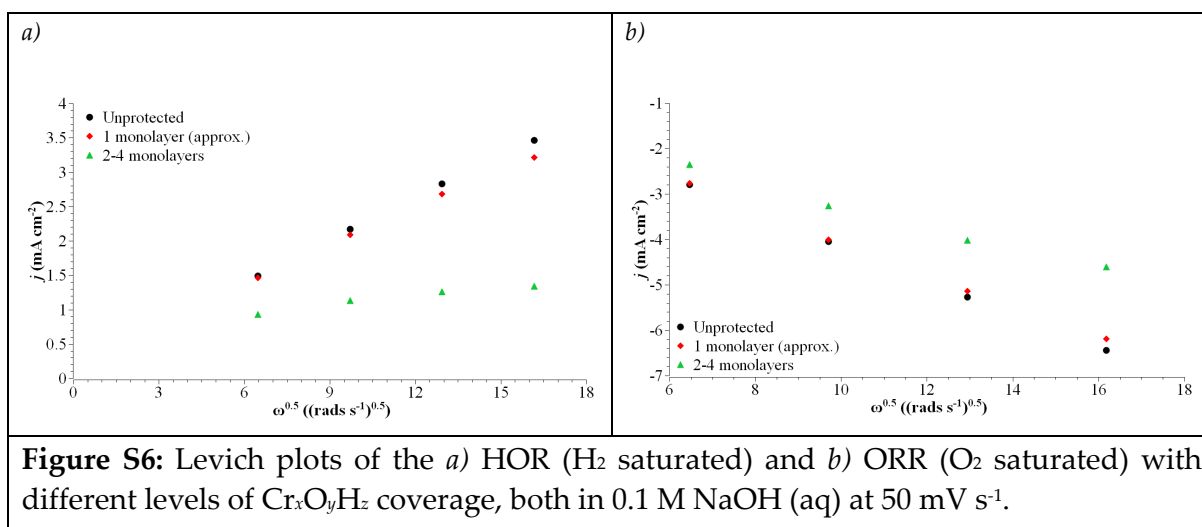


Figure S5: ORR linear sweep voltammograms (LSVs) at different rotation rates of the *a)* bare Pt, *b)* 1 monolayer $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$, *c)* 2-4 monolayer $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$ and *d)* 4+ monolayers $\text{Cr}_x\text{O}_y\text{H}_z/\text{Pt}$ in O_2 saturated 0.1 M NaOH (aq) at 50 mV s^{-1} .



CO stripping

CO stripping was undertaken in either N_2 saturated 0.1M NaOH (aq) electrolyte for the different levels of $\text{Cr}_x\text{O}_y\text{H}_z$ 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^2 , with unprotected Pt taken to represent 100% CO coverage.

