Supplementary information

We consider reactions 2 and 3 in an attempt to explain the role of a passive oxide in the time dependent current decay. A simplified version of the r_2 and r_3 with the appropriate material balances may be expressed as the following.

$$\frac{\partial \theta_{vac}^{\#}}{\partial t} = -\frac{k_3}{[\#]}\left\{\left(\theta_{vac}^{\#}\right)^{x} \exp\left[\frac{\alpha_{a,3}F}{RT}\left(V-U_3\right)\right] - \theta_{CxO}^{\#} \exp\left[-\frac{\alpha_{c,3}F}{RT}\left(V-U_3\right)\right]\right\} \tag{S1}$$

$$\frac{\partial N_c}{\partial t} = -k_2 \theta_{vac}^{\#} \exp\left[\frac{\alpha_{a,2}F}{RT}\left(V-U_2\right)\right] SN_cM \tag{S2}$$

If we take the limit of high overpotentials and create a lumped rate parameter A', we may ignore the cathodic term in Equation S1, resulting in Equations S3 – S6.

$$\frac{\partial \theta_{vac}^{\#}}{\partial t} = A'\left(\theta_{vac}^{\#}\right)^{x} \tag{S3}$$

$$\theta_{vac}^{\#} = \left[(1-x)(A't)\right]^{\frac{1}{1-x}} \tag{S4}$$

$$\frac{\partial N_c}{\partial t} = -k_2 A'' t^{-n} \exp\left[\frac{\alpha_{a,2}F}{RT}\left(V-U_2\right)\right] SN_cM \tag{S5}$$

$$-n = \frac{1}{1-x} \tag{S6}$$

The empirical power law decay equation is now approximated by a simplified reaction sequence with the power *n* being related to the stoichiometry of the passive oxide.

The rate expression chosen to represent the passive oxide growth, r_3, is based upon the following postulated elementary steps. First, the carbon lattice is oxidized.

$$x[\#] \leftrightarrow [\#]_x^+ + e^- \tag{S7}$$

This step is slow in the anodic direction and taken to be the RDS for oxidation. The consumption of multiple carbon atoms has been previously suggested by Binder *et al.* and Choo *et al.* for example [16, 44]. Binder *et al.* also assumed oxidation and hydrolysis as separate steps. This results in a kinetic expression independent of water concentration. Next, the oxidized carbon site reacts with water. Both the anodic and cathodic directions of this reaction step occur quickly compared to the others.

$$[\#]_x^+ + H_2O \leftrightarrow [\#]_x OH + H^+ \tag{S8}$$

The final step in the oxidation process is deprotonation of the oxide. This step is taken to be slow in the cathodic direction and the RDS for the reduction process. Thus a simplified rate expression, r_3, for reactions S6-S8 includes the anodic portion of S6 and cathodic portion of S8 assuming the same equilibrium potential, U_3, and rate constant, k_3.

$$[\#]_x OH \leftrightarrow [\#]_x O + H^+ + e^- \tag{S8}$$

Supplementary Material (ESI) for PCCP