

Study of Elemental Processes on a Co_3O_4 Supercapacitor

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Among the electro-active materials, Co_3O_4 is considered as a good candidate of electrochemical pseudo-capacitors which is widely used in supercapacitors due to its excellent electrochemical capacitive behaviour, affordability and environment safety [1]. The redox reactions occurring at the Co_3O_4 oxide surface are believed to be at an outer, near-surface region of the oxide/electrolyte interface which is because of the redox transformations between species of $\text{Co}_3\text{O}_4/\text{CoOOH}$, $\text{Co}(\text{OH})_2/\text{CoOOH}$ and $\text{CoO}_2/\text{CoOOH}$, which can be enhanced at different redox potentials $\sim 0.01\text{-}0.420$ V versus SCE [2].

In this work we employed *in situ* Neutron Reflectometry (NR) and Electrochemical Impedance Spectroscopy (EIS) techniques to study structural changes of Co_3O_4 thin film electrodes and the behaviour of the electrode/electrolyte interface at different KOH concentrations, electrode polarization and time. The thin film Co_3O_4 electrode which was prepared by magnetron sputter coating on either a bare Si slab ($\text{Si}/\text{Co}_3\text{O}_4$) or on carbon coated Si wafer ($\text{C}/\text{Co}_3\text{O}_4$) provided a suitable reflective surface for NR measurements.

The NR data showed that a passive layer was formed at the Co_3O_4 /electrolyte interface at open circuit potential before any potential application. In Figure 2, the Nyquist diagrams of EIS data for $\text{C}/\text{Co}_3\text{O}_4$ electrode at different added volumes of 2M KOH are shown. Additional EIS and NR studies on different electrodes of $\text{Si}/\text{Co}_3\text{O}_4$ and $\text{C}/\text{Co}_3\text{O}_4$ at different concentrations of OH^- showed that the oxide film was hydrated faster when carbon under layer is present in comparison with the electrode without carbon layer. However, NR data collected at different steps of the contrast matching experiment did not show the existence of any passive layer at the oxide/electrolyte interface of the $\text{C}/\text{Co}_3\text{O}_4$ electrode. The comparison between the SLD profiles of the oxide layer of the $\text{Si}/\text{Co}_3\text{O}_4$ electrode (Figure 3) as a function of time showed that the existence of the passive layer at the oxide/electrolyte interface is more stable than the

passive layer built-up at the $\text{C}/\text{Co}_3\text{O}_4$ /electrolyte interface.

The study as a function of time, concentration and potential dependant behaviour of different electrode systems showed that the existence of carbon in the $\text{C}/\text{Co}_3\text{O}_4$ electrode increased the porosity of the film which then also increased the hydrophilicity and wettability of the Co_3O_4 layer that lead to faster hydration of the oxide layer.

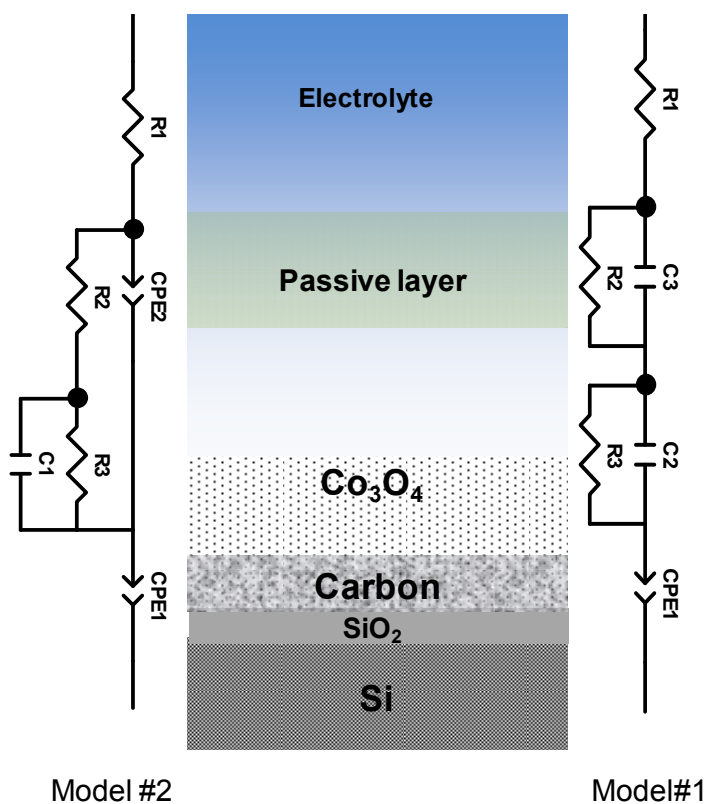


Fig. 1 Two equivalent circuit models used to fit the EIS data. Different existing layers were observed including the Silicone wafer, native SiO_2 layer, Carbon layer, Co_3O_4 film, passive layer and electrolyte.

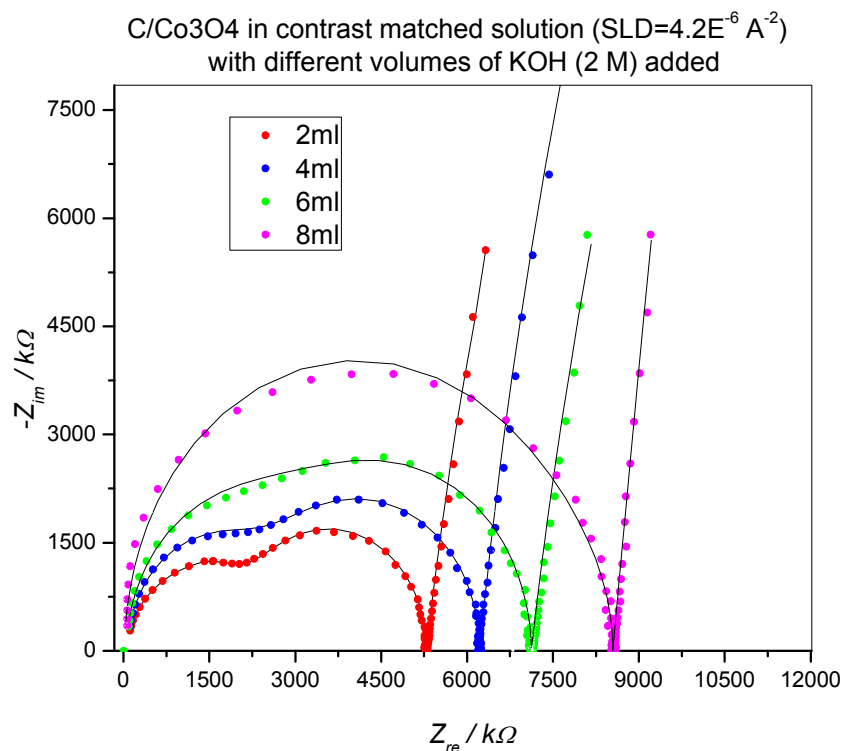


Fig. 2 Least-squares fitted raw EIS data using the equivalent circuit #1 shown in Figure 5. Panel A and B show the overlay of Nyquist plot of EIS data from C/Co₃O₄ system at different OH⁻ concentrations.

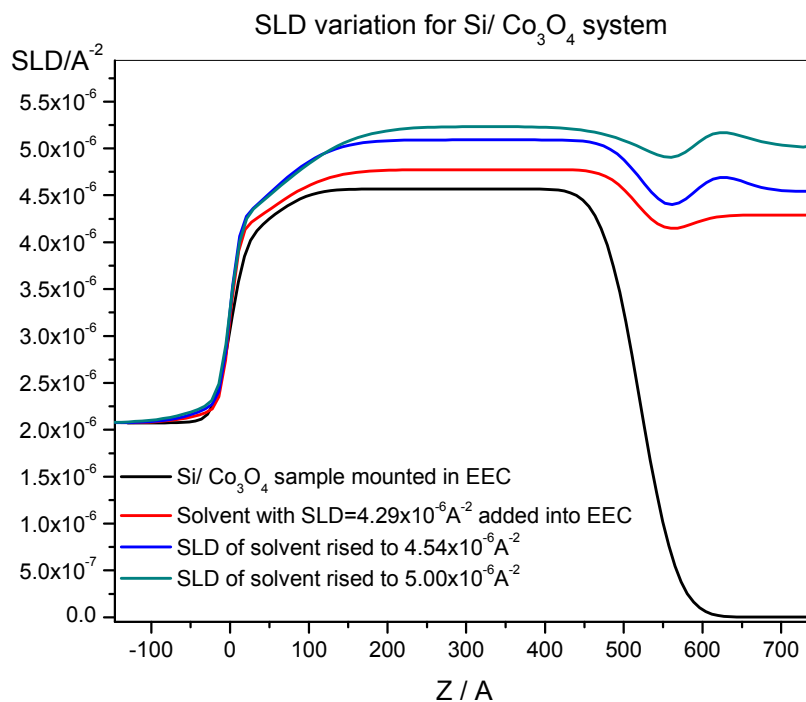


Fig. 3 The comparison between the SLD profiles of the Si/Co₃O₄ sample mounted in the empty electrochemical cell, after filling the cell with electrolyte and during the contrast matching experiment.

References

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