

Moving Reaction Fronts in Supercapacitors with Pseudocapacitance

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A way to enhance the capacity of electrochemical double layer capacitors is the utilization of the so-called pseudocapacitance, which involves surface redox reactions as an additional charge storage mechanism. Although there are numerous works on such faradaic supercapacitors in literature, modeling papers are rare.

In the current work, a model of a supercapacitor with pseudocapacitance focusing on effects along the thickness of the electrode was developed. Especially fast charging processes, i.e. high power densities, were analyzed because this is the target region for application. Simulations of galvanostatic charging showed that with fast charging, i.e. high current densities, the charging takes place non-uniformly across the thickness of the electrode. At very high current densities this leads to the occurrence of moving reaction fronts (see Fig. 1). Because of the limited ion transport, the reaction takes place in a thin reaction zone. At first a thin layer at the electrode-separator interface is oxidized until the material is depleted. Thus, the reaction zone is forced to move further into the inside of the electrode. With this, a moving reaction zone is formed that oxidizes the electrode from the electrolyte side to the current collector side of the electrode.

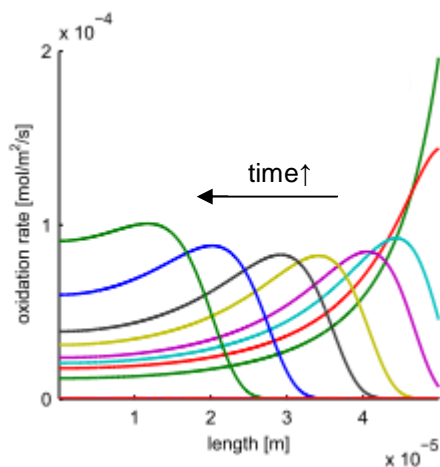


Figure 1: Reaction rate distribution during galvanostatic charging with $10\text{A}/\text{cm}^2$

The influence of this moving reaction front on the performance of the supercapacitor was investigated by analyzing the energy that is needed for the charging process. For reference, a 0D model which neglects the ion transport in the electrode was used. It was found that upon fully oxidizing the electrode the effect of the ion transport and the resulting non-uniform oxidation and moving reaction fronts was an ohmic loss. However, if the electrode was only partially oxidized, i.e. the supercapacitor partially charged with a high current density, the losses due to the ion transport were less than

an ohmic loss. The reason for this is that only a thin part of the electrode was used for faradaic charge storage thus decreasing the length of ion transport and with this the transport losses.

A practical problem in supercapacitor development is the scale up of the electrodes. While most fundamental research is done on thin electrodes, a key target is to achieve an increasing mass loading without sacrificing capacity per mass [1]. In order to draw conclusions about the scale-up of the electrodes, the influence of the electrode thickness was investigated. Increase of the electrode thickness leads to losses especially at the end of oxidation phase. However, the losses of a thick electrode under high current densities can be kept small if the electrode is only partially charged. Thus, the obtained simulation results can be used as an "operation map" for a given current density.

In the next step, the influence of the moving reaction fronts on the classical analysis techniques cyclic voltammetry and electrochemical impedance spectroscopy were investigated. As seen in Fig. 1, in cyclic voltammograms the moving reaction fronts occur at high scan rates and lead to an asymmetric broadening of the oxidation peak which could be misinterpreted as a merged second oxidation peak.

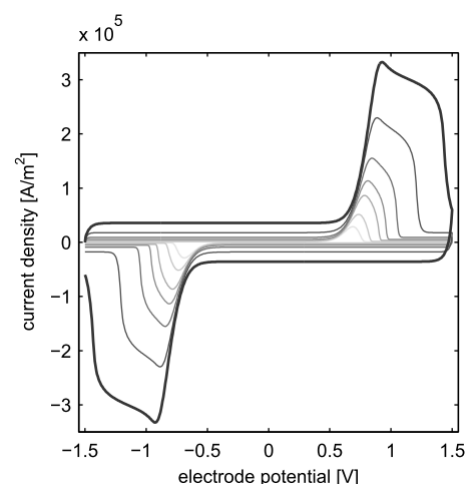


Figure 2: Cyclic Voltammograms of a supercapacitor electrode with pseudocapacitance at different sweep rates ($50\text{mV}/\text{s}$ - $4\text{V}/\text{s}$).

In electrochemical impedance spectra the transport processes in the porous electrode lead to a typical Warburg-like 45 degree line in the Nyquist plot.

Finally, measures for the occurrence of moving reaction fronts were developed. The analysis of the reaction front velocity shows a minimum which defines a critical current density, above which distinct reaction fronts occur. Additionally, the derivation of the reaction penetration depth is a useful tool to estimate the occurrence of moving reaction fronts.

[1] H. Wang et al. J Phys Chem C 2011, 115, 17599 – 17605