ABSTRACT

The effects of self-discharge on the performance of symmetric electric double layer capacitors (EDLCs) and active electrolyte enhanced supercapacitors (AEESCs) were examined by incorporating self-discharge into electrochemical capacitor (EC) models during charging and discharging. The effects of self-discharge on the performance of asymmetric ECs were also studied by including applicable self-discharge mechanisms into mass transfer and charge conservation equations during charging and discharging. Sources of self-discharge in capacitors are several impurities, side-reactions, redox reactions and electric double layer's (EDLs) instability. Incorporation of self-discharge into symmetric and asymmetric EC models, created a platform to reduce the number of experiments to determine the minimum allowable amount of impurities and redox species in components of the device for maximum performance. It was observed that key self-discharge parameters to be tuned in order to suppress the EC self-discharge rate are concentration of shuttle impurities, concentration of redox species, and thickness of the separator. Tuning key self-discharge parameters of a symmetric device with both side-reactions/redox reactions and EDLs instability self-discharges, improved first and second charge-discharge cycle efficiency η_{E1} and η_{E2}. These charge-discharge cycle efficiencies (η_{E1} and η_{E2}) were enhanced from 38.13% and 38.14% to 80.54% and 81.56% respectively, compared with 84.24% and 84.25%, respectively in similar capacitor without self-discharge. The tuning process also improved energy efficiencies η_{E1} and η_{E2} of the asymmetric device with both side-reactions/redox reactions and EDL's instability self-discharges from 67.21% and 75.00% to 87.21% and 88.70% respectively, compared with 90.72% and 90.82%, respectively in a similar capacitor without self-discharge. Energy loss by self-discharge in the symmetric capacitor with

tuned key self-discharge parameters was reduced from 28.38Wh in untuned to 5.60Wh, while that of the asymmetric capacitor with tuned key self-discharge parameters was reduced from 59.53Wh in untuned to 7.43Wh. Fast charging and discharging of the EC greatly reduced the self-discharge rate, compared with slow charging and discharging. In symmetric and asymmetric capacitors, both EDL's instability and side-reactions and/or reactions self-discharges occurs in significant measure but side-reactions or reactions contributed to the majority of the self-discharges. It was shown that models that incorporated self-discharge give more practical evaluation of voltage decay and energy dissipation during self-discharge.

The influence of different charging current densities, charging times and several structural designs on symmetric EC performance such as capacitance, energy density and power density was investigated through modelling and simulation. The effects of different charging current densities, charging times and several structural designs on asymmetric EC performance via modelling and simulation can be investigated, and the results would be similar. The difference between symmetric and asymmetric ECs is that symmetric use the same type of electrode while asymmetric use different types of electrodes. Clear understanding of the effects of different structural design variables and operating conditions on capacitors' performance will guide in optimal design and fabrication of high performance ECs. The operating conditions and design configurations examined are charging current density, charging times, electrode and electrolyte effective conductivity, electrode thickness and electrode porosity. It was revealed that ECs with low electrode and electrolyte effective conductivities can only be effectively charged at a low current density for extended periods of time. ECs with high concentrations of impurity ions and redox species exhibit high self-discharge rates, which result in voltage decay after charging. Reduction of charging time by charging the EC fast, greatly reduced the rate of self-discharge compared with the slow charging process. The simulation showed that the typical electrode length scale over which the liquid potential drop occurs and electrode utilization can be used as a design parameter to optimize electrode thickness (effective thickness) of the EC which should function within a specific current density range. This is also a guideline that can be used to determine the optimum electrodes thickness (100% electrodes utilization), optimum charging current density and optimum charging time for cells of a given voltage, electrode's thickness, and electrodes and electrolyte’s effective conductivities. The energy density of the capacitor with specific electrodes and electrolyte effective conductivities was increased 2.125, 4.750 and 10.75 folds by reducing the electrode's thickness 1.33, 2.00, and 4.00 folds, respectively. The power density of the capacitor, with specific electrodes thickness, and given electrode and electrolyte effective conductivities charged at a specific current density, increased by a factor of 10, 100 and 1000, when the charging rate was increased 10, 100 and 1000, times respectively. The power density of the capacitor with specific electrodes thickness, and a given electrodes and electrolyte effective conductivities, also increased approximately eleven-fold when the electrode's thickness was reduced four-fold under a given charging conditions. The ragone plots generated for different electrode sizes via modeling and simulation, can be used to select optimum electrode dimensions to attain certain energy and power densities specifications. Theoretical expressions for performance parameters of different ECs were optimized by writing MATLAB scripts to solve them and also via the MATLAB R2014a optimization tool box. Performances of different kinds of ECs at given circumstances were compared through theoretical equations and simulation of various models, subject to the conditions of device components using optimal K_{BMopt} and K_{Eopt}, as well as the symmetric EDLC experimental data.

The storable energy E_{ch}, maximum energy density ED_{max} and power density PD_{max} of symmetric and asymmetric EC using suitable electrode mass, operating potential range ratios and proper organic electrolyte (optimum K_{BMopt} and K_{Eopt}) were 562.78Wh, 382.42Wh/kg & 76.29W/kg and 1304.30Wh, 837.00Wh/kg & 167W/kg, respectively. Estimations of performance parameters were feasible and achievable once details of electrodes mass ratio, operating potential range ratio and specific capacitance of electrolyte are known. Performances of asymmetric EC with suitable electrode mass and operating potential range ratios using aqueous electrolytes, and that with suitable electrode mass, operating potential range ratios and organic electrolyte with appropriate operating potential range and specific capacitance were 2.20 and 5.56 folds, respectively, greater than those of symmetric EDLC and asymmetric EC using the same aqueous electrolyte. This enhancement came together with reduction in cell mass and volume. Storable and deliverable energies of the asymmetric EC with suitable electrode mass and operating potential range ratios using proper organic electrolyte were also a factor of 12.9 greater than those of symmetric EDLCs using aqueous electrolyte reduction in cell mass and volume by a factor. Storable energy, energy density and power density of asymmetric EDLCs with suitable electrode mass and operating potential range ratios, using proper organic electrolyte, were a factor of 5.56 higher than those of similar symmetric EDLCs using aqueous electrolyte reduction in cell mass and volume by a factor 1.77. These results can obviously reduce the number of experiments needed to determine the optimum manufacturing state of ECs. They also demonstrated that introduction of an asymmetric electrode and organic electrolyte was very successful in improving performance of the EC with reduction in cell mass and volume. Introduction of an asymmetric EDLC with the same type of electrode, and suitable electrodes mass ratio, working potential range ratios and proper organic electrolyte, equally enhanced the performance of a conventional symmetric EDLC using aqueous electrolyte with reduction in cell mass and volume. These results can be a guideline for design, fabrication and operation of electrochemical capacitors with outstanding performance in terms of high storable energy, energy and power densities.