ASYMMETRIC TYPE ELECTROCHEMICAL CAPACITORS

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The paper reveals the main principles of Asymmetric Type Electrochemical Capacitors development. Besides, the concept of asymmetry is represented , electrode processes are analyzed, and the main dependencies and criteria of electrode selection for cell assembling are pointed out.

Lately, the interest to the so called Hybrid Combined, Asymmetric Electrochemical Capacitors considerably increased. Asymmetric concept uses two different electrochemical processes, proceeding on different electrodes of one cell. For instance, positive electrode – faradaic process, negative electrode – double electric layer. The use of one of the capacitor electrodes as non-polarizable, i.e. changing little of potential during current flow, let us "exclude" one of the capacitors, connected in serial inside the cell. In this case, the capacitance of the cells is doubled at least. There is a possibility to reach the higher voltage in the cell owing to the use of non-polarizable electrode with higher equilibrium potential, for instance: in C/NiOOH system, KOH electrolyte – 1.4V, comparing to carbon/carbon system, KOH electrolyte – 1…1.2V. All of this in total raise the energy density of asymmetric capacitor in 3 – 4 times, comparing to the symmetric one, with one similar electrode.

The key moment of Asymmetric Electrochemical Capacitor (EC) development is the selection of the operating potential windows for each electrode. Basically, it is defined by ratio of absolute electrode capacitances in the cell. As a result, the following requirement should be fulfilled: in critical points of electrodes potential changing (the end of charge and the end of discharge) it shouldn't reach the potential of electrolyte decomposition or transition to the irreversible electrochemical reaction.

Asymmetric EC, using different by nature electrochemical processes, means by itself asymmetric operation of electrodes. This, in it's turn, leads to some limitations, defined by the difference of processes proceeding speed on each of the electrodes. Let's write down the scheme of polarisation restrictions for electrochemical capacitor of the system:

PbO_2 H_2SO_4 C(carbon)

$E_{oa} + E_o$ | E_{oc} | E_{or} where:

E_{oa} – activation overpotential (charge transfer);

E_{oc} – concentration overpotential (transfer of H_2SO_4 into the active mass);

E_{or} – resistance overpotential (ohmic: ions, electrons).

Obviously, in case of current flowing through this cell, electrochemical process will proceed more effectively in carbon electrode. During the dynamic process: fast charge – discharge, the effectiveness of capacity use in PbO_2 electrode will be lower than in carbon electrode. That's why initially chosen ratio of PbO_2 and C capacities will differ in reality. At the moment of $CPbO_2$ and C_{carbon} leveling the asymmetric principle gets broken and EC capacity decreases sharply.

While developing Asymmetric EC, main criteria of pseudocapacitive electrode selection are:

- Higher specific capacity and absolute capacity comparing to polarization electrode;
- Ability to operate in long cycling mode (>100K cycles), with good reversibility of electrode reaction;
- High speed of electrode reaction (Low Ohmic and Polarization loses at high density of discharge current).

And the most significant aspect – the provision of the required ratio of capacities of nonpolarizable and polarizable electrodes in any operating modes, taking in consideration uneven electrodes degradation during service life.

First approach to classify Asymmetric EC:

1. Capacitors with aqueous electrolytes:
   - 1.1. Oxide electrodes (RuOx/C, NiOx/C,…);
   - 1.2. Metallic type electrodes (C/Cd, C/Methydride);
   - 1.3. Electrodes with specific sorption of ions, incl. Recombinant type.
2. Capacitors with nonaquous electrolytes:
   - 2.1 Oxide electrodes (RuOx/C,…)
   - 2.2 Intercalation Systems ($C/Li_4Ti_5O_{12}$, Graphite/C, …).
     - 2.2.1. Conductive Polymers (PFPT/C, …).

Appropriate spheres of application of Asymmetrical EC are defined by their RC-time constant and by the guaranteed service life.

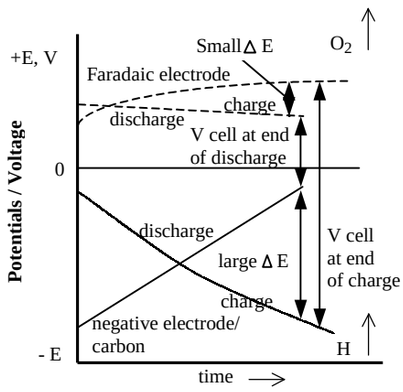

Fig. 1. Voltage window of cell and potential windows of electrodes in Asymmetric Capacitor

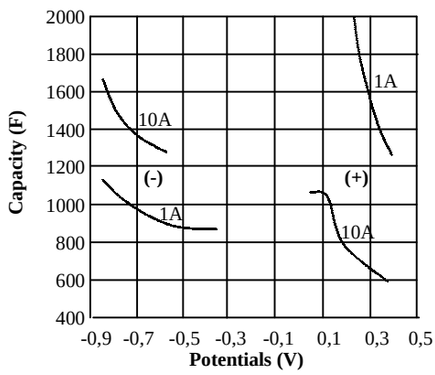

Fig. 2 Asymmetric operation of electrodes at the different current densities (C/NiOx)