Commentary

Toward a realization of nanogate capacitors—for want of practical advices

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We propose a new energy autarkeia system extracting full power of a quickly charging capacitor If a nanogate capacitor is realized, then the system will work ideally. With the present EDLC, the needed system is too costly and bulky and is suitable only for a mega-size electricity storage system. There is no danger of thermal runaway and a great number of capacitors can be connected without any fear of fire. If a nanogate capacitor is realized in the lines of the late M. Okamura, EDLC will prevail and work as safe storage of electric energy as electric enrgy.

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1. ECaSS(R)

The present MS is a preliminary report calling for practical suggestions and advices for realizing nanogate capacitors. The present capacitors (electric double layer (super)capacitor—EDLC) are already very effective but they are bulky and expensive. But except for these two weak points, they are ideal storage of electric energy, with no danger of thermal runaway. One representative example is “Frequency and voltage support for dynamic grid stability” by Siemens (§3). This is a large-scale energy storage system using a bulk number of supercapacitors and the afore-mentioned weak points are not relevant. But for small-size use, these weak points are blocking the way and give way to li-ion batteries which have a danger of thermal runaway. Nanogate capacitors were about to be multi-produced [Okamura (1999)], [Okamura and Konoshita (2010)], [Okamura et al. (2004)], and [Takeuchi et al. (1998)]. But to our great regret, unfortunate demise of M. Okamura, the total plan was abandoned and there seems to be no research going on toward realization of nanogate capacitors. There are some researches going on using porous graphen etc., different from Okamura's material. Once nanogate capacitors are realized and multi-produced, the world will get a safe and the most effective storage of electric energy and then the further progress is assured in the book [H.-Y. Li et al.(2023)]. If someone or some lab takes this as a research project and make any progress, it'll have a tremendous positive effect on the global situation and will make a great saving of energy. Our lab is being engaged in the project and we would be glad to share any progress. The main part is §2 and substantiating nanogate capacitors by trial and error a lá Okamura.

Definition 1. *A* **capacitor** *(or also called a* **condenser***) is a device for storing charge consisting of two conducting plates (or surfaces) of any shape, with one carrying positive charge $+Q$, say and the other negative charge $-Q$. If the voltage difference between two plate is V and the positive charge is Q, then $C = \frac{Q}{V}$ is called the* **capacitance***, whence it follows that*

$$Q = CV. \qquad (1.1)$$

A **parallel plate capacitor** *is a special type of capacitor with two conducting plates of the same shape and of area A distance d being apart. The capacitance C is given bt $C = \frac{A}{4\pi d}$, whence the shorter the distance, the bigger the capacitance, whence the bigger amount of charge.*

An **electric double layer** *generally means an aggregate of electric dipoles on two thin surfaces, close to each other, on one of which positive charges (holes) are uniformly distributed and on the other of which negative charges (electrons), found by Helmholz in* 1879*.*

Here we restrict to the electric double layer (EDL) occurring naturally on the **interface** of each of a pair of conductive poles (electrodes) and electrolyte. Statistically, on the immediate interface there is a thin layer (consisting of inner and outer layers, see below)

and outside there is a diffused layer, constituting a double layer. For water electrolyte, the BDM model describes a detailed structure of EDL, [Okamura (1999), pp. 28-29]. The Inner Helmholtz Layer (IHL) is the next to the interface of width d_1 which consists of molecules of electrolyte and specifically adsorbed ions (and other molecules). The Outer Helmholtz Layer (OHL) is the next outer layer of IHL of width d_2 which is the radius of those solvated (electrolyte) ions that are attached to the surface of IHL. From the data on voltage V_d of the diffused layer and V_h of the layer to d_2, the capacitance C_d of the diffused layer and the capacitance C_h of the Helmholtz layer can be found. It turns out that the higher the density of electroryte (whence the smaller d_2), the smaller the voltage V_d and that C_d is negligible compared with C_h.

We define **breakdown voltage** V to be the maximum voltage difference that can be applied across the insulator before it starts conducting. If higher voltage than V is exerted, then **electrolysis** occurs but **within breakdown voltage, poles and electroryte are insulated by the double layer and it works as a**

capacitor. For an EDL capacitor to have higher energy density, we find from (1.5) below that the one with smaller d_2 and bigger breakdown voltage is what is wanted.

M. Okamura [Okamura (1999)] was led to a great discovery of an electric double layer super-capacitor ECaSS(R) being guided by the **similarity** between a *parallel-plate capacitor* and an *electric double layer*.

ECaSS(R)—energy capacitor system, neé ECS—is a *(super-)capacitor controlled by an electronic circuit* was invented by M. Okamura and it stores electricity as electric energy, whence almost no loss of energy under transformation. And the cycle life can be as long as its calendar year. The problem is that it is high-cost. But one could argue that a towncar type compact EV having an ECaSS(R) as the source of electricity is to have a very long life. It can have a *large output density* and can absorb most of electric energy generated by regenerative braking, thus prolonging the driving range. The only defect is the smaller energy density and the original driving range is similar to that of lead acid EV. A compact EV with ECaSS(R) can compete other vehicles and supersede them in many respects. Driving range is not so long as LIB EVs but as it so happened in 1996-1999 with GM EV1, drivers will find that normally they drive some max 50 km per day. And when they come home, the super-capacitor can be charged in a few minutes. It will turn out that they just drive their EVs rather than other cars.

Below we shall dwell on some details of ECaSS(R). To emphasize the energy-aspect, we write electric energy for power. The electric energy spent by the resistance for time period t is

$$W_R = W_R(t) = \int_0^t i^2 R\,\mathrm{d}t \qquad (1.2)$$

The limit as $t \to \infty$ of $W_R(t)$ is the total energy spent in the resistance, which is the total electric energy W stored in the capacitor

$$W = \lim_{t\to\infty} W_R(t) = \int_0^\infty i^2 R\,\mathrm{d}t. \qquad (1.3)$$

In the case where the capacitor is **charged by a constant voltage** V, the current i at time t is given by

$$i = i(t) = \frac{V}{R} e^{-\frac{t}{CR}}. \qquad (1.4)$$

Then (1.3) amounts to

$$W = \int_0^\infty i^2 R\,\mathrm{d}t = \int_0^\infty R\frac{V^2}{R^2} e^{-\frac{2t}{CR}}\,\mathrm{d}t = \frac{CR}{2}\frac{V^2}{R} = \frac{1}{2}CV^2. \qquad (1.5)$$

By (1.1), (1.5) reads

$$W = \frac{1}{2}\frac{Q^2}{C}, \qquad (1.6)$$

which is the energy stored in the capacitor when charged by constant **current source** (which is used in ECaSS(R)). The charge Q charged/discharged by constant current i for time period t is

$$Q = i \cdot t. \qquad (1.7)$$

and (1.2) reads

$$W_R = i^2 R \cdot t = R\frac{Q^2}{t}, \qquad (1.8)$$

on substituting from (1.7). Hence the ratio of the loss is $\frac{W_R}{W} = \frac{2CR}{t}$, whence the loss is smaller if charging time is longer. However, the ratio of loss of charge and discharge by voltage source is $\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$ by (1.5).

As is seen in (1.5) and (1.8), only capacitors do not work because of high internal resistance and one needs a magic to get rid of $i^2 R$. Okamura's idea is to **combine the capacitors in series connection with an ingenious electronic circuit**, [Okamura (1999)]. As mentioned above, all capacitors have the property that their efficiency is $\leq 50\%$ if charged/discharged by voltage source by (1.5). To use current source, the current pump (switching converter) is to be installed in the circuit (step-down chopper) which charges the capacitor by current. A hint is indicated in [Okamura (1999), p. 129, footnote] as to how one can get a current source: here again one has to have a masterly knowledge about (circuit) elements C and L that C stores energy as voltage and L stores energy as current. For discharging, we note that (1.5) leads to $V = \sqrt{\frac{2}{C}}\sqrt{W}$, i.e. the voltage varies too much and to avoid this, another current pump (output converter) is to be installed which allows to get constant output voltage with efficiency S.

In order to connect capacitors of the same capacitance in series effectively, there is a problem of different allotted voltage because of different amount of leak current of each capacitor. In ECaSS(R), each capacitor is squeezed by a parallel monitor having the effect of initialization.

Thus, Okamura's ECaSS(R) is an ingenious combination of EDL capacitors in series connection charged by current source which can be utilized up to $\frac{15}{16} \approx 94\%$ efficiency until energy is spent to $\frac{1}{4}$ of full charged voltage (by (1.5)).

For a real ECaSS(R) model, the energy is a modified form of (1.5):

$$W = \frac{1}{2}PSCV^2, \qquad (1.9)$$

where P resp. S is the efficiency of power resp. integration efficiency of the current pump. For the data $P = \frac{15}{16}$, $S = 83\%$, we have 28.2 Wh, [Okamura (1999), p. 173].

Once the principle is established by Okamura, there can be a lot of improvements possible since ECaSS(R) has flexibility of replacing the electrodes and electrolyte. There are many experimental results on improved ECaSS(R) which hopefully will be realized as commercial products.

2. Nanogate capacitor

In a nanogate capacitor, electrolyte is non-aqueous, e.g. $\mathrm{Et_4NBF_4}$ (tetraethilammonium tetra-fuluoroborate) and electrodes are activated non-porous graphen. Energy density is 15Wh/kg, out put density 13.5Wh/kg. Then with 10 capacitor in serial connection will surpass the ordinary energy density of secondary batteries.

[Okamura (1999), p. 34, 68,79] claims that electrolyte is to be 0.8 mol/ℓ of $\mathrm{Et_4NBF_4}$ dissolved into PC (propylene carbonate) and dewatered up to 100 ppm. This electrolyte is available from Mitsubishi Chemical Corp., Mitsui Chemical, Toyama Pharmacological Co. as elctorolyte for EDLC.

For electrodes, the carbons are used which are calcinated from petroleum cokes, meso-phase carbons (pitches), at around 700°. They consist of well-grown graphite-like layers with an average inter-layer distance $d_{002} = 0.35 \sim 0.365$ nm。 After they are additionally treated by heating with KOH (potassium hydroxide) at 700°, they provide the expansion of inter-layer distance up to $d_{002} = 0.36 \sim 0.385$nm and they have a much smaller BET (Brunauer-Emmett-Teller) surface area $70 - 900 m^2/g$.

The carbons are mixed up with carbon black (acetylene black—conductive material) (Denki Kagaku) and PTFE (Dupont-Mitsui Fluoro Chemicals) binder under 18° at the ratio 8:1:1, where PTFE=Polytetrafluoroethylene. The mixture is kneaded by a motor-driven mortar and pestled at temperature higher than 58° to make slightly adhesive powder. It is then rolled with the aid of an aluminium foil wrapping and then without foil, it is made into a sheet with thickness of about 0.4mm at temperature over 50°. Then it is punched to make a coin shape of diameter 20mm.

Several of the above coin sheets are set in the vessel with several sheets of separators (PTFE), where the separator is inserted between two carbon sheets on which there are pre-set aluminium electrodes (collecting electrode). The vessel is specifically designed to soak the coin sheets and the separators in electrolyte. These are dried up in a vacuum vessel at 208° for 2 hours. Then the vessel is cooled down to room temperature and it is soaked in the electrolyte solution by opening the drain line connecting to a bottle containing electrolyte. The carbon sheets absorb electrolyte as the separator does. Then all these are inserted in a laminated polymer-envelope, sealed in vacuum, producing an Nanogate capacitor cell.

The envelope has a small extra area which can accommodate the gass generated by over-voltage charging. The above processes are carried out in a glove box which is kept dry. But the elctrodes expand in the direction of their depth. Activated non-porous carbon electrodes are used [Okamura et al. (2004)].

For possible EV use we need smaller-size capacitors and we use the full specks of the system—inertia force and regenerative braking. For M_1 in Item 4 we may use a variable speed PM motor which can charge the supercapacitor by regenerative braking. But since we can make a full force of the supercapacitor, regenerative braking may be disposed of in the future (in which case we use M_1 just as a motor). Then the system will be very simple consisting of two PM motors and a supercapacitor which is to have energy density as large as a lead-acid battery.

3. Possible use of the present ECaSS

- Siemans' SVC PLUS (STATCOM) Frequency Stabilizer.

  The equilibrium point for the European network, which operates on alternating current, is at a frequency of 50 Hertz. In the USA, the reference frequency is 60 Hertz. This frequency must be kept stable, with the tolerance threshold within $\pm 0.5\%$.

  In case of imbalance by some disturbance, the frequency can only be stabilized by an **inertial response** from generator-turbine sets. The mechanical kinetic energy determines the frequency drop after disturbance until the **operating reserve** is activated in several seconds by the primary frequency reserve (PFR). Grids are undergoing the drastic change of power generation by renewable energy, and there are less and less synchronous power generations, i.e., rotating machines. This results in shrinking of instantaneous reserves, which increases the risk of exceeding critical frequency levels. This may lead to load rejection or a blackout. Some source of fast frequency response (FFR) is urgently needed to cover the gap between inertial response and operating reserves. Siemens has been developing SVC PLUS (STATCOM) Frequency Stabilizer which makes use of a bulk number of supercapacitors and gives a cost-effective, compact solution that can emulate system inertia by boosting high active power into the grid when needed. It also offers voltage support by means of reactive power compensation.

- Torishima 100kW wind power generator TWE100.

  output power/frequency: 400V/50/60Hz.

  short period leveling control (10s)/ control of output voltage within $\pm$2kW/s variation for 10s. According to [Okamura and Konoshita (2010), pp. 233-235], the output enrgy of EDLC is 100kW$\times$

10s=1000kWs. Hence the required capacitance C of EDLC is $C = \left(120^2 - 80^2\right)/2 = 1000 \times 1000J$, whence $C = 25F$.

medium period leveling control (10m)/ control of variation of output voltage within 10% of the fixed output voltage. According to [Okamura and Konoshita (2010), pp. 233-235], the output energy of EDLC is 100kW$\times$10s=3000kWs $C\left(440^2 - 360^2\right)/2 = 1000 \times 1000J$, whence $C = 31.25F$.

- Rapid charger (using EDLC) of an EV from commercial power supplies of 200V.

  EDLC specs.

  Max. charging power: 150kW.

  Direct current circuit voltage: between 600V~400V. max. vol. 600V, min. vol. 280V.

  For 20s, rapid charge by EDLC of its max. power 150kW. Then the voltage of EDLC goes down from 600V to 400V. Then in the succeeding 100s, EDLC is charged by power supplies with Vol. 35kW, say. As we see below, the output energy of EDLC (charged energy) is 833Wh. Repeating this 120s rapid charging n times, the whole power is $833n/2$ Wh. Suppose the EV can be charged up to 40kWh. Then 96min. is needed. If the driving range is 322km, then for going to and back from work may be some 40km and 1/8th power is enough. Then charging time may be 12min, similar to the supplying fuel to traditional inner combustion cars. The case of Ioxus Japan: the module iMOD96V83A : 96V83F in which 36 cells are connected in series. Dim. H 22.4cm, W 24.7cm, L 88.5cm, wt 35kg. $-40^\circ \sim 65^\circ$

  To achieve 600V, we need 7 modules (600/96=6.25). In case of 6 modules, capacitance of the modules connected in parallel 11.8F is (83/7=11.8). 13.8 F(83/6=13.8).

  The needed capacitance of the system is 30F as we show below. Therefore we need 2 parallel connected modules (30/11.8=2.54). (30/13.8=2.17).

  Altogether we should have $6 \sim 7$modules times $2 = 12 \sim 14$ modules. One module costs, 350,000yen+shipping cost. Suppose it is 20,000 RMB max. Then total amount needed is $12 \sim 14 \cdot 20,000 = 240,000 \sim 280,000$ RMB.

  Dim. H 1.56m, W 1.73cm, L 6.2m, wt 245kg.

  But it will last for over 10 years and no maintenance or BMS needed. No special addition needed, only connect to commercial power supply of 200V.

  1. Calculation of the output energy of EDLC (charged energy) $150\mathrm{kW} \cdot$ 20s=3000kWs=833Wh

  2. The needed capacitance C of the system is calculated by the formula $(600^2 - 400^2)C = 3000\mathrm{kWh} = 3000 \cdot 1000J$, whence $C =$ 30F.

- SUDA energy autárkeia system (SEAS) is stated as a quadri-layer visions of 4 different cases [H.-Y. Li et al.(2023), §25.2].

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1. In the fundamental **factory use version**, the SEAS consists of any kind of machine M_1 that is driven by electric current (motors of various kinds--several hundreds) and a fly wheel M_2 that can be charged by current and (some packs of) ECaSS, parallel connection of 10 packs of 10 cells in series connection, say. There is no regenerative braking circuit.

   To start the system, S_3 is disconnected first and M_2 is given energy through switches S_1, S_2, then immediately disconnected from the circuit and it keeps energy as inertia force. Then S_3 is on and M_1 is supplied electricity from the supercapacitor and the system starts working. During operation, if the monitor D detects insufficient energy in the supercapacitor, it sends a signal to the switch-control system C to disconnect M_1 by switch S_3 and make M_2 charge the supercapacitor through switch S_4 in an instant. Then the system restarts and repeats the process: charge M_2 first and then start M_1.
2. The simplest use of the system is to use it as solar energy saving system (energy from photo-voltaic generation). Here no other components. 1997-2000 4.3kWh. 84% efficiency. [Okamura (1999)].
3. The second simplest is to use the system as the power system of the bullet train or tramcar etc. This case makes full use of the regenerating braking energy. If the power of the system is large enough to absorb all energy from regenerating braking, it may even possible to reach Beijing from Xi'an without charging. This will make the electricity cables unnecessary.

   Both will be of great use.

   2006 Tokai Passengers Travel Co.

   Absorption of energy arising from regenerative breaking of a 1500 V direct current train

   EDLC: 570 Wh, 594 cells in series connection.

   2009 (reported) Mannheim City Traffic Office, Germany

   Electric train, saving energy

   EDLC: 850 Wh, 4 parallel connection of 160 cells in series connection.

   Cf. [Okamura (1999)]

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