Studies on Au colloid-embedded active-carbon based supercapacitors

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Abstract

Supercapacitors (S-C) are short-term energy storage elements that find many applications, e.g., electronic charging devices and suppressors of power fluctuations in grids that are interfaced with sustainable sources. For a double-layer S-C, one takes advantage of the very narrow interface at an electrolyte and the large-surface of the porous conductors. Capacitance of an ordinary capacitor is increased when dispersing metallic colloids in its dielectric. It is not clear, though, if the same strategy works for S-C since its double layer region is so narrow. Here we explore the addition of functionalized Au nano-particles (AuNPs) to active-carbon electrodes in S-C to find a large specific capacitance increase.
I. Introduction

Originally devised for microwave lenses, Artificial Dielectrics (AD) are man-made materials that contain metal features much smaller than a characteristic propagating wavelength (e.g., mm-size ball bearings at a wavelength of 3 cm) [1-3]. These features alter the effective permittivity and permeability of the dielectric through creation of locally induced dipoles. A microwave lens is but one example. This concept was extended later to include nano-size semiconductor embedded dielectrics [4,5]. While there is a large body of work on AD at the high-frequency range, little if at all, has been investigated at the low frequency end.

Supercapacitors (S-C) take advantage of the large capacitance at the interface between a porous electrode and an electrolyte [6-11]. Here, we concentrate on carbon-based S-C that exhibit electrical double-layer. S-C are used in a wide-range of applications, such as consumer electronic products, memory back-up devices, hybrid electric vehicles, power supply system [12-13]. They were also proposed as buffers to highly fluctuating power grids that are equipped with sustainable sources [14]. Our intent is to gain basic knowledge on the capacitance changes when incorporating very low dispersion of gold colloids into active carbon (A-C) based, S-C electrodes.

AD may be understood in terms of local-fields theory [2]. In a quasi-DC approach one analyzes the effect of a single colloid per unit cell, made of two parallel conductors. Originally, the electrode’s charge is \( Q \) under a bias of \( V_{in} \). The metal colloids, acting as dipoles induce additional charge, \( q \), in the capacitor’s electrodes. For a given bias, the increased charge is translated into an increased capacitance. The unit cell is defined by the colloid spacing, \( a \). The cell's capacitance is \( C_0 \) without the colloid and \( C' \) with it. Assume the colloid as a capacitor of equal dimensions \( d^3 \), the cell dimension as \( a^2b \) with electrode spacing of \( b \), and external potential \( V_{in} \), expressed by the external field as, \( E_0 \) [2]:

\[
C' = C_0 (1 + q/Q) = C_0 \left[ 1 + C_{coll} \cdot V_{col}/C_0 \cdot V_{in} \right] = C_0 [1 + (d^2/d) \cdot (E_0 \cdot d)/(a^2/b) \times (E_0 \cdot b)] = C_0 (1 + N \cdot d^3).
\]

The last step is achieved when the lateral area of a unit cell is inversely proportional to the number of colloids per area, \( N \) and there is one colloid per cell. When adding more and more colloids, the local field at a particular colloid position is a linear combination of the external field and an interaction field. The local interaction field on a particular colloid is exerted by all other colloids excluding the colloid itself. The effect of all other colloids is characterized by an interaction parameter, \( C \). At very low frequencies, the interaction field is mostly of electric nature. The polarization is summarized in a self-consistent form, the Clausius-Mossotti relation when the distance between colloids is much smaller than the wavelength of interest; this is easily achievable at low frequencies:

\[
p = N \alpha_e E_0 / (1 - \alpha_e C).
\]

Here: \( N \) is the concentration of the metallic colloids, \( \alpha_e \) is the electrical polarizability of the colloid and \( E_0 \) is the external field, applied by two parallel conductors. The relative, effective dielectric constant in comparison to the background material is derived from the Eq. 2 as,

\[
k = 1 + N \alpha_e / (1 - \alpha_e C).
\]

Thus, capacitance increase is achieved by an increased number of dipoles and the interaction between them.

The surface of the porous electrode is a few orders of magnitude larger than its geometrical flat surface counterpart. The surface of the porous electrode is proportional to the geometrical volume of the sample; namely a larger film volume amounts to a larger effective surface. A large surface is capable of adsorbing many colloids. It makes, therefore sense to normalize the capacitance results by the electrode volume for a proper comparisons [15]. In our case,
volumetric specific capacitance amounts to gravitonic specific capacitance since the area of all samples was the same.

Dispersions of Au nano-particles (AuNPs) have been known for a long time and the preparation methods are well-established [16]. In order to ensure a good suspension, the colloids are coated with a ligand that is negatively charged. The charged surface enhances the electrostatic bond between the neutral, yet conductive A-C electrode and the AuNPs. The suspension in water exhibits red-wine color for ca 50 nm particles, and purplish/brown color for larger size colloids [17]. The larger size colloids of ~100 nm tend to aggregate and exhibit sedimentation. Here, data on two colloid sizes and various polymeric binders exhibit an enhanced specific capacitance when the AuNPs are incorporated in A-C based S-C.

II. Materials and Methods

Preparation methods: gold colloids

Nano-size AuNPs were synthesized following literature method using citrate as a reducing agent and stabilizer [18]. In brief, chloroauric acid (HAuCl₄) water solution (10 mg HAuCl₄ in 90 ml of water) was heated to boiling and sodium citrate solution (0.5 ml of 250 mM) was introduced. The mixture was stirred for 30 min until the color turned to wine red. AuNPs were then purified by centrifuge and washed with DI water three times. The concentration of AuNPs in water was 1 mg/mL; the titration experiments were made with increasing amounts of 10μL per batch and are translated to μg when referenced to the amount of A-C in the batch; otherwise, they are quoted in μL.

There were 2 batches of suspended AuNPs in water: medium size exhibiting blue/wine color, Figs. 3-7) whose light absorption data is shown in Fig. 1 and an aggregated batch (~100 nm Fig. 9) exhibiting sedimentation.

Figure 1. Absorbance for the smaller size AuNPs, suspended in water. DLS data indicates an averaged size of 45 nm.

Preparation methods: porous electrodes

(a1) A single batch of active-carbon (A-C) with a 5% Cellulose Acetate Butyrate (CAB) binder was prepared. The 20 mL of acetone contained 2 gr of A-C and 100 mg of CAB. Six samples, each containing 1 mL of the slurry were prepared. To these, succession amounts of 10 μL of AuNPs, suspended in water were added. Each mixture was first sonicated with a horn antenna, dropped casted on grafoil electrodes (area of contact 1.27x1.27 cm², or 0.5”x0.5 inch²), baked on a hot plate at <90°C and then soaked with an electrolyte (1 M of Na₂SO₄, or NaCl). A fiberglass filter
(Whatmen 1851-055) was used as a membrane. The Au colloid concentration was 1 mg/mL. The pores in the A-C electrodes were of the order of sub-microns [19-20].

(a2) Variation on (a1) includes the suspension of A-C and AuNPs in acetone, sonication, and addition of dissolved CAB in 1 mL acetone, sonication and drop casting. 1 M of NaCl was as an electrolyte.

(b) Similar to (a1) but with Poly-Vinyl Alcohol (PVA) as a binder and 1 M of NaCl as an electrolyte. The Au colloids sizes were of order of \( \sim 100 \) nm, exhibited some sedimentation and deemed as aggregates.

The samples: Cuts of 200 micron thick grafoil electrodes with back adhesive (1.27 cm x 2.54 cm) were placed on similar cut microscope slides. Before placing it on the slides, the grafoil electrodes were placed in 1 M NaOH container and were exposed for 30 sec to microwave radiation in a microwave oven to improve adhesion between the binder materials to the grafoil. The two slides were held by tweezers (or clips) and the boundaries of the sample were left unsealed while soaking it in the electrolyte. The sample configuration is shown in Fig. 2a and its picture in Fig.2b.

![Figure 2](image_url)

Figure 2. (a) A cross section of sample with grafoil coated active-carbon (A-C) electrodes, and (b) a picture of the cover area ca, 12.7x12.7 mm².

Electrochemical Techniques:

Potentiostat/Galvanostat (Metrohm) was used. Each sample was tested using three electrochemical methods: Cyclic Voltammetry (C-V), Charge-Discharge (C-D) and Electrochemical Impedance Spectroscopy (EIS). These methods all agreed on the titration trend.

Initial Characterizations:

By itself, un-coated grafoil electrodes exhibited very small capacitance values (Fig. 3a). Thicker grafoil electrodes exhibited an inferior capacitance to the thinner ones, probably due to manufacturing differences. Electrochemical Impedance Spectroscopy (EIS) (Fig. 3b) reveals that there is little change in the differential capacitance as a function of light when the A-C films were placed on ITO electrodes and subjected to irradiation by a 75 W incandescent light [as done in refs. 19-20]. There is relatively a large change of the electrode resistance (up to the knee of the curve). A light induced increase in the cell polarization is observed around the curve’s knee indicating reduction in ion diffusion [21]. Overall, the optical effect is small (~6%) and is attributed to optical excitation in the A-C itself and to a lesser extent by the ITO electrodes.

Low concentration of AuNPs, drop-casted on grafoil-only electrodes exhibited little capacitance variations as a function of colloid concentration (Fig. 3c). The capacitance values are smaller than those achieved with A-C coated electrodes. The concentration of the AuNPs was referenced to its suspension in 1 mL of acetone and the electrolyte was 1 M NaCl.
Figure 3. (a) Initial C-V traces for A-C deposited (pink and black curves) and uncoated (grey curve) on various grafoil based current collectors; thick and thin electrodes refer to thickness values of 500 and 200 micron, respectively. (b) EIS curves under 75 W white light for colloidal embedded sample on ITO substrate (instead of the grafoil electrodes). (c) Low concentration of AuNPs on grafoil only electrodes exhibited little capacitance variations. The concentration of the AuNPs is referenced to the solvent: 1 mL of acetone. The electrolyte was 1 M NaCl.

Titration experiments have been carried out to study the effect of AuNP loading. The initial idea was that larger AuNP concentration will lend itself to larger capacitance values as more colloids will find itself at the electrolyte/electrode interface. Initial C-V experiments with 1 M of Na₂SO₄ were made as shown in Fig. 4a. These experiments exhibited a capacitance peak at AuNPs concentration of 40 µg/mL. The related capacitances as a function of AuNP concentration are shown in Fig. 4b. Note a capacitance increase by a factor of ~2 as a result of AuNPs presence when compared to a reference sample without them (the sample with 0 AuNP concentration). The amount of active carbon in each vial was 100 mg/mL.

The area of each sample was the same and the related capacitance values of Fig. 4a may be viewed as specific areal capacitance. For examples, the peak capacitance of 110 mF at 40 µg/100 mg is translated to 110 mF/1.27² cm²=68.2 mF/cm². The trend in Fig. 4 is also exhibited in Fig.5a,b and Fig. 6a,b for C-D and EIS experiments, respectively.
Two reference experiments were additionally made: (1) a repeat of the 50 μg experiment on another grafoil substrate to assess variations in sample preparation. That variation was estimated at ±5%. (2) 30 μg of AuNPs were added to the mixture holding 30 μL of AuNPs (in total 60 μL of AuNPS in 1 mL) to assess an increase in colloid concentration.

![Figure 4](image1.png)

Figure 4. (a) Successive C-V plots for various concentrations (in μL per mL of solvent) depicted on the right. (b) Capacitance as a function of AuNPs concentration exhibits a peak at 40 μL/mL. The electrolyte was 1 M of Na₂SO₄.

![Figure 5](image2.png)

Figure 5. (a) C-D plots for various AuNPs concentration (in μL per 1 mL of solvent). (b) Capacitance as a function of AuNPs concentration exhibits a peak at 40 μL/mL. The electrolyte was 1 M of Na₂SO₄.

Finally, Electrochemical Impedance Spectroscopy (EIS) for the maximum capacitance is shown in Fig. 6a. The slope of the curve in Fig. 6b is proportional to the inverse of the differential capacitance, \( C_{\text{diff}} \), as, \( 1/(2\pi C_{\text{diff}}) \) [21]. \( C_{\text{diff}} \) may be calculated as 0.194 F, corroborating the value obtained from Fig. 2b. Overall, the electrode resistance (ca 3-5 Ohms for all samples) is rather small.
Figure 6. (a) Capacitance values, derived from EIS curves. The concentration of the AuNP is in mL per 1 μL of solvent. (b) The slope of the linear curve for the sample exhibiting capacitance maxima at 40 μL/mL of AuNPs is proportional to 1/C_{diff}. The electrolyte was 1 M of Na_2SO_4.

One could argue that values of film capacitance, or even values of specific capacitance with respect to the area (in units of [F/cm^2]), do not provide for a full picture; as pointed earlier, the effective (porous) film's surface scales as its volume. Plots of the specific gravitonic capacitance in units of F/g were made for different set of films at various conditions (various thicknesses, binders and electrolytes) as outlined below. As outlined below, the gravitonic capacitance is directly related to the volumetric capacitance in our case:

The area of the sample is the same, 1.61 cm^2. The density of the composite film, d_{film}, is a weighted density of its components: 95% of A-C and 5% of polymeric binder which are kept the same throughout all tests: d_{film}=0.95×(d_{A-C}=0.375 g/cm^3) + 0.05×(d_{polymer}=1.21 g/cm^3) ~ 0.42 g/cm^3. The volume is A×t and the film thickness is t=w_{film}/(d_{film}×A) with w_{film} being the film weight. The gravitonic specific capacitance in units of F/g is related to the volumetric specific capacitance in units of [F/cm^3] as: [F/cm^3]=[(g/cm^3)×F]/g=[F×d_{film}/g]. Therefore, gravitonic and volumetric specific capacitance values are proportional to one another through a constant: the film density, or, d_{film}=0.42 g/cm^3.

III. Results

Two sets of experiments were first carried out: one for thicker (~450 μm) and the other for thinner (~75 μm) films. Their results are shown in Fig. 7. The thin films were obtained by further dilution of the original batches by 1 + 1 mL of acetone + ethanol for a total of 3 mL solution. The concentration of the AuNPs is referenced to the amount of the A-C in the sample because both the AuNPs and the A-C were diluted by the same amount. The trend exhibited by the thicker and thinner films is the same; thinner films exhibited larger specific values [22]. The consistent results for the reference sample (0 μg/100 mg) alludes to the repeatability of the experiments. Of interest are the relatively large values at 20 and 50 μg/100mg. As also suggested by Fig. 9, the large variability of values at 50 μg/100 mg in Fig. 7 may be attributed to lower film integrity due to a mixture of hydrophobic and hydrophilic components; the AuNPss are suspended in water while the A-C and the CAB binder are hydrophobic.
Figure 7. Specific capacitance, $C_{\text{specific}}$ in units of F/g from C-V data for thick and thin films with a CAB binder. The concentration of AuNPs is referenced to the amount of A-C in the slurry. The value for 10 $\mu$g per 100 mg of A-C is identical for both films. The electrolyte was 1 M of Na$_2$SO$_4$.

Another set of tests was conducted with the smaller size AuNPs colloids (~45 nm of Fig. 1), yet with 1 M NaCl as an electrolyte. Better film homogeneity was achieved by first sonicating the AuNPs with A-C in 1 mL of acetone following with 1 mL of 6% CAB by weight in acetone, as well; the latter mixture was re-sonicated. The results shown in Fig. 8 are consistent with the previous results. The peak value seem to shift a bit towards a larger concentration.

We found out that incorporating the AuNPs in the electrolyte did not yield any capacitance increase. This is due to screening by the ions in the electrolyte. Administering the AuNPs in polymeric binder before adding the A-C was not efficient, either. Adding the AuNPs to a thin polymeric layer directly on the grafoil film resulted in a very poor capacitor because it blocked the collection of current.

Figure 8. Specific capacitance values derived from C-V data for CAB binder and 1 M NaCl electrolyte. Similar trend is obtained with C-D data. The concentration of AuNP in $\mu$g is referenced to 100 mg of A-C in the batch.

Another set of experiments was conducted with a PVA binder and larger amount of A-C (200 mg per 1 mL of water). Judging by the suspension color and sedimentation, the AuNPs appeared to be aggregated and of larger size (~100 nm). Unlike the hydrophobic CAB, PVA is hydrophilic and better matches with the water suspended AuNPs as alluded to by [23]. PVA is less compatible
with the hydrophobic current collector and the treatment with the NaOH helped the adhesion of the film to the grafoil. The electrolyte here was 1 M NaCl. Two sets of experiments were conducted and their averages are shown in Fig. 9 by the blue dots. The data are consistent up to 40 \( \mu g \) per 200 mg of A-C after which film homogeneity could become an issue.

Figure 9. Specific capacitance values derived from C-V data for PVA binder and 1 M NaCl electrolyte. The black dots are the results from two sets of experiments; the blue dots are averages of these two experiments. The concentration of AuNP in \( \mu g \) is referenced to 200 mg of A-C in the batch.

Simulations:
In the simulations, one compares two cases: (1) a cell without metal colloids; (2) a cell with colloids extruding into the neutral region. A portion of the S-C was modelled by a parallel plate capacitor with a graphitic film of finite conductance that is deposited on top of a metallic current collector. The gold particle is partially embedded inside the graphitic film. The neutral region is situated at the cell's center and a bias is provided between the two current collectors: \( \pm V_{\text{in}} \). The surface potential of the neutral region and the surface potential of the metal colloids are floating. The colloid radius was 10 nm. Larger particles would result in larger polarization effect, though experimentally, one would need to balance their size with the pore size of the A-C. The otherwise capacitance increase is diminished when the colloids are embedded away from the extended electrode. This corroborates the experiments; when the AuNPs were mostly part of the electrolyte, the efficiency of the capacitor was substantially diminished. The conductivity of the graphitic material matters only if its conductance is comparable to the current collectors' value.

The potential distribution inside the cell with and without the metallic colloids is shown in Fig. 10. The local polarization is shown in Fig. 11. The latter points to polarization increase in the cell upon the presence of the AuNPs.
The capacitance of the cell is proportional to the charge on the electrode. Fig. 12 shows the change in the electrode charge as a function of the cell bias. The electrode charge, \( Q \), is related to the bias, \( V_{in} \), as, \( Q=C\cdot V_{in} \), with \( C \), the cell capacitance. The cell capacitance is therefore, \( C=Q/V_{in} \) and it is constant since the charge on the electrode varies linearly with \( V_{in} \). The slope of the curve (the capacitance) increases upon presence of the AuNPs. The curves of Fig. 12 are translated to cell capacitance values of: 0.133 and 0.22 nF, for respectively, cells without colloids and cells with them.

While not shown, packing more colloids, say two AuNPs on each surface, obviously increases the cell capacitance but up to a point. The cell capacitance for very closely packed colloids on each surface is actually smaller than when they are placed apart. Simulation wise, the change is not large (ca 2.5%), yet noticeable and is attributed to a strong dipole-dipole interaction.
One may point out that capacitance increase may also be deduced by the concept of capacitor-within-capacitor [24], where the metal colloid is modeled by a small metallic dipole, which is embedded in a larger capacitor (the cell). The large capacitance in that case is attributed to the large polarization between the uppermost dipole surface and the electrode as alluded to by Fig. 11b.

IV. Discussion

Experimentation and simulations exhibited enhancement of specific capacitance upon treating active-carbon electrodes with AuNPs. This effect occurred under various conditions (hydrophobic and hydrophilic polymeric binders, electrolytes and various AuNPs/A-C mass ratios). The effect was quite strong exhibiting an enhancement of close or larger than a factor of 2 despite the small amount of AuNPs used. The concentration used for the AuNPs is three orders of magnitude smaller than the concentration used for (neutral) semiconductor colloids [19-20]. Optical excitations of the semiconductor particles make their oscillator strength similar to that of metallic colloids. Yet, the dispersion of these neutral particles was throughout the entire film, including the binder. This observation, and the simulations point to the possible role of placing the metallic colloids within the double layer region, close to the conductive A-C medium.

It was also found that the cell's capacitance was not affected by adding the colloids to the electrolyte, most likely due to ion screening. Flat surfaces exhibited small capacitance variations in the AuNP concentration range of interest, which points to the important role played by the porous A-C film. The increase of A-C concentration in the batch (100 mg/mL in Fig. 8 vs 200 mg/ml in Fig. 9) did not affect the presence of a large specific capacitance peak in our experiments. This suggests that the AuNPs were mostly adsorbed by the porous electrode regardless of it starting concentration. It also reaffirms the use of gravitonic, or volumetric specific capacitance because such normalization method factors out contributions from the film thickness. One takes advantage that the colloids were coated with a negatively charged ligand, enabling it to better attach to the active-carbon electrode. Proof that the interaction between AuNPs and the A-C electrode was electrostatically strong is provided by Fig. 2; further dilution of the batch did not alter the titration trend.
The ligand, coating the AuNPs enables a better colloid suspension. It may also limit the packing of the colloids on the sample's surface. One may argue that such effect would eventually lead to saturation in the value of the specific capacitance. At the same time, beyond the specific capacitance peak one may observe large value fluctuations (e.g., Figs. 7, 9), which suggest that larger packing of AuNPs may increase the inhomogeneous colloid dispersion in the A-C electrode.

V. Conclusion

Incorporating gold particles in aqueous, active-carbon-based supercapacitors exhibited a substantial specific capacitance increase (gravitonic or volumetric). Simulations point to the enhancing effect of AuNPs dipoles when placed at the electrode/electrolyte interface.

References:

1. Brown, John, and Willis Jackson. "The properties of artificial dielectrics at centimetre wavelengths." Proceedings of the IEE-Part B: Radio and Electronic Engineering 102.1 (1955): 11-16.
2. R. E. Collin, *Field Theory of Guided Waves*, Wiley-IEEE Press, 2nd edition, 1990.
3. Shih-Chang Wu and H Grebel, "Phase shifts in coplanar waveguides with patterned conductive top covers," J. Phys. D: Appl. Phys. 28 437-439 (1995)
4. H. Grebel and P. Chen, "Artificial dielectric polymeric waveguides: metallic embedded films ", JOSA A, 8, 615-618 (1991). [https://doi.org/10.1364/JOSAA.8.000615](https://doi.org/10.1364/JOSAA.8.000615)
5. H. Grebel and P. Chen, "Artificial dielectric polymeric waveguides: semiconductor-embedded films", Opt. Letts, 15, 667-669 (1990). [https://doi.org/10.1364/OL.15.000667](https://doi.org/10.1364/OL.15.000667)
6. Keh-Chyun Tsay, Lei Zhang, Jiujun Zhang, Electrochimica Acta 60 (2012) 428–436.
7. Yudong Li, Xianzhu Xu, Yanzhen He, Yanqiu Jiang and Kaifeng Lin, Polymers 2017, 9, 2; doi:10.3390/polym9010002.
8. M. Kaempgen, C. K. Chan, J. Ma, Y. Cui, and G. Gruner, Nano Letts., , 9 (2009) 1872.
9. Michio Inagaki, Hidetaka Konno, Osamu Tanaike, Journal of Power Sources 195 (2010) 7880–7903.
10. Zhang, S and Pan, N, 2015. DOI:10.1002/aenm.201401401. https://escholarship.org/uc/item/26r5w8nc
11. Mohammad S. Rahmaniifar, Maryam Hemmati, Abolhassan Noori, Maher F. El-Kady, Mir F. Mousavi, Richard B. Kaner, Materials Today Energy 12 (2019) 26-36. https://doi.org/10.1016/j.mtener.2018.12.006
12. B.K. Kim, S. Sy, A. Yu, J. Zhang, Electrochemical supercapacitors for energy storage and conversion, Handbook of Clean Energy Systems (2015) 1–25.
13. Xin Miao, Roberto Rojas-Cessa, Ahmed Mohamed and Haim Grebel, "The Digital Power Networks: Energy Dissemination Through a Micro-Grid", Proceedings - IEEE 2018 International Congress on Cybermatics, 230-235. DOI: 10.1109/Cybermatics_2018.2018.00068
14. Roberto Rojas-Cessa, Haim Grebel, Zhengqi Jiang, Camila Fukuda, Henrique Pita, Tazima S. Chowdhury, Ziqian Dong and Yu Wan, "Integration of alternative energy sources into digital micro-grids", Environmental Progress & Sustainable Energy, (2018) 37, 155-164. DOI 10.1002/ep.
15. Y. Gogotsi and P. Simon, "True Performance Metrics in Electrochemical Energy Storage", Science 334, 917 (2011). DOI: 10.1126/science.1213003

16. John Turkevich, "Colloidal Gold. Part I: HISTORICAL AND PREPARATIVE ASPECTS, MORPHOLOGY AND STRUCTURE", Gold Bull., 1985, 18, 86-91.

17. John Turkevich, "Colloidal Gold. Part II: COLOUR, COAGULATION, ADHESION, ALLOYING AND CATALYTIC PROPERTIES", Gold Bull., 1985, 18, 125-131.

18. Mercado-Lubo, R.; Zhang, Y.; Zhao, L.; Rossi, K.; Wu, X.; Zou, Y.; Castillo, A.; Leonard, J.; Bortell, R.; Greiner, D. L.; Shultz, L. D.; Han, G.; McCormick, B. A. Nature Communications 2016, 12225.

19. H. Grebel, "Asymmetric Supercapacitors: Optical and Thermal Effects When Active Carbon Electrodes Are Embedded with Nano-Scale Semiconductor Dots", C 2021, 7(1), 7; https://doi.org/10.3390/c70100072.

20. H. Grebel, "Optically Controlled Supercapacitors: Functional Active Carbon Electrodes with Semiconductor Particles", Materials 2021, 14(15), 4183; https://doi.org/10.3390/ma14154183

21. Bing-Ang Mei, Obaidallah Munteshari, Jonathan Lau, Bruce Dunn, and Laurent Pilon, "Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices", J. Phys. Chem. C 2018, 122, 194–206. DOI: 10.1021/acs.jpcc.7b10582.

22. Suvi Lehtimäki, Anna Railanmaa, Jari Keskine, Manu Kujala, Sampo Tuukkanen Donald Lupo, "Performance, stability and operation voltage optimization of screen-printed aqueous supercapacitors", Scientific Reports, 7:46001 (2017). DOI: 10.1038/srep46001

23. Qinxing Xie, Xiaolin Huang, Yufeng Zhang, Shihua Wu, Peng Zhao, "High performance aqueous symmetric supercapacitors based on advanced carbon electrodes and hydrophilic poly(vinylidene fluoride) porous separator", Applied Surface Science 443 (2018) 412–420.

24. H. Grebel, "Capacitor-within-capacitor", SN Appl. Sci. 1, 48 (2019). https://doi.org/10.1007/s42452-018-0058-z