Composite electrolytes in capacitors and energy storage

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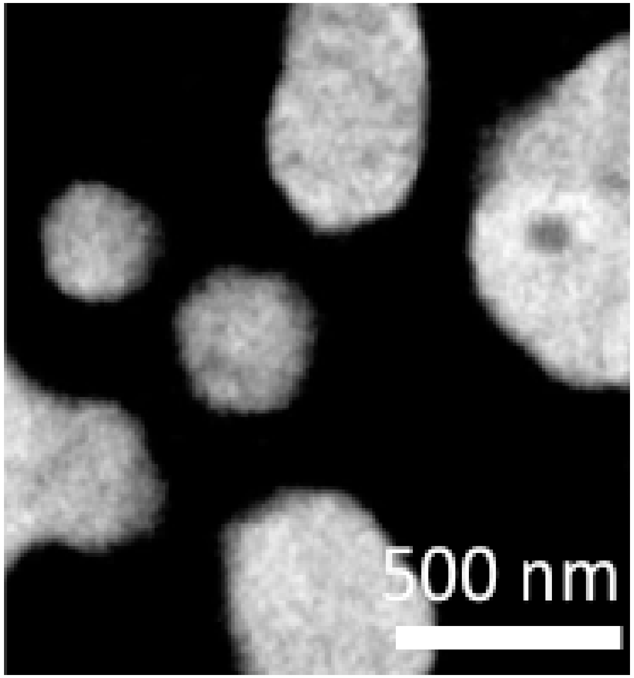
1.) Energy in an electrolyte: which are the relevant quantities?
Global variables: voltage U, capacitance C?
Local variables: electric field **E,** displacement field **D** ?

2.) The problem of estimating energy storage and 'normal' composites:
inhomogeneous fields and field dependent permittivity matrix **є**

3.) energy density in an electrolyte
a) symmetric permittivity matrix **є**
b) general permittivity matrix **є**

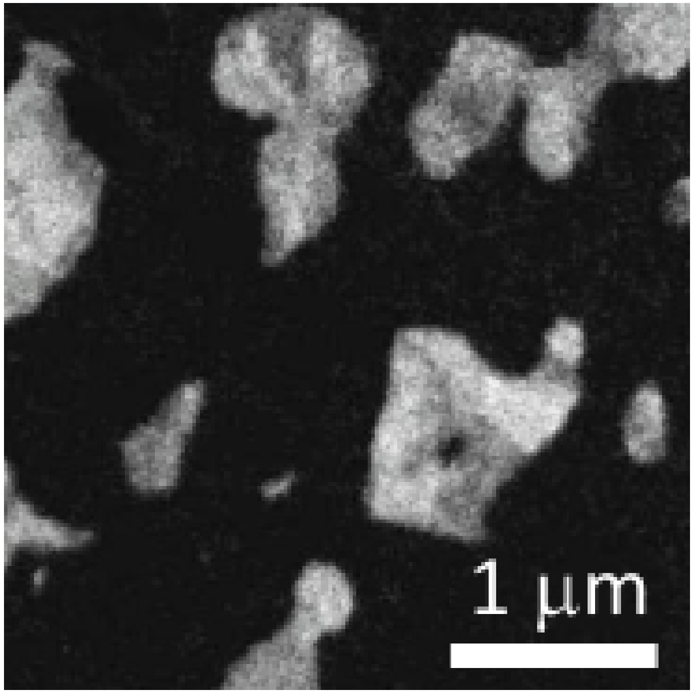
4.) Conclusion: 'Normal' composites may have higher capacitance, but homogeneous electrolytes are superior in storing energy.
Recommendations

From super-cap to super-super-cap?



Komposit **$BaTiO_3$** **+ Ni**

Concentration 27%



Komposit **$BaTiO_3$** **+ Cu**

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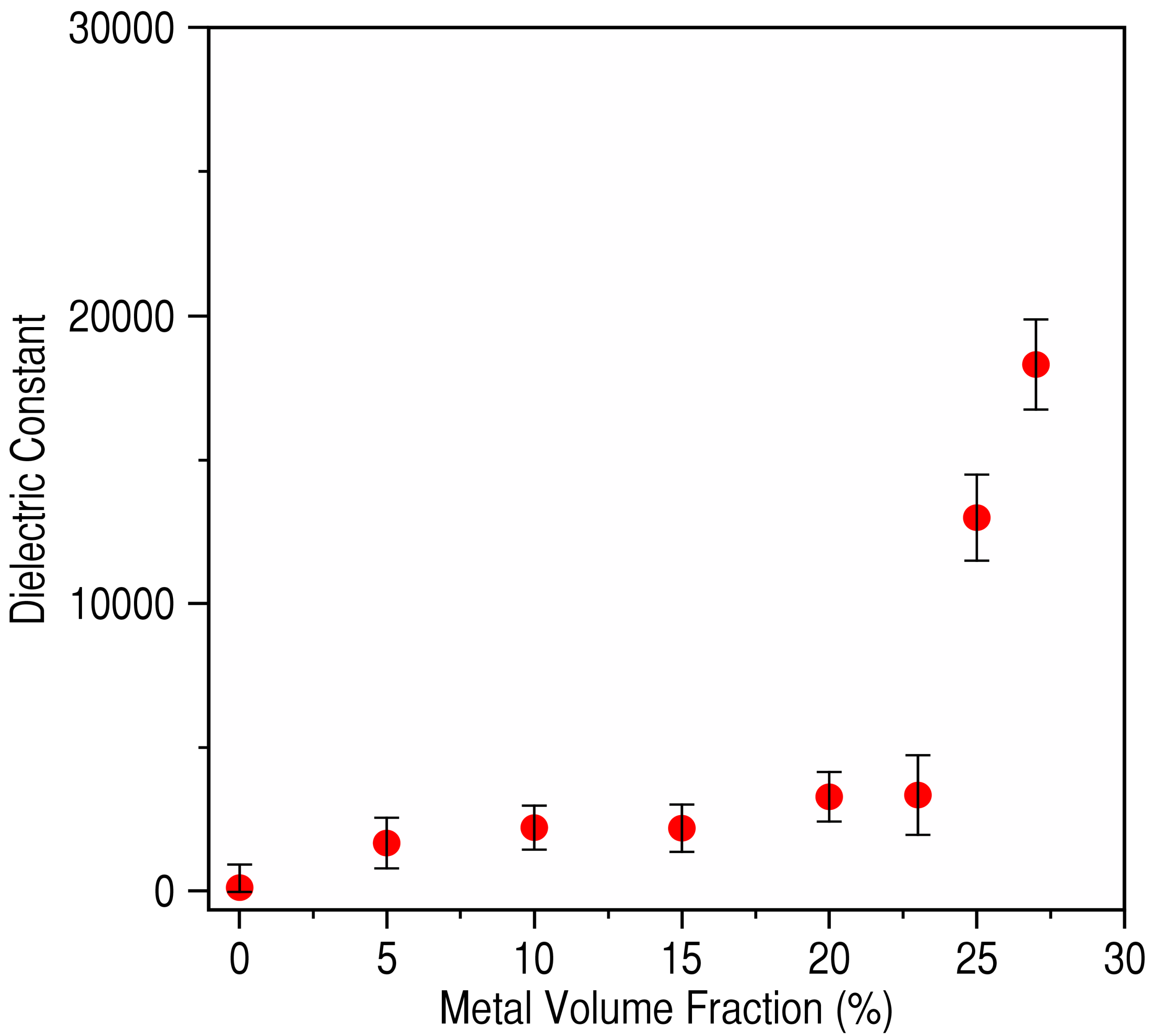


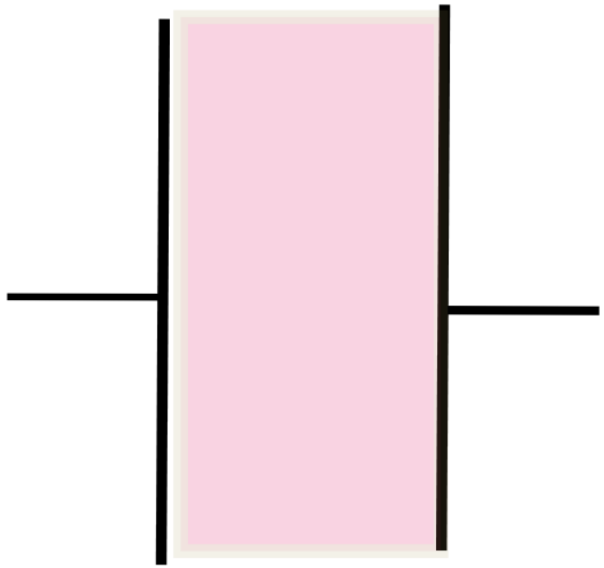
Dornseiffer, Pithan etal 2008 - 10 (private communication)

Komposit $BaTiO_3$ + Cu

H. Lustfeld, C. Pithan and M. Reißel, J Eur Ceram Soc 32 (2012) 859

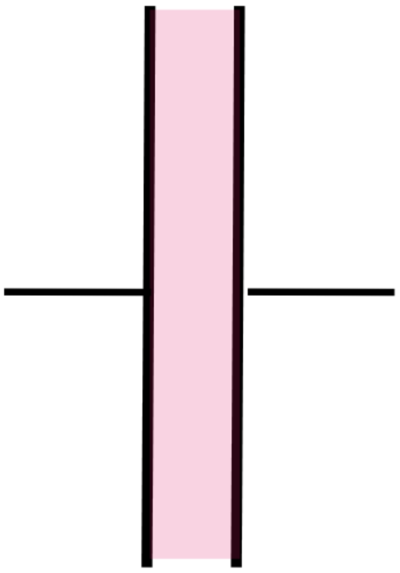
Energy in an electrolyte

Simple example: Electrolyte between parallel plates,
local and global representation



$$\mathcal{E} = \varepsilon_0 \varepsilon E^2 V$$

$$C = \varepsilon_0 \varepsilon F/d \qquad \mathcal{E} = 1/2 C U^2$$



$$\mathcal{E} = \varepsilon_0 \varepsilon E^2 \cdot V/3$$

$$C \to 3C \qquad U \to U/3$$

Result: For energy storage calculating the local energy density is appropriate.

$$\mathcal{E}(\mathbf{r}) = \frac{1}{2}\varepsilon_0 \varepsilon \mathbf{E}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}), \qquad \mathbf{D}(\mathbf{r}) = \varepsilon_{\mathbf{0}} \varepsilon \mathbf{E}(\mathbf{r})$$

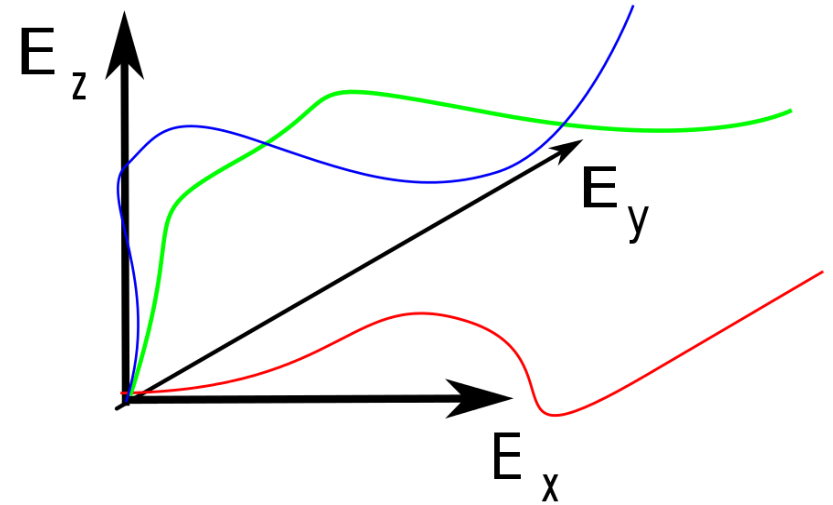
$$\mathcal{E}(\mathbf{r}) = \int \mathbf{E}(\mathbf{r}) \cdot d\mathbf{D}(\mathbf{r})$$

Local energy density in a composite

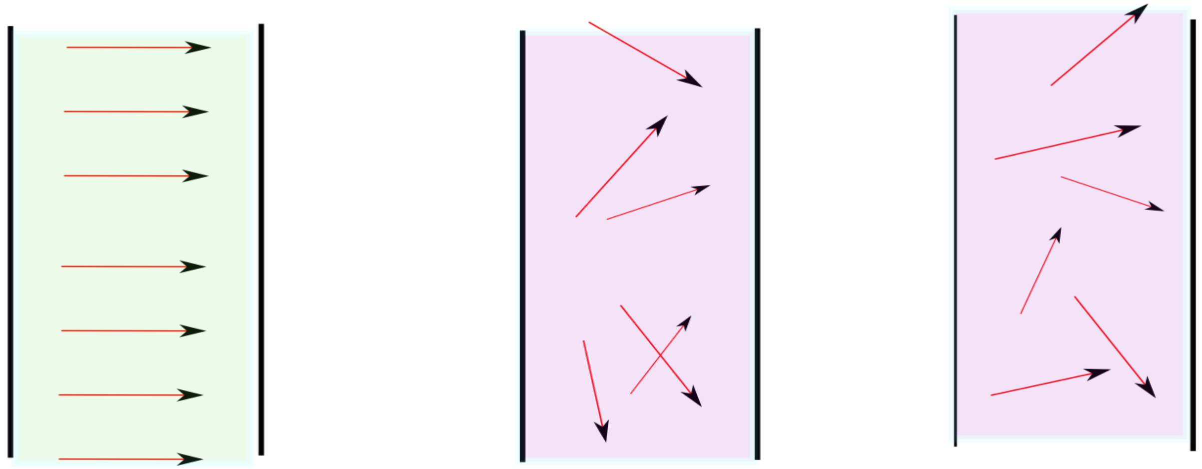
$$\mathcal{E}(\mathbf{r}) = \int \mathbf{E}(\mathbf{r}) \cdot d\mathbf{D}(\mathbf{r})$$

$$\boldsymbol{\varepsilon}(\mathbf{r}, \mathbf{E}) = \frac{1}{\varepsilon_0} \frac{\partial \mathbf{D}(\mathbf{r})}{\partial \mathbf{E}(\mathbf{r})}$$

$$\mathcal{E}(\mathbf{r}) = \varepsilon_0 \int_{P(\mathbf{r})} \mathbf{E}' \cdot \boldsymbol{\varepsilon}(\mathbf{r}, \mathbf{E}') \cdot d\mathbf{E}'$$



Paths of a composite electrolyte in E-space for different locations in real space

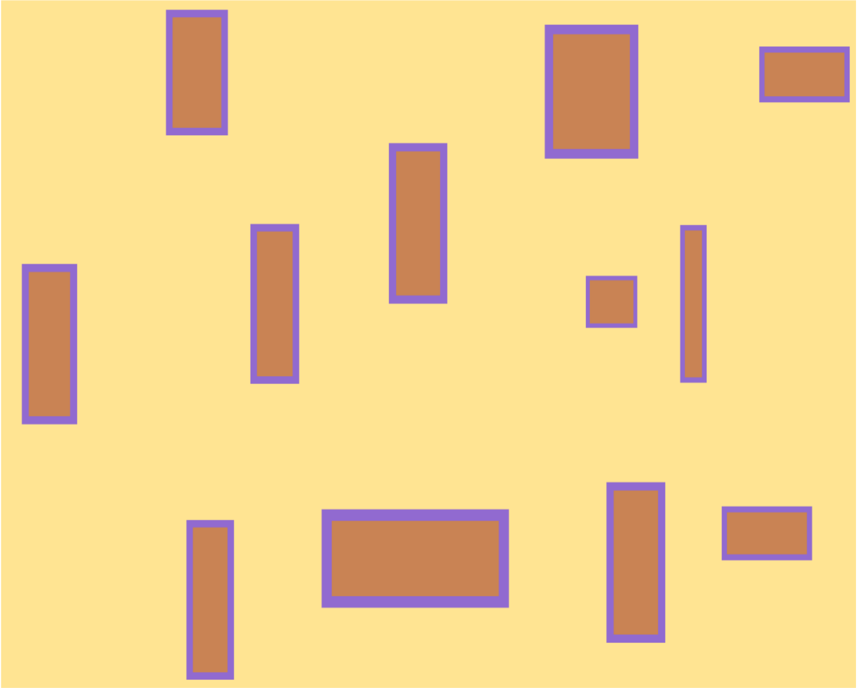


Homogeneous electrolyte

Composite: Electric field changes modulus and direction during charging

We define 'normal' composites in the following way:

a) Apart from surface- and interface layers each component of the composite has bulk properties.
b) Surface- and interface layers of the various components contribute only marginally to the energy storage.



$$\mathcal{E} \approx \sum_{\nu=1}^{N} \cdot \int_{V^{(\nu)}} d^3r \cdot \int_{\mathbf{P}(\mathbf{r})} \mathbf{E}' \cdot \boldsymbol{\varepsilon}^{(\nu)}(\mathbf{E}') \cdot d\mathbf{E}'$$

$$\mathcal{E}^{(\nu)}(\mathbf{r}) = \cdot \int_{\mathbf{P}(\mathbf{r})} \mathbf{E}' \cdot \boldsymbol{\varepsilon}^{(\nu)}(\mathbf{E}') \cdot d\mathbf{E}'$$

Estimate for the symmetric case: $\varepsilon_{ik}^{(\nu)} = \varepsilon_{ki}^{(\nu)}$

$$\mathcal{E}^{(\nu)}(P_S) = \int_{\mathbf{P}_S} \mathbf{E}' \cdot \boldsymbol{\varepsilon}^{(\nu)}(\mathbf{E}') \cdot d\mathbf{E}'$$

Integral is path-independent

$$\mathcal{E}^{(\nu_{max})} \geq \mathcal{E}^{(\nu)}$$

Result:
A homogeneous electrolyte with highest energy density $\mathcal{E}^{(\nu_{max})}$
Is superior to a 'normal' composite !

The problem of estimating energy storage and 'normal' composites

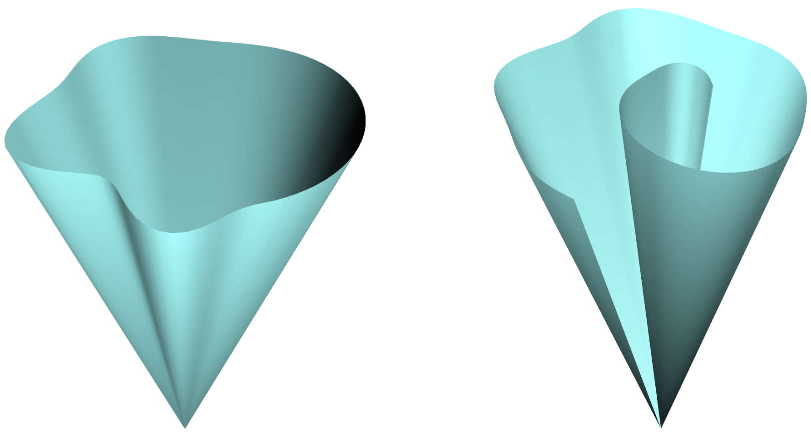
Estimate for the general case:

$$\varepsilon_{ik}^{(\nu)} \neq \varepsilon_{ki}^{(\nu)}$$

$$\mathcal{E}^{(\nu)}(P_S) = \int_{\mathbf{P}_S} \mathbf{E}' \cdot \boldsymbol{\varepsilon}^{(\nu)}(\mathbf{E}') \cdot d\mathbf{E}'$$

Integral is now path-dependent, but not on relevant surfaces

$$\mathcal{E}^{(\nu_{max})} \geq \mathcal{E}^{(\nu)}$$



Result again:
A homogeneous electrolyte with highest energy density Is superior to a 'normal' composite !

$$\mathcal{E}^{(\nu_{max})}$$

Conclusions, reommendations

1.) Energy in a composite electrolyte: the relevant quantities:
Local variables: electric field **E,** displacement field **D, local ε**

We define a class of 'normal' composite electrolytes:

a) Apart from surface- and interface layers each component of the composite has bulk properties.
b) Surface- and interface layers of the various components contribute only marginally to the energy storage.

With this definition of 'normal' composites we have shown

2.) Normal Composites may have higher capacitance, but homogeneous electrolytes are superior in storing energy.

This work has been done as part of a cooperation between FH-Aachen and FZ.-Juelich (PGI-1, PGI-7)