

3D image-based modeling of hierarchical porous electrodes: mechanical strength and effective conductivity

D. Roussel, D. Jauffrès, C.L. Martin



A. Lichtner



R. Bordia



J. Villanova



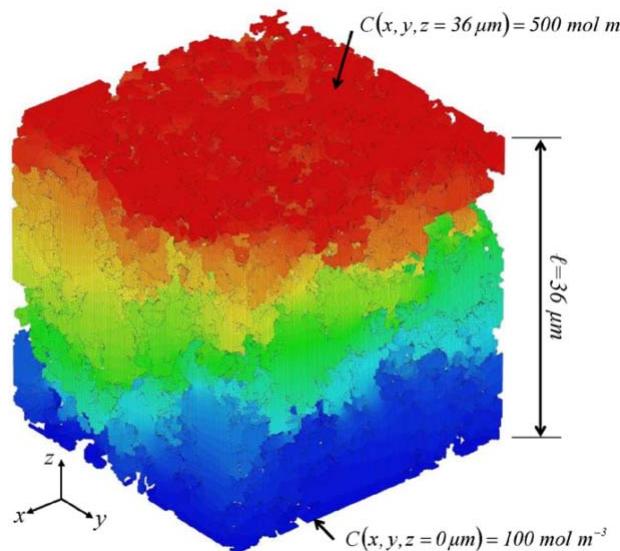
Funding : OPTIMA-SOFC project



- Image-based calculation of material properties

Well-established for porosity, pore size distribution, tortuosity, elasticity, thermal conductivity ...

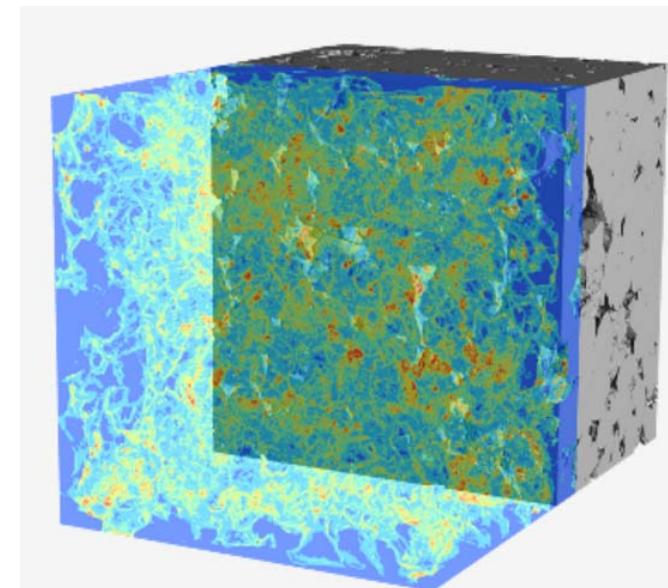
Finite Element Method



Laplace's equation for diffusion → tortuosity factor

Laurencin, J. et al. J. Power Sources 198, 182–189 (2012).

Voxel-based FFT method



Von Mises stresses during compression of sandstone

www.math2market.de (Geodict software)

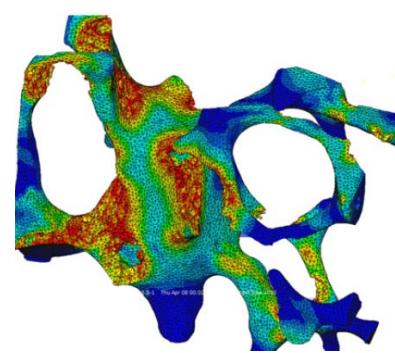
- Image-based calculation of material properties

→ *Difficult for fracture or electrochemical modeling*

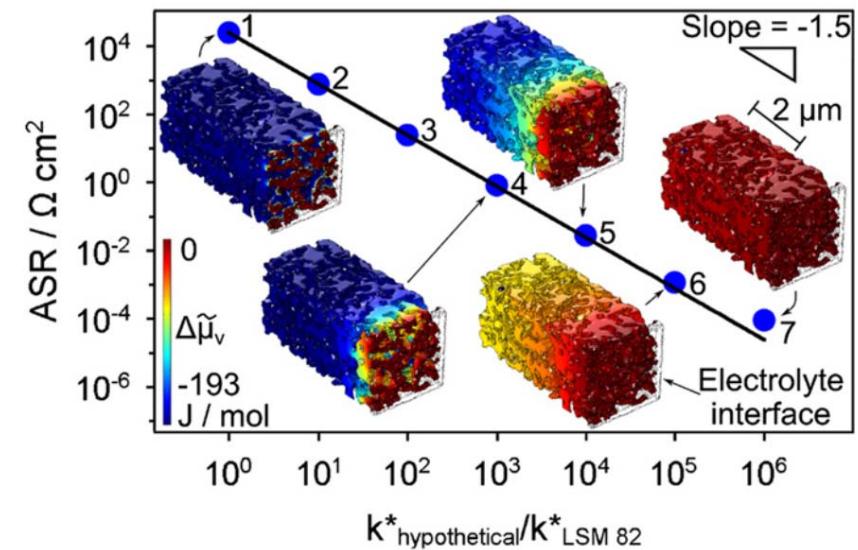
X-ray tomography



FEM model



Zhang, L. et al. *Acta Mater.* 60, 4235–4246 (2012).

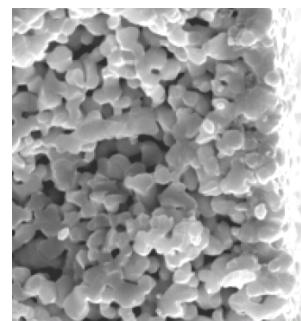
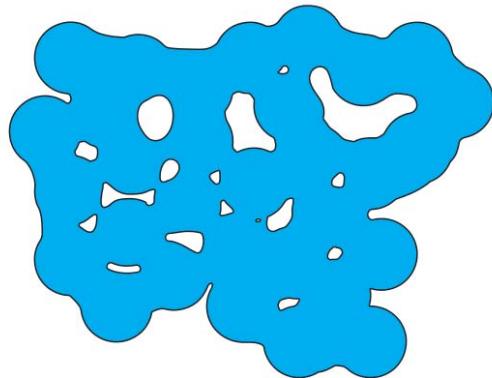


Lynch, M. E. et al. *Nano Energy* 2, 1–11 (2013).

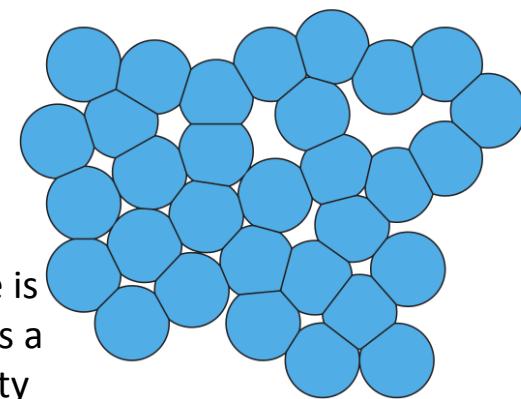
→ *Difficult if two scales (hierarchy) are involved*

- Image-based calculation of material properties : DEM approach

Porous continuum approach



Discrete approach



≠

Each particle is
considered as a
distinct entity

Finite Element Method, FEM
Voxel-based FFT (Geodict, CraFT)

*Continuous domain to be meshed
Limited to small systems ($\sim 10^2$ to 10^3 particles)*

Discrete Element Method, DEM

*No meshing
Can handle very large systems (up to 10^6 particles !)*

Elasticity, tortuosity ... 😊

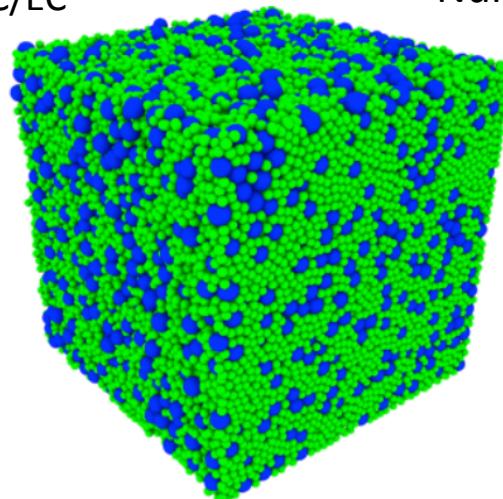
Fracture & damage, electrochemistry 😊

Elasticity, tortuosity ... 😊

Fracture & damage, electrochemistry 😊

- Image-based calculation of material properties : DEM approach

Volume fraction IC/EC
Particles size
Green density
Microporosity



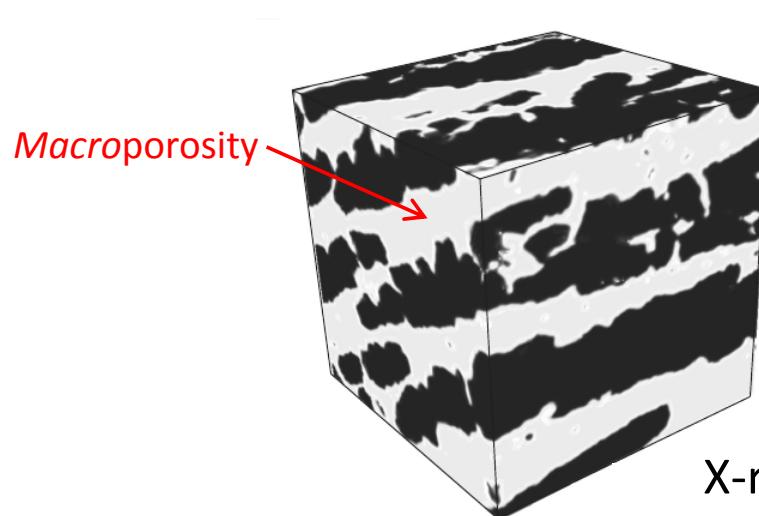
Numerical compaction + Numerical sintering



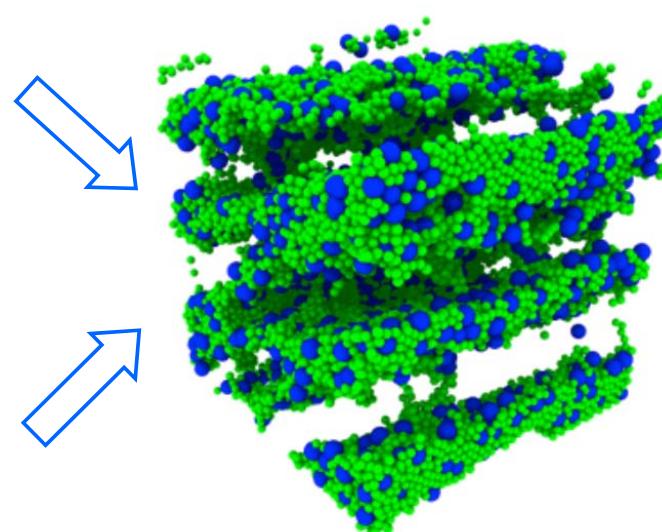
« sintered » packing

C.L. Martin and R. Bordia, 2008,
Phys Rev E 77, 031307

C.L. Martin and R. Bordia, 2009,
Acta Mater 57, 549-558



X-ray tomography

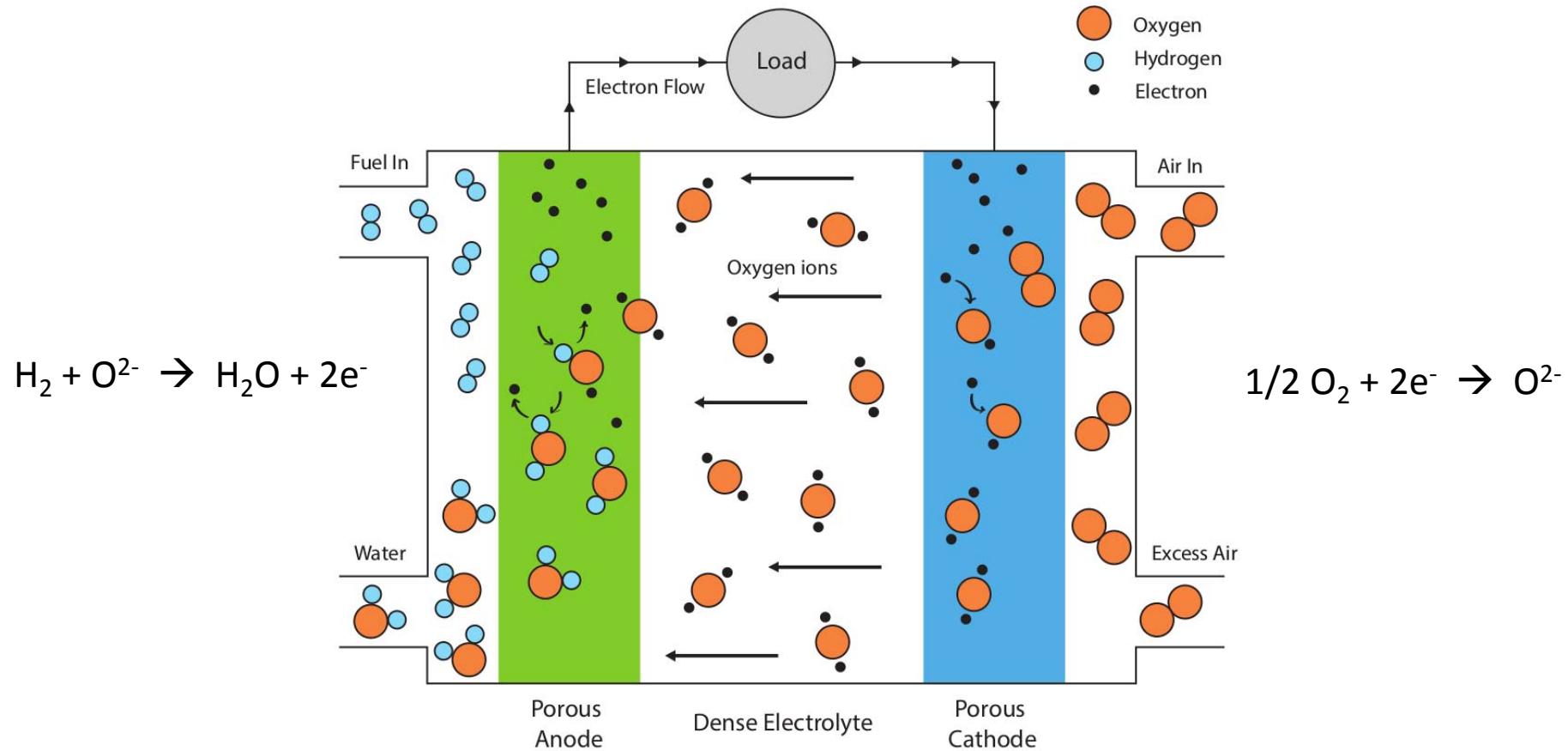


DEM simulations

- Outline

- Hierarchical SOFC electrodes & X-ray nanotomography
- Electrochemical modeling
- Fracture modeling

- SOFC (Solid Oxide Fuel Cell) : principle

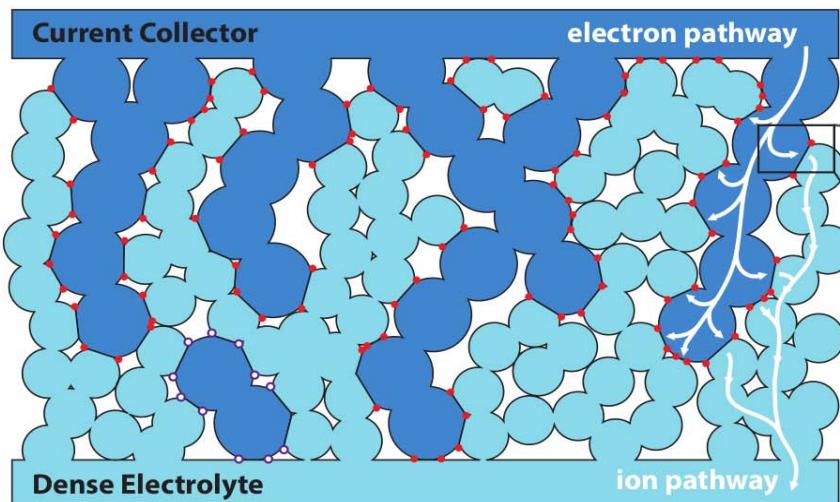


T = 700 to 900°C

- SOFC (Solid Oxide Fuel Cell) : cathode material

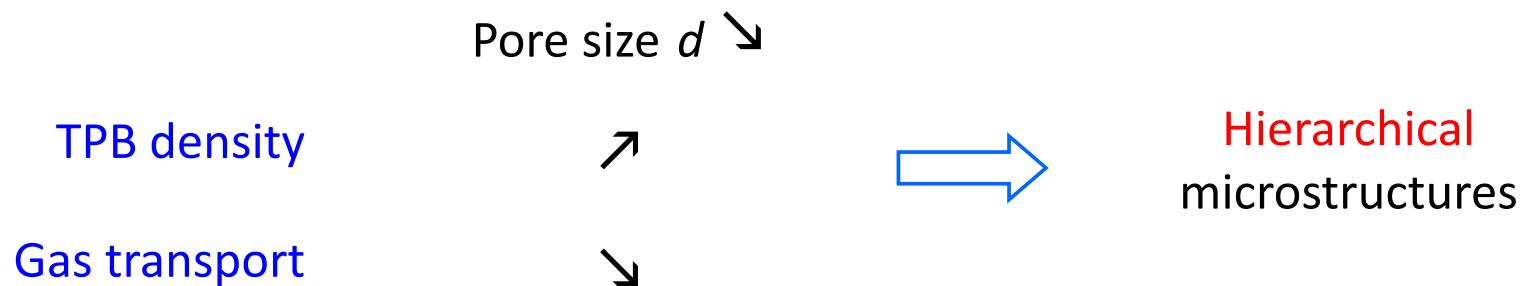
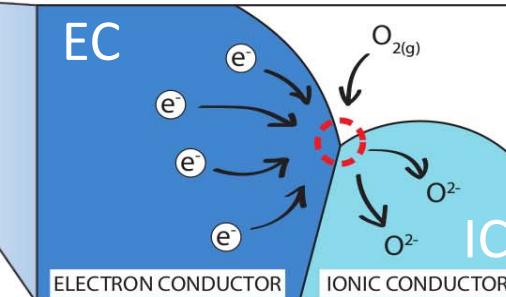
Ionic Conductor = Yttria-Stabilized Zirconia

Electronic Conductor = Lanthanum Strontium Manganite



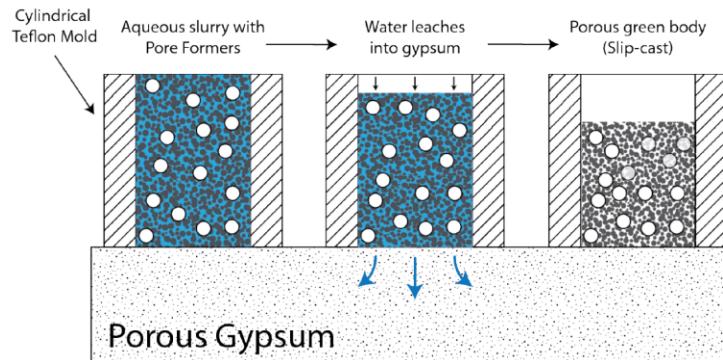
Composite Cathode Microstructure

- Triple Phase Boundary (TPB)

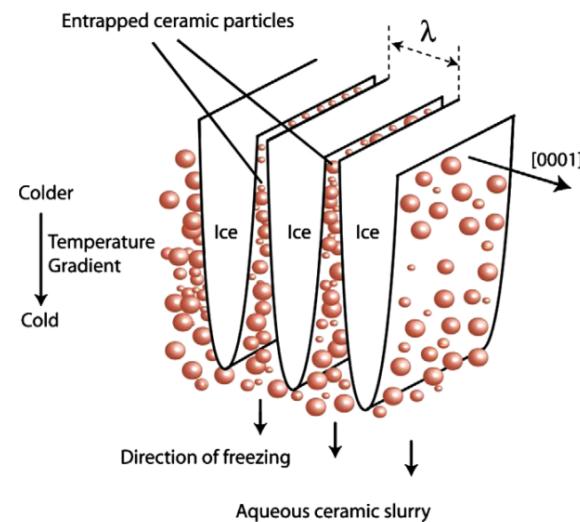


- SOFC (Solid Oxide Fuel Cell) : cathode material

Pore former



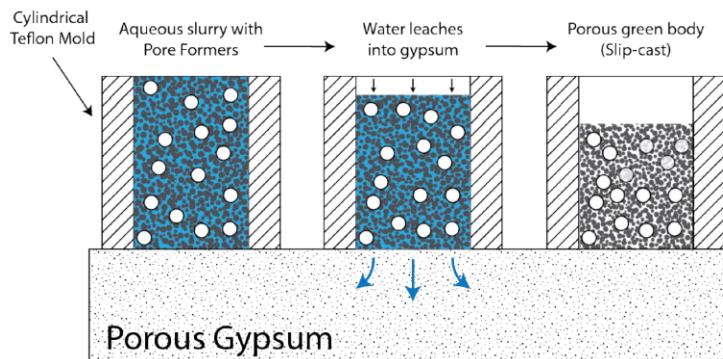
Freeze-casting



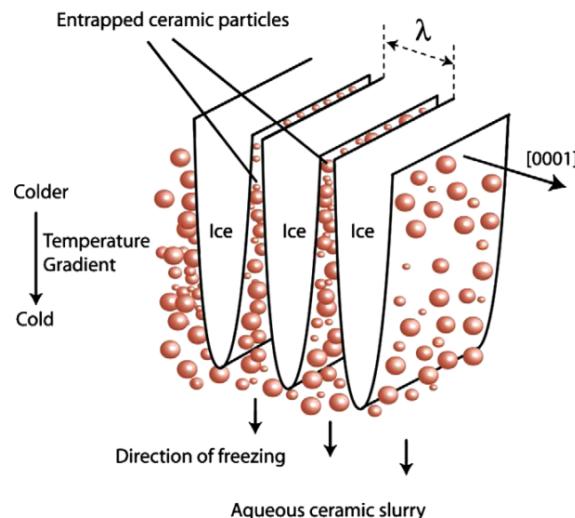
Deville, S. et al., Acta Mater. 55, 1965–1974 (2007).

- SOFC (Solid Oxide Fuel Cell) : cathode material

Pore former



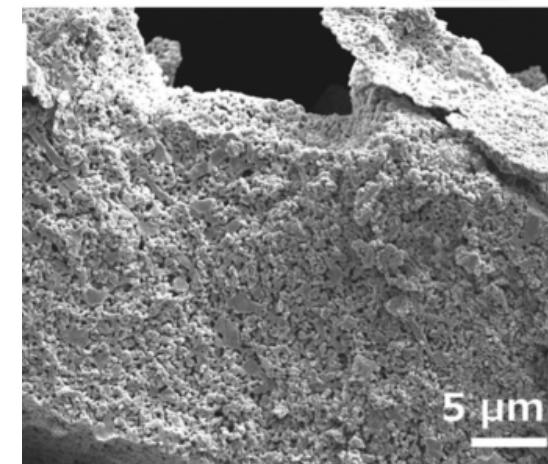
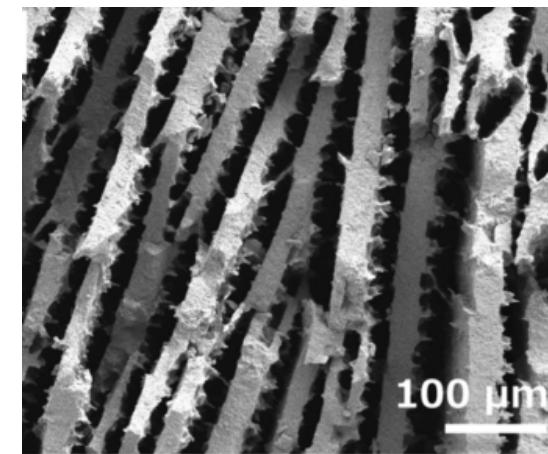
Freeze-casting



Deville, S. et al., Acta Mater. 55, 1965–1974 (2007).

Hierarchy in porosity

Oriented macroporosity
15 to 25%

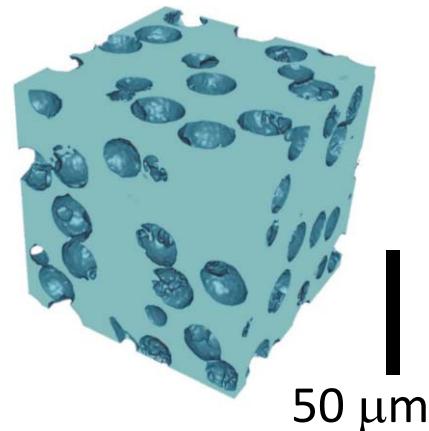
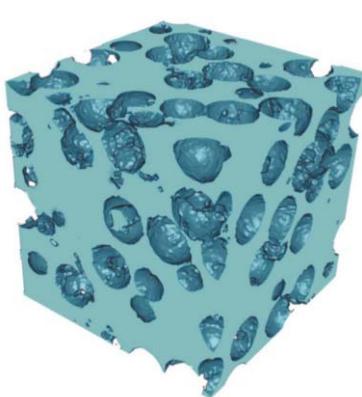


LSM + YSZ composite

Lichtner, A. Z. et al. J. Eur. Ceram. Soc. 35, 585–595 (2015).

- Synchrotron X-ray nanotomography

Pore former

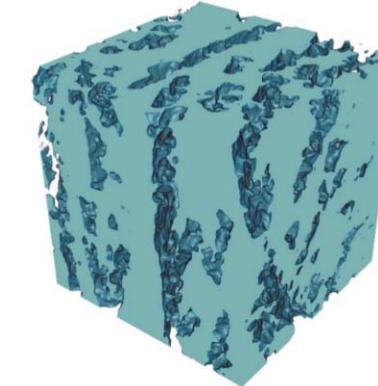
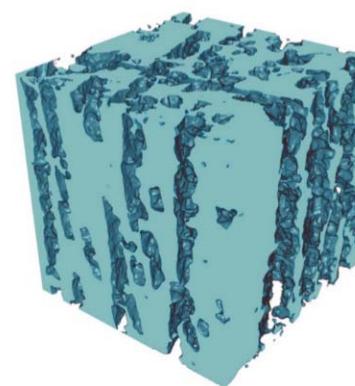
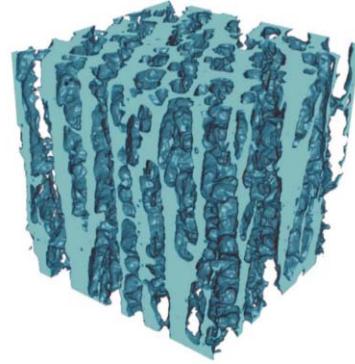
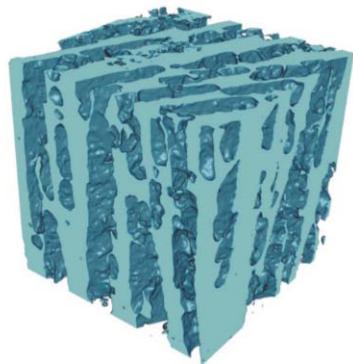


50 μm

Voxel size 75 nm
Scan time \sim 4 hours



Freeze-cast



Solid loading 20%
Freezing rate 20°C/min

20%
40°C/min

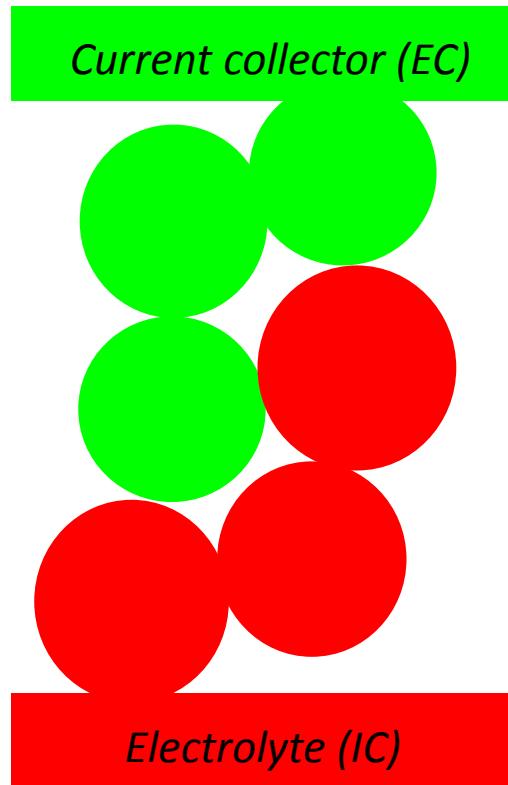
30%
20°C/min

30%
40°C/min

Electrochemical modeling $\rightarrow K_{\text{eff}} = 1/\text{ASR}$
Mechanical modeling \rightarrow Strength

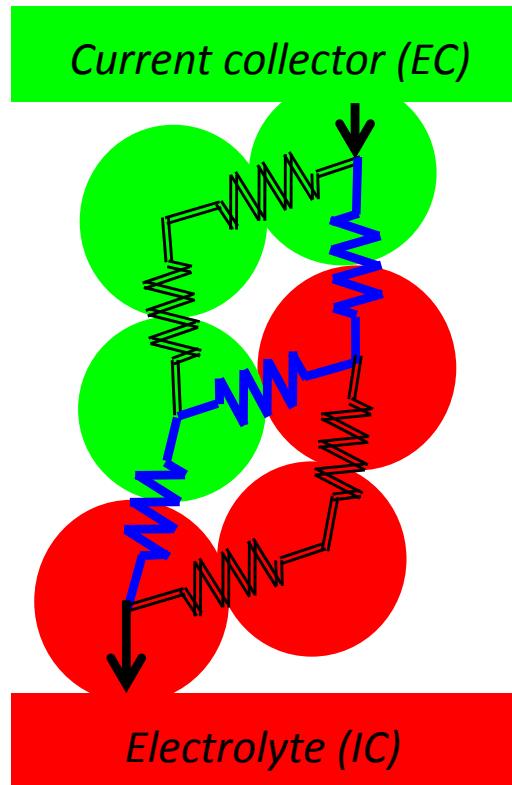
- Electrochemical model

Resistance Network



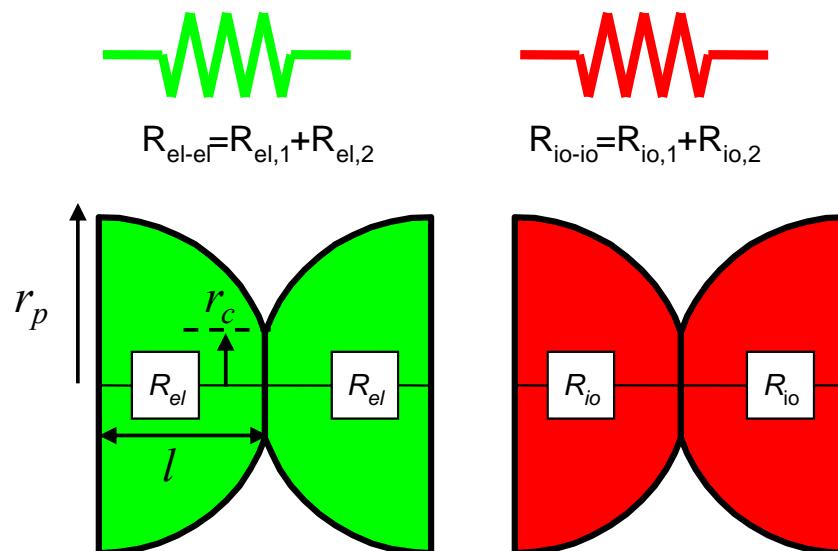
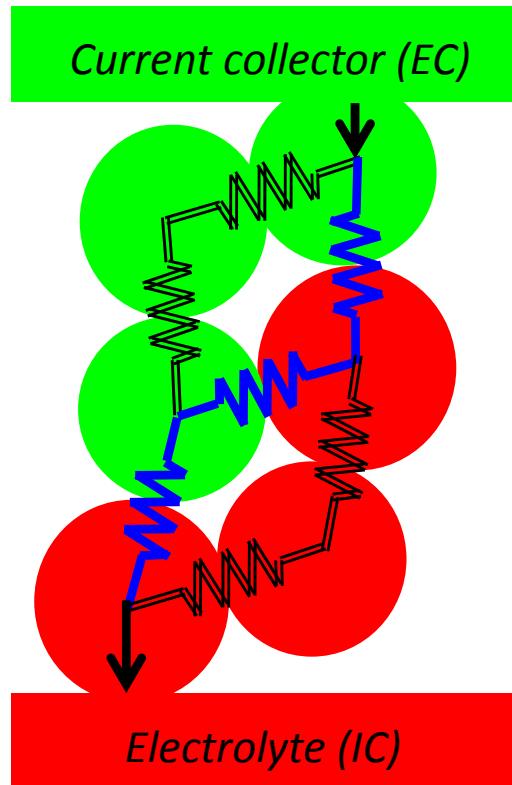
- Electrochemical model

Resistance Network



- Electrochemical model

Resistance Network



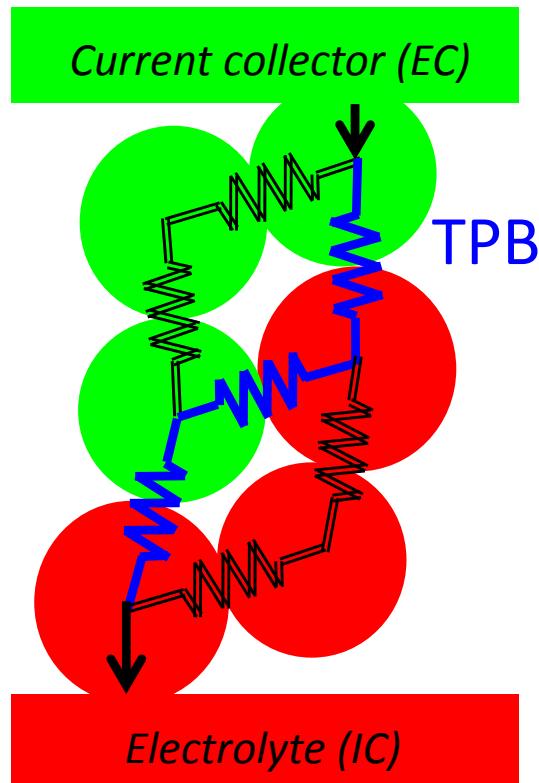
Resistance of a truncated half-sphere

$$\begin{cases} R = 0.899 \frac{r_c}{r_p} \frac{1}{\sqrt{1 - (r_c/r_p)^2}} R_{cyl} & \text{for } \frac{r_c}{r_p} < 0.744 \\ R = R_{cyl} = \frac{l}{K\pi r_c^2} & \text{for } \frac{r_c}{r_p} > 0.744 \end{cases}$$

Argento, C. & Bouvard, D. Int. J. Heat Mass Transf. 39, 1343–1350 (1996).

- Electrochemical model

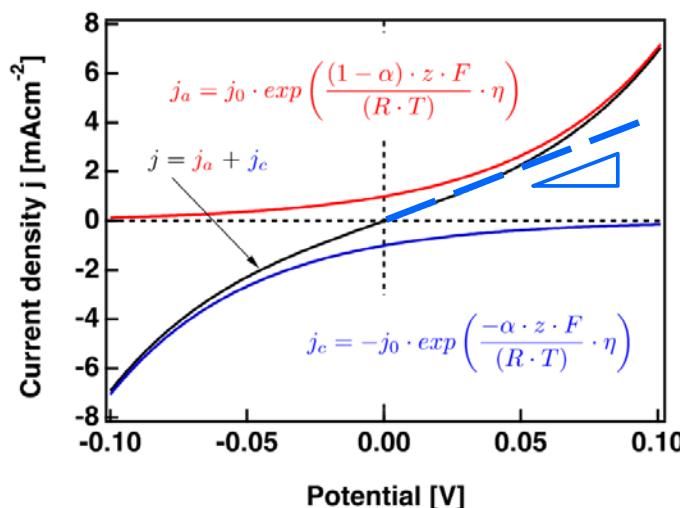
Resistance Network



Charge transfer

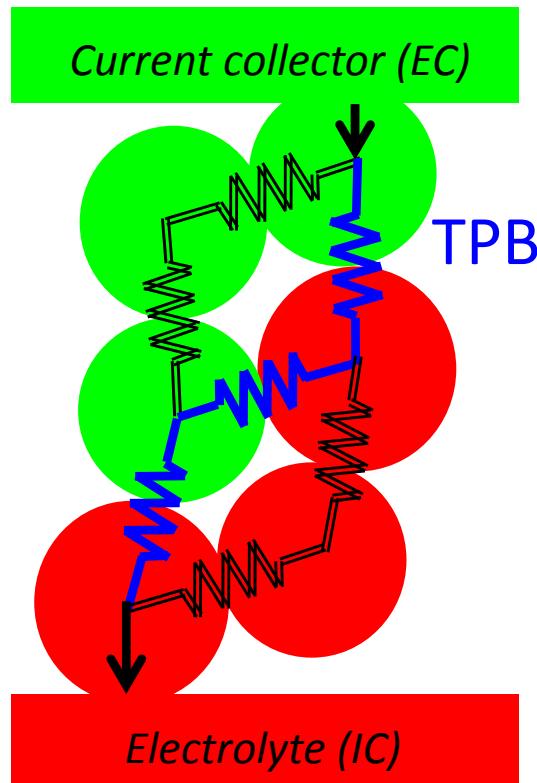


Butler-Volmer law



- Electrochemical model

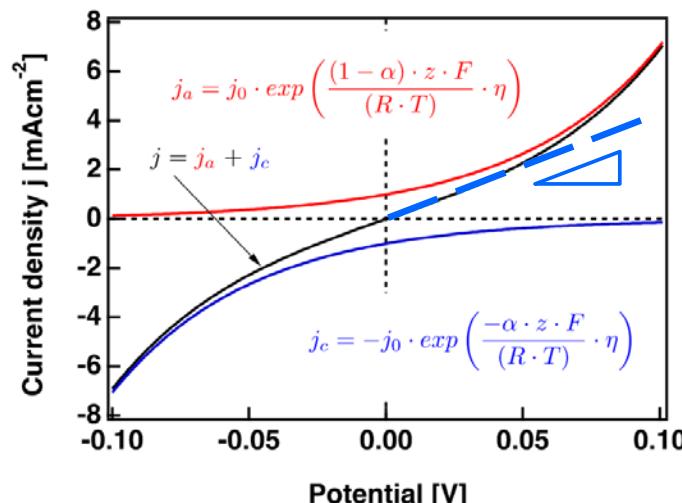
Resistance Network



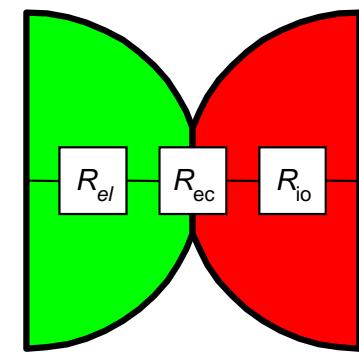
Charge transfer



Butler-Volmer law



$$R_{\text{el-io}} = R_{\text{el}} + R_{\text{ec}} + R_{\text{io}}$$



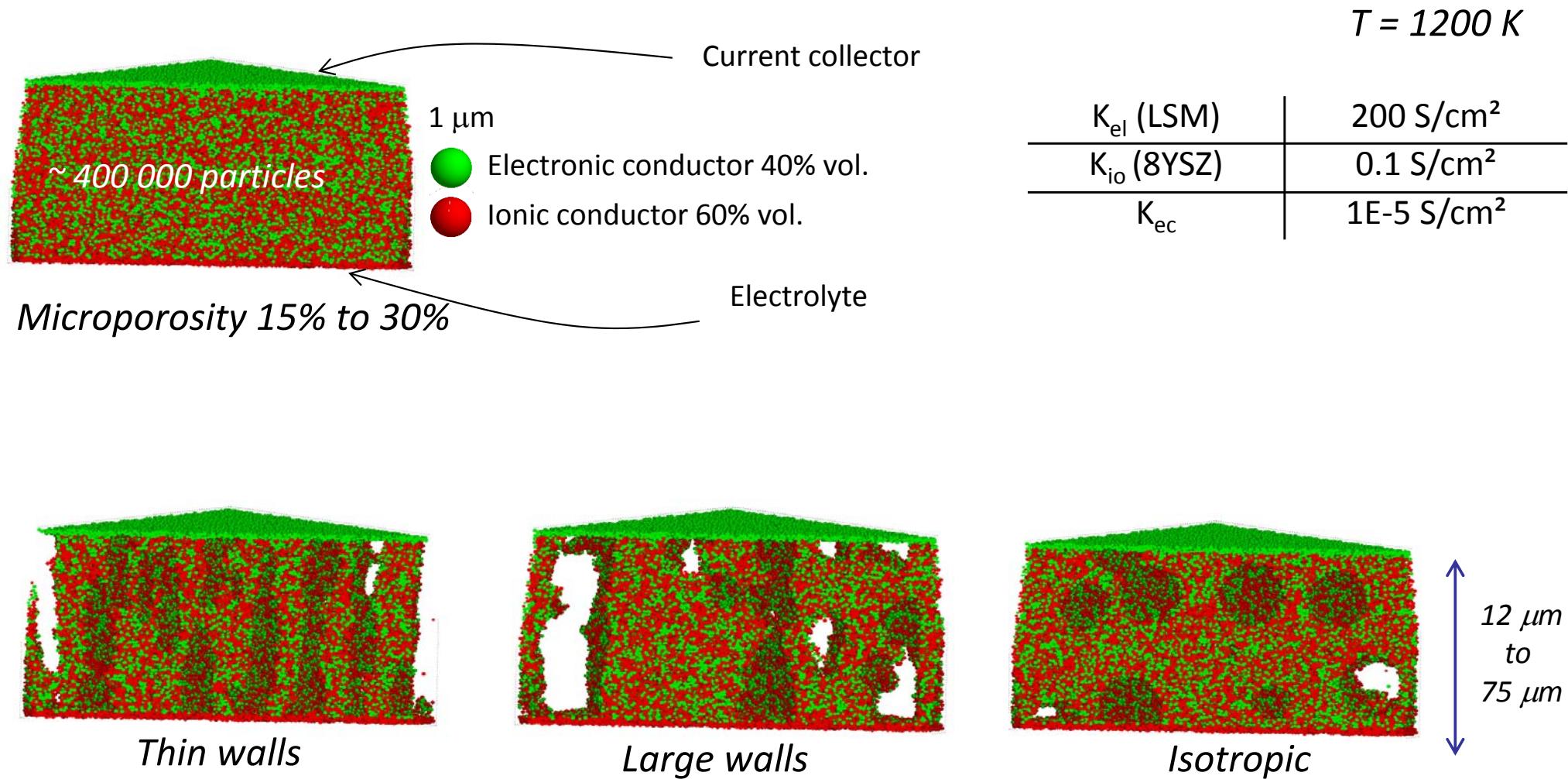
$$R_{\text{ec}} = \frac{1}{K_{\text{ec}}} \frac{1}{2\pi r_c}$$



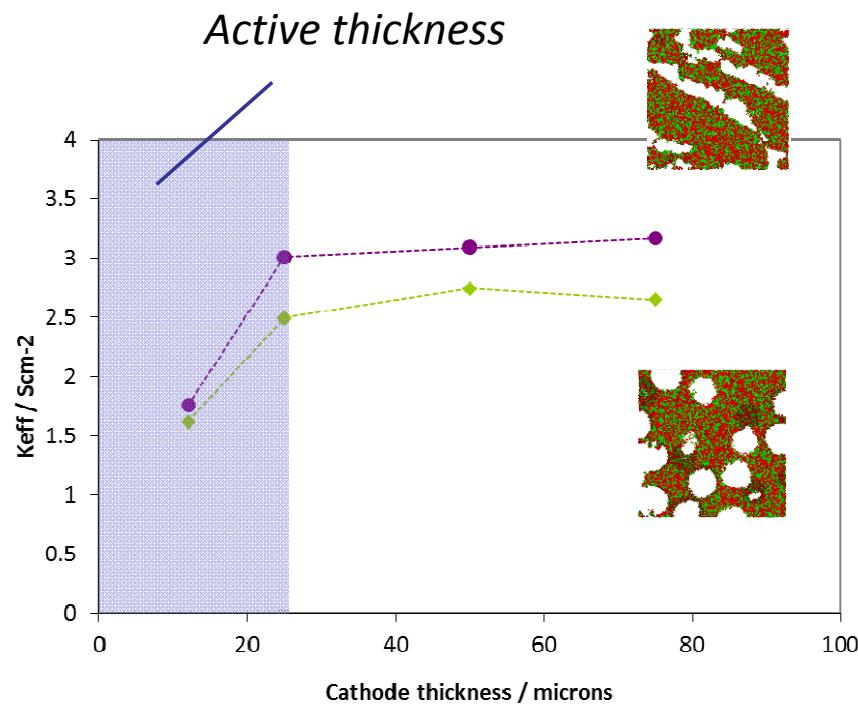
Assumption : gas transport is facile

Schneider, L. et al., *Electrochim. Acta* 52, 314–324 (2006).

- Numerical samples



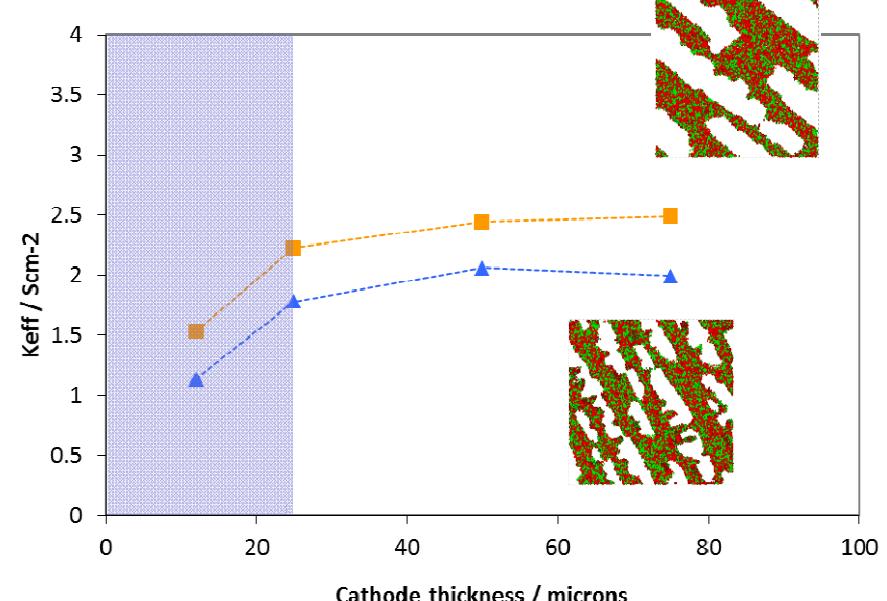
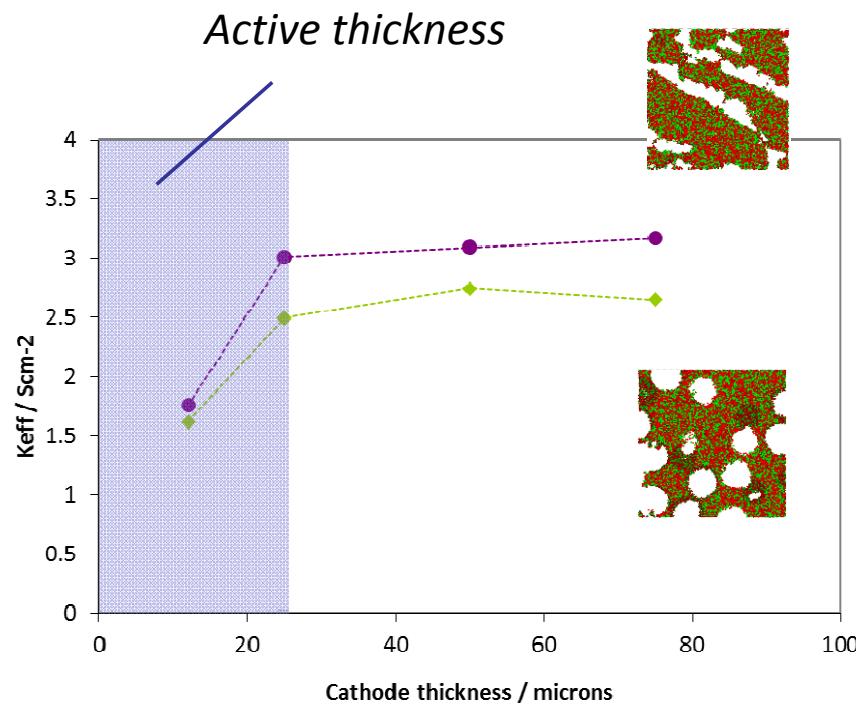
- Results : influence of macroporosity



Anisotropy performs better

$$K_{eff} (\text{Scm}^{-2}) = 1/\text{ASR} (\Omega\text{cm}^2)$$

- Results : influence of macroporosity

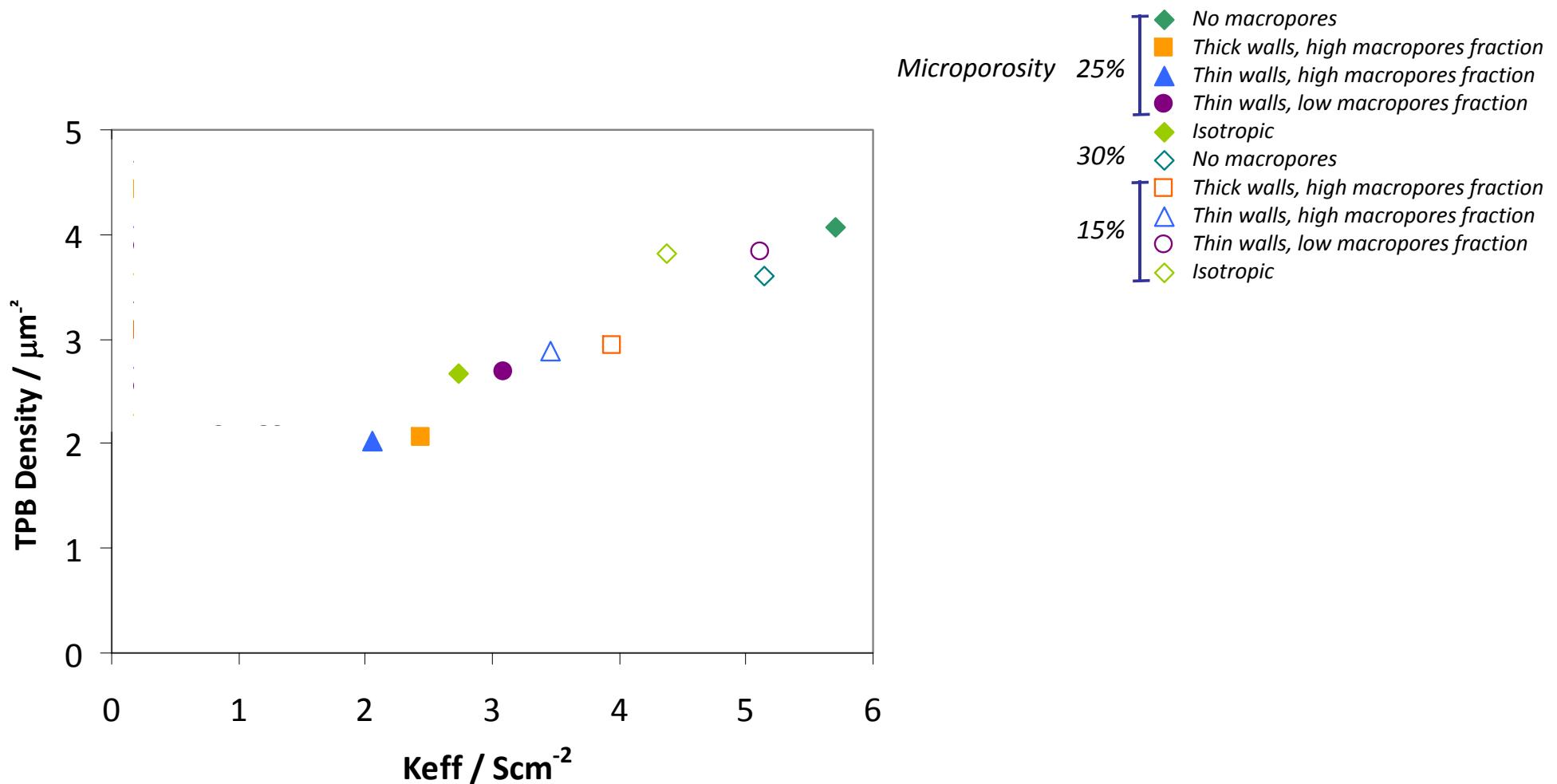


Anisotropy performs better

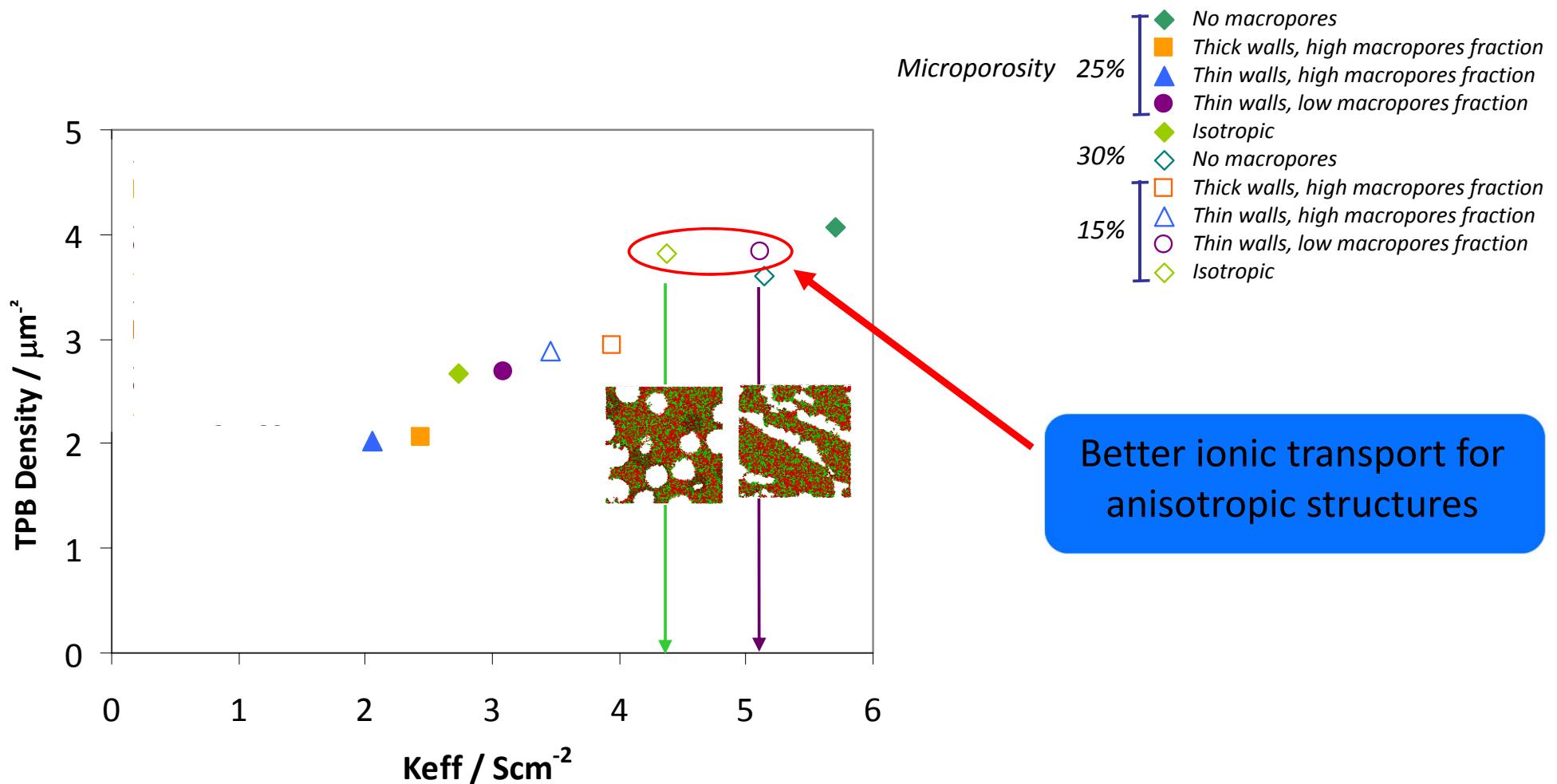
Thick walls perform better

$$K_{eff} (Scm^{-2}) = 1/ASR (\Omega cm^2)$$

- Results : correlation with TPB Density



- Results : correlation with TPB Density

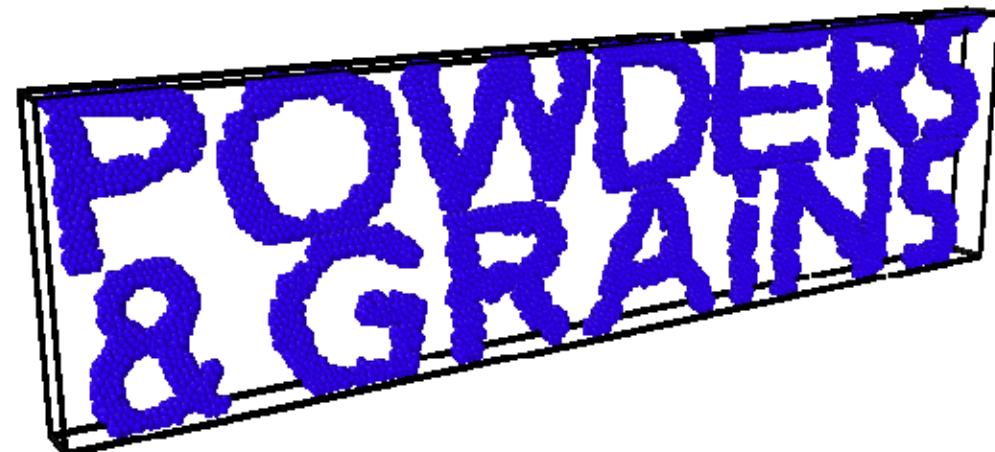


Performance is not governed only
by TPB density

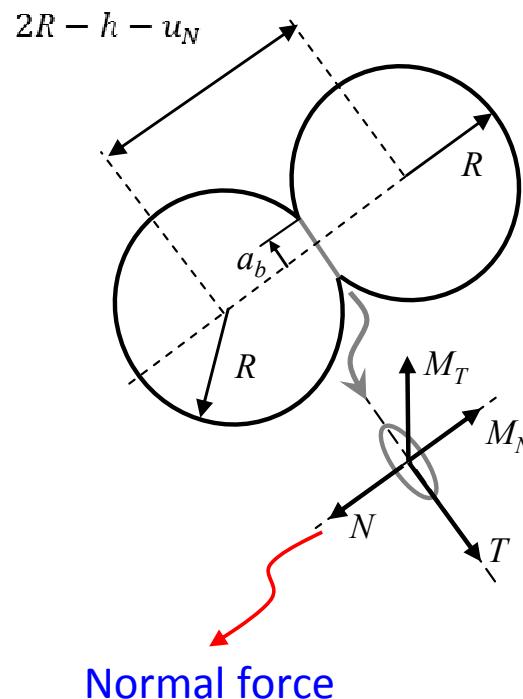
- Discrete Element Method to model fracture of porous materials
 - Each particle is represented by a **sphere**
 - The motion of **each particle** is dictated by the 2nd law of Newton
 - New contacts appear and contacts break **naturally**
 - The physics of the problem is embedded in the **contact law**
 - **Fracture** dictated by local failure criteria

In-house : dp3D

Open source : LIGGGHTS
(LAMMPS modified for granular)



- Solid neck between two particles → bond contact model



$$N = E_p \cdot f_N \left(\frac{a_b}{R}, \nu \right) a_b u_N$$

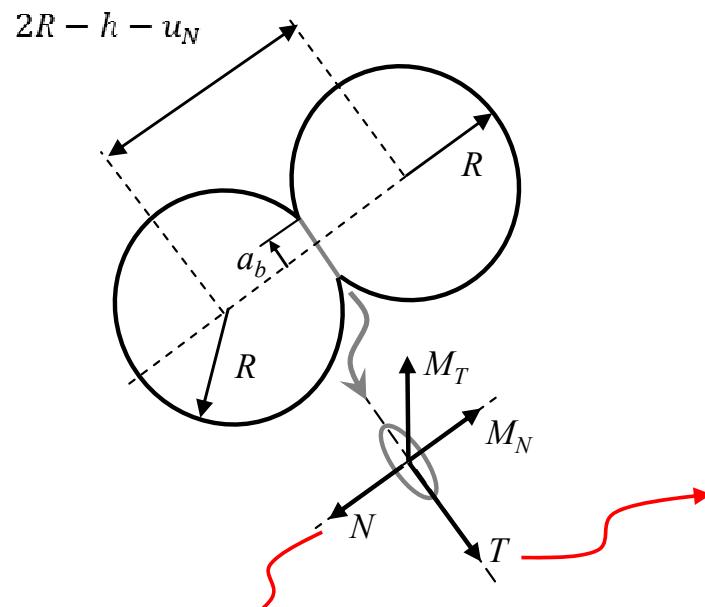
Finite element calculation

G. Jefferson et al., 2002, J Mech Phys Solids, 50 2539-75

D.O. Potyondy and P.A. Cundall, 2004, Int J Rock Mech & Mining Sci 41, 329-1364

D. Jauffres et al., 2012, MSMSE 20, 045009

- Solid neck between two particles → bond contact model



Normal force

$$N = E_p' f_N \left(\frac{a_b}{R}, v \right) a_b u_N$$

Tangential force

$$T = -E_p'' f_T \left(\frac{a_b}{R}, v \right) a_b u_T$$

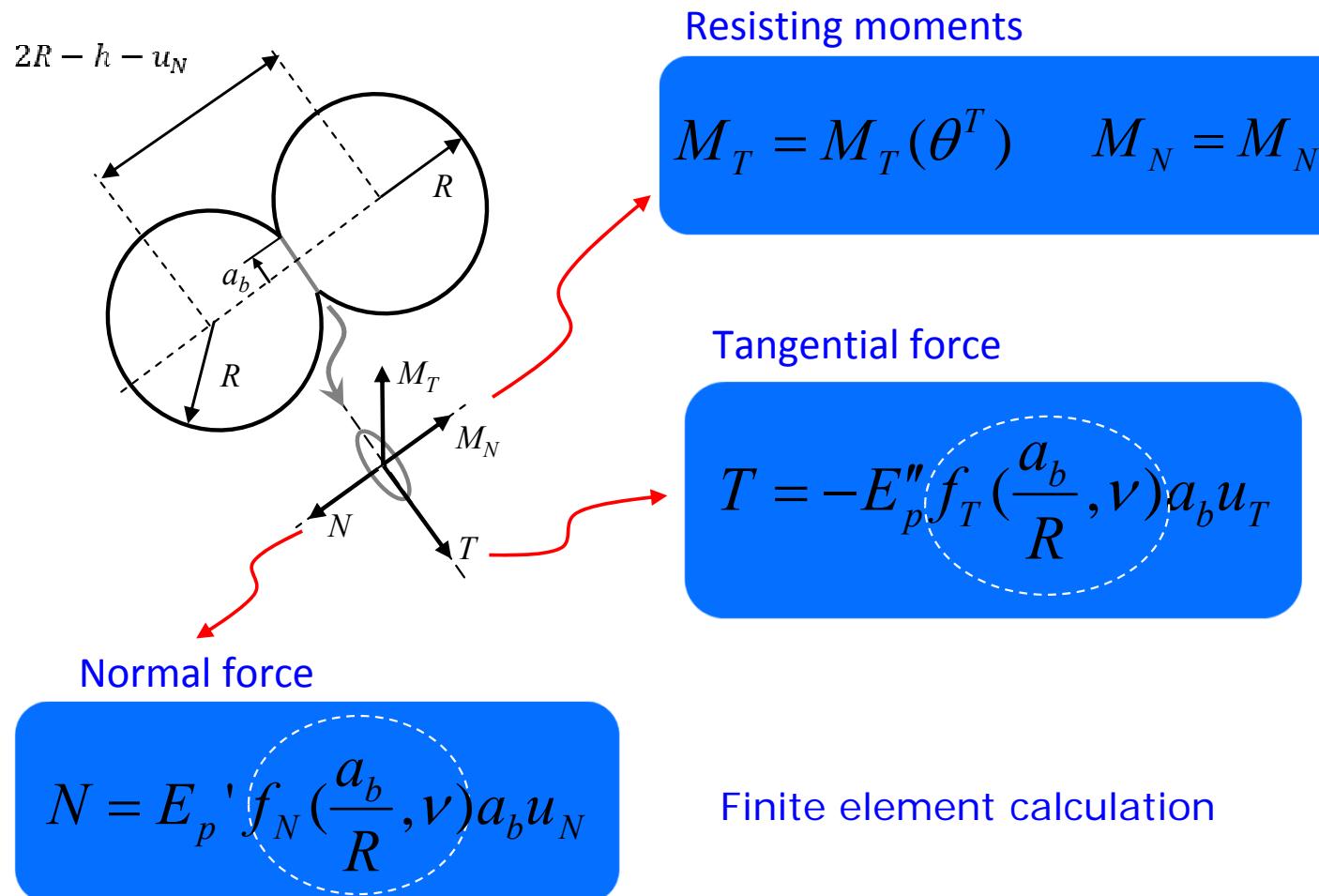
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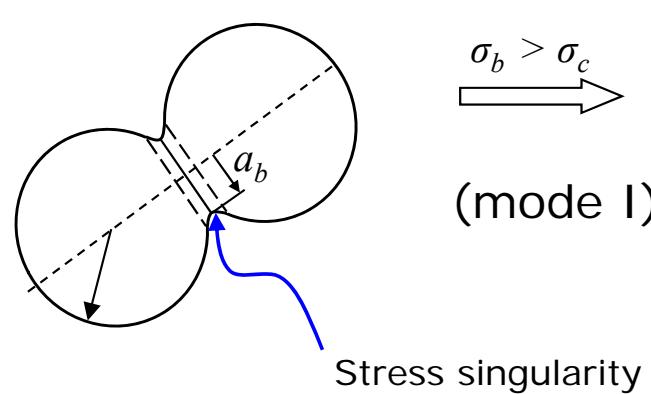
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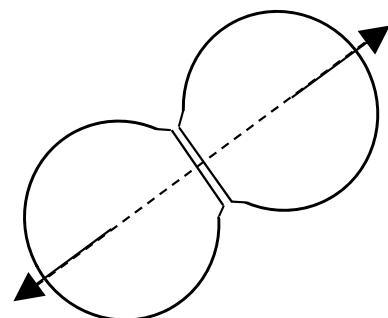
G. Jefferson et al., 2002, J Mech Phys Solids, 50 2539-75
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 D. Jauffres et al., 2012, MSMSE 20, 045009

- Solid neck between two particles → bond fracture criteria



$$\sigma_b > \sigma_c$$

(mode I)

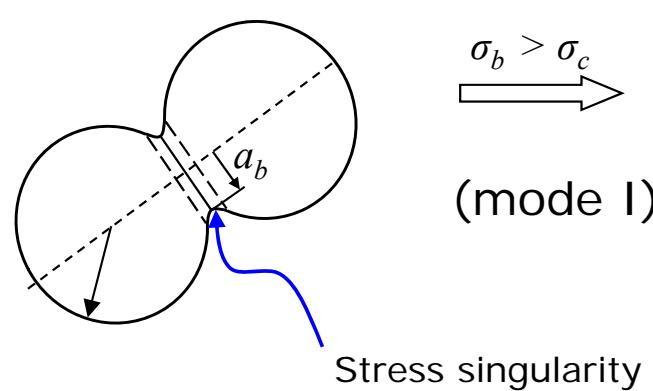


Fracture energy
 $\Gamma = 2\gamma_s \sim 2J/m^2$

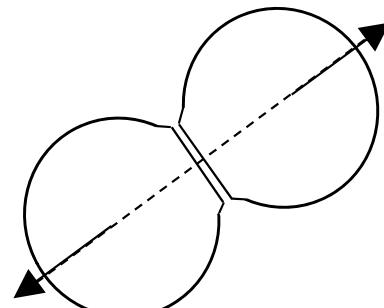
$$\sigma_c = 2 \sqrt{\frac{E_p}{1-\nu_p^2} \frac{\Gamma}{\pi a_b}} f_N$$

D. Jauffres et al., 2012, Acta Mat 60, 4685-4694

- Solid neck between two particles → bond fracture criteria



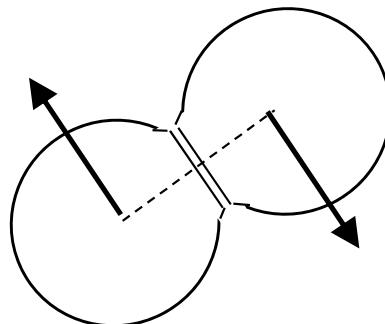
(mode I)



Fracture energy
 $\Gamma = 2\gamma_s \sim 2J/m^2$

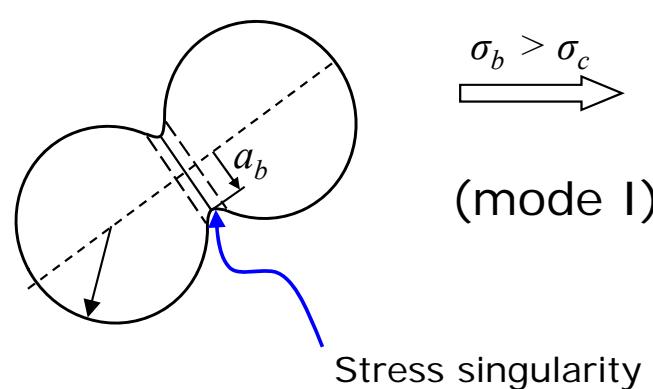
$$\sigma_c = 2 \sqrt{\frac{E_p}{1-\nu_p^2} \frac{\Gamma}{\pi a_b}} f_N$$

- + Similar in tangential mode (mode II)



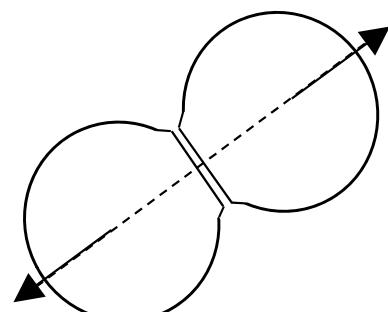
D. Jauffres et al., 2012, Acta Mat 60, 4685-4694

- Solid neck between two particles → bond fracture criteria



$\sigma_b > \sigma_c$

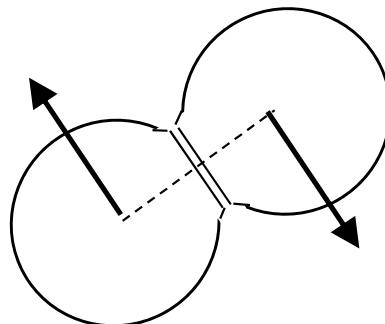
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Fracture energy
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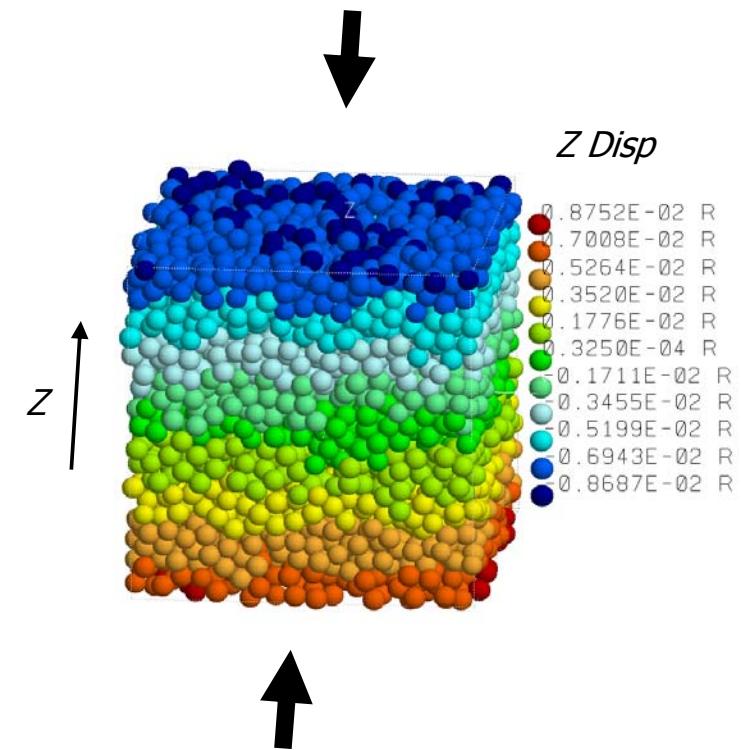
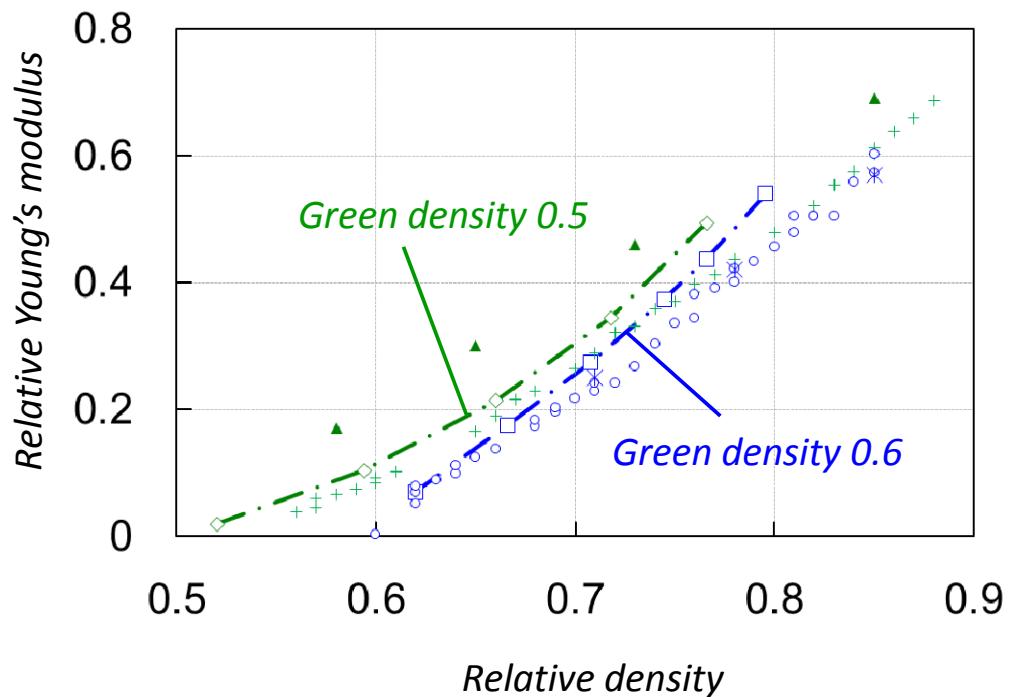


material parameters

- elasticity (E_p, ν_p) of particles
- Γ
- porosity ($\rightarrow a_b$)

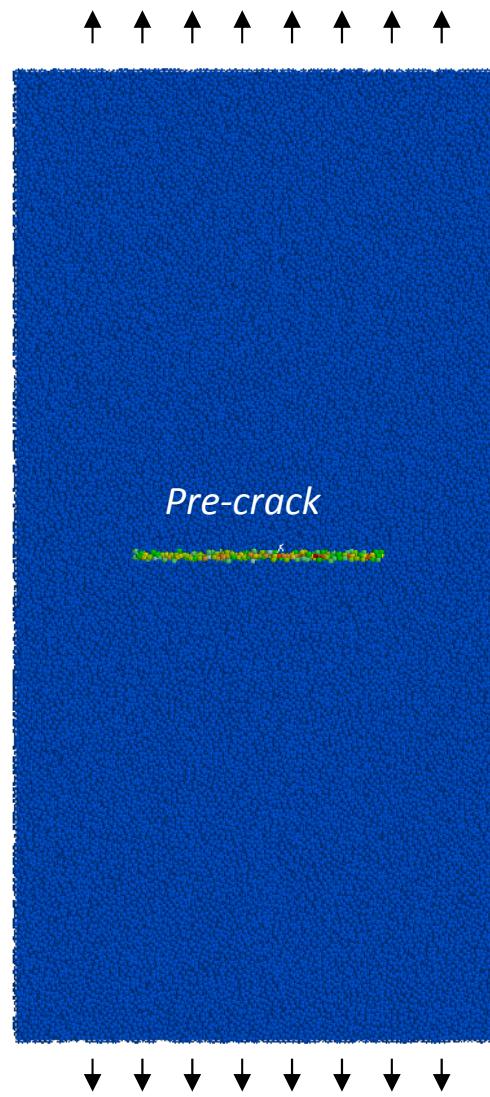
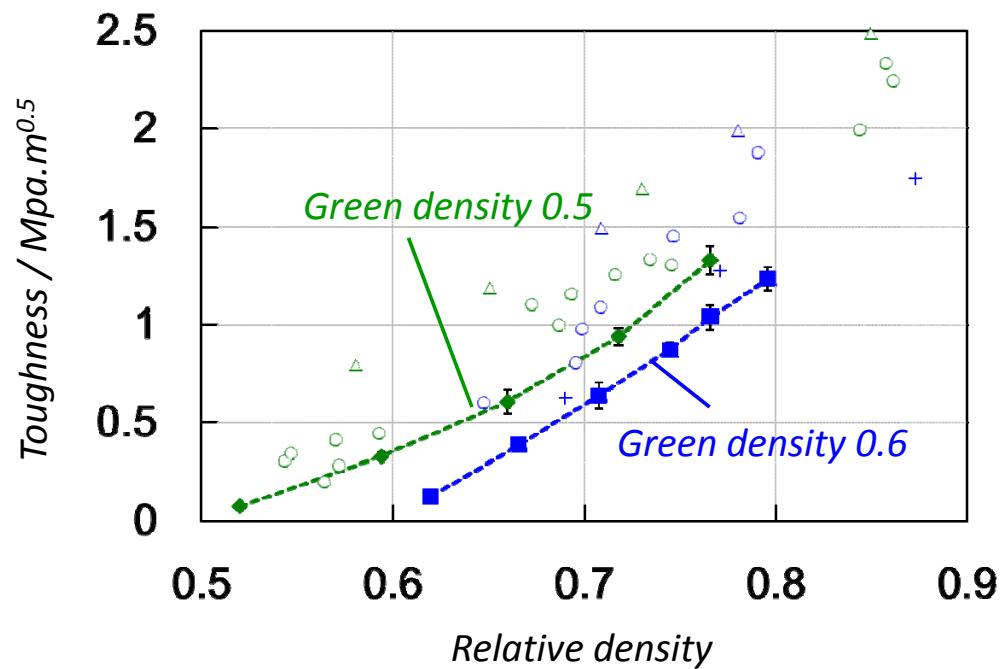
D. Jauffres et al., 2012, Acta Mat 60, 4685-4694

- Validation: elasticity



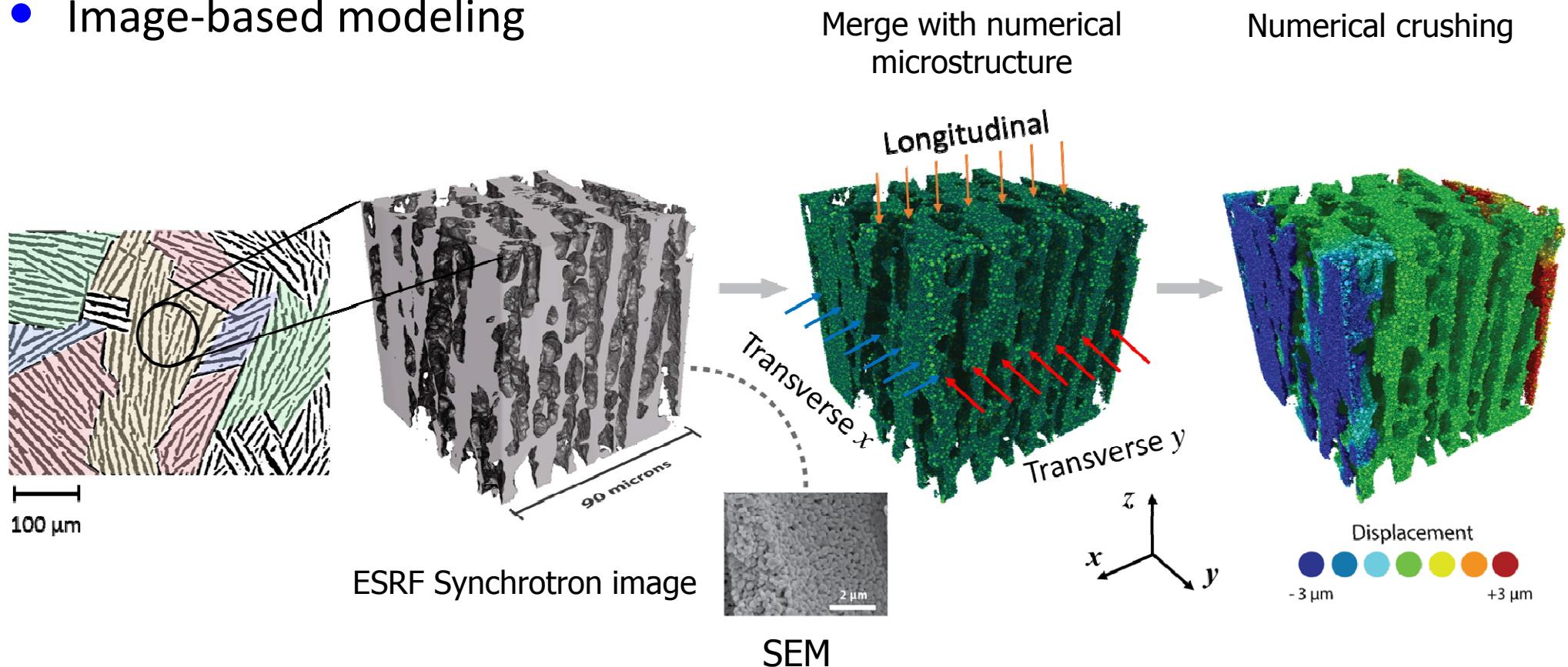
D. Jauffres et al., 2012, MSMSE 20, 045009

- Validation: toughness



D. Jauffres et al., 2012, Acta Mat 60, 4685-4694

- Image-based modeling

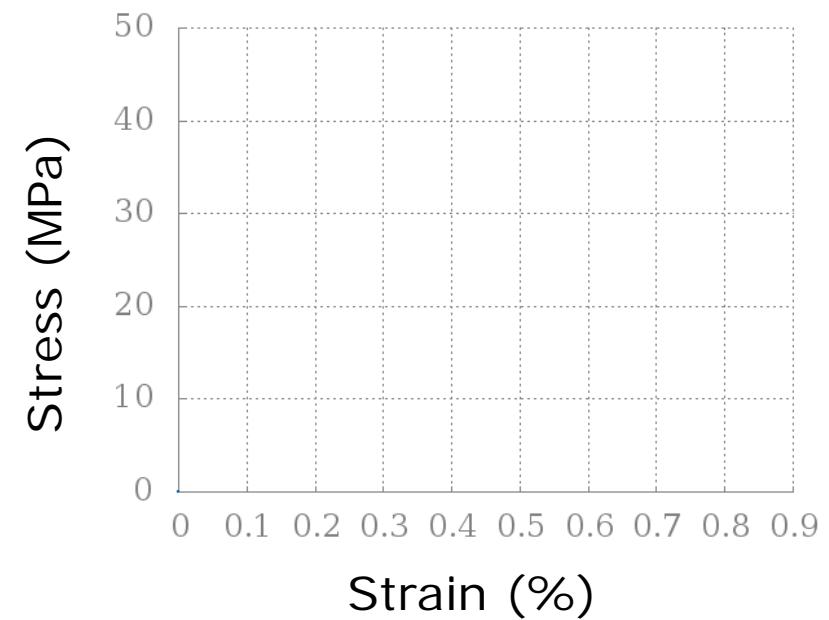
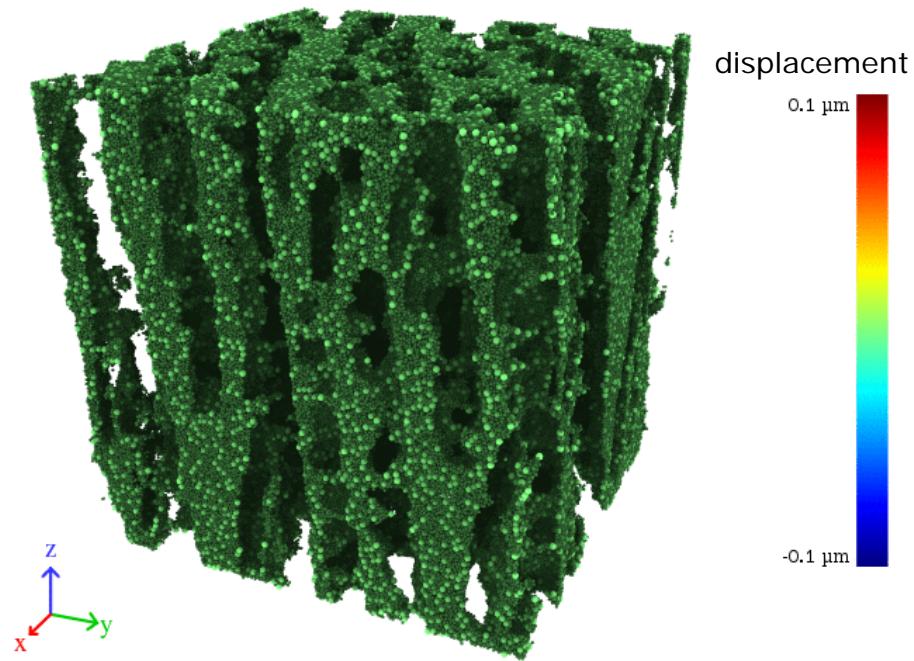


D. Roussel, et al., *Scr. Mater.*, **113** 250–253 (2016)

Mixture of YSZ and LSM particles

| E (LSM) | E (YSZ) | γ_s (J/m ²) | $2R$ (LSM) | $2R$ (YSZ) |
|-----------|-----------|--------------------------------|-----------------|-------------------|
| 130 GPa | 220 GPa | 0.5 | 1 μm | 0.5 μm |

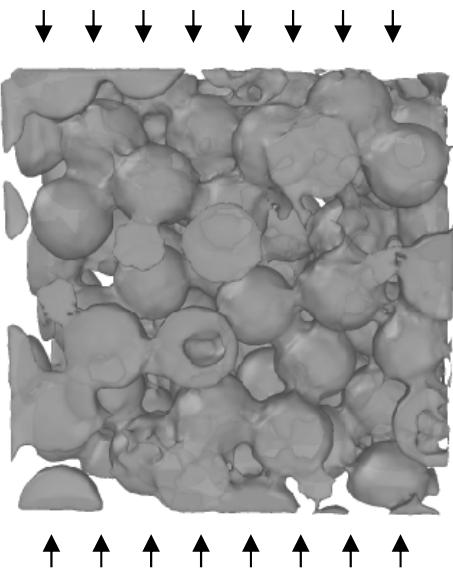
- Compression



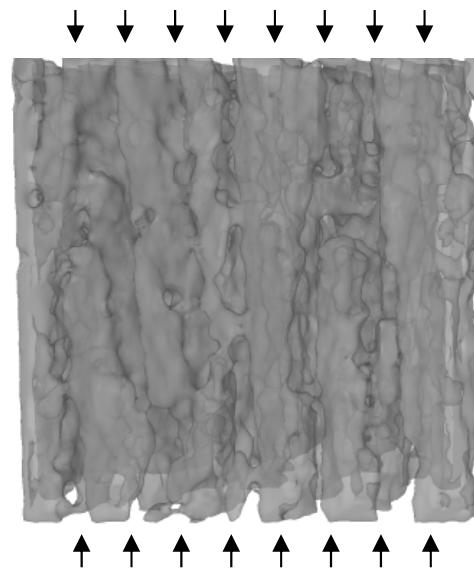
D. Roussel, et al., *Scr. Mater.*, 113 250–253 (2016)

- Damage evolution

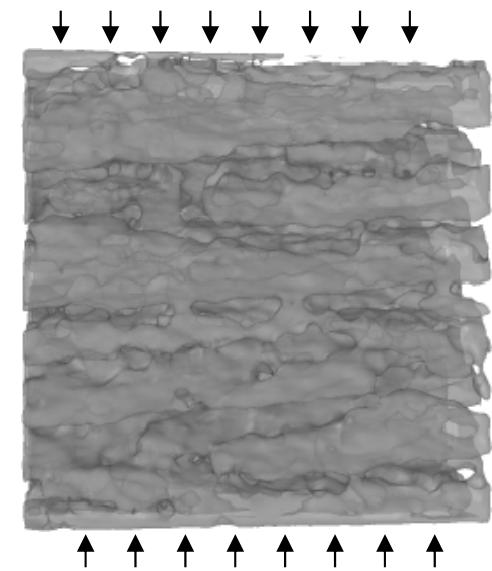
Isotropic structure
Pore formers



Anisotropic structure
Longitudinal

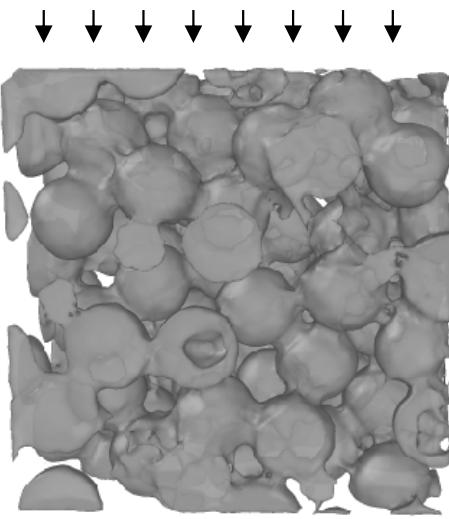


Anisotropic structure
Transverse y (weak)

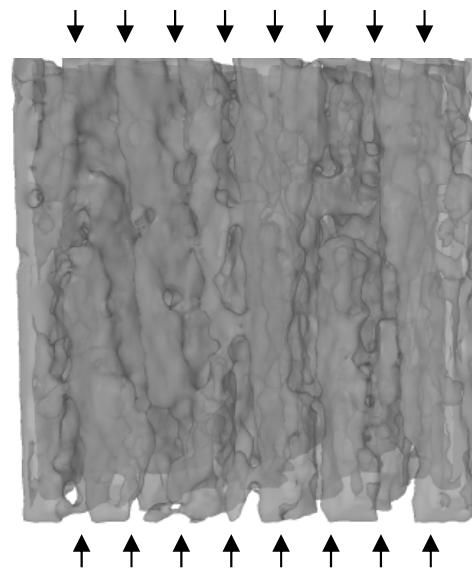


- Damage evolution

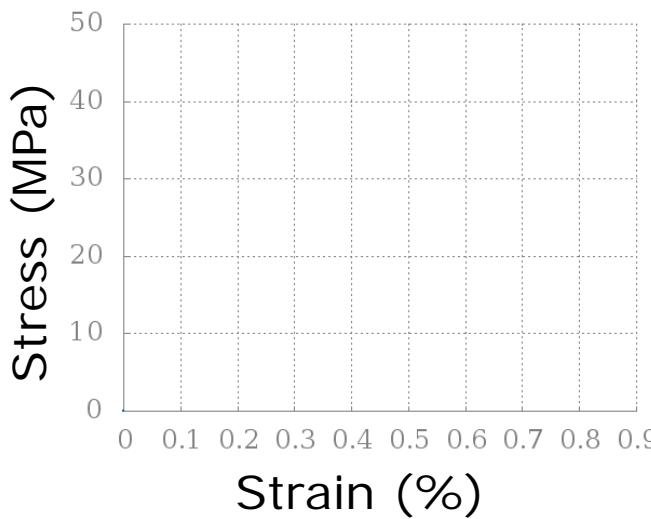
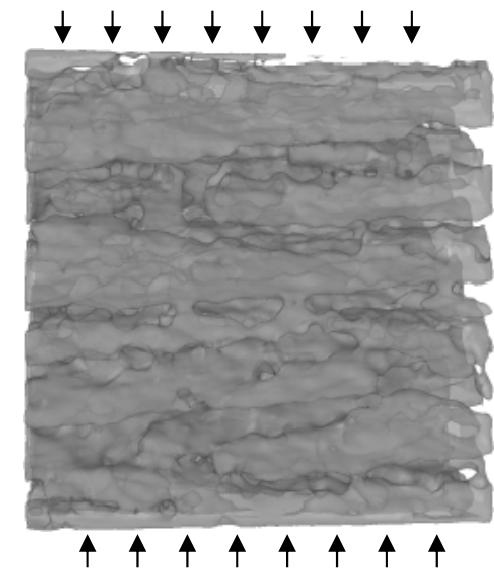
Isotropic structure
Pore formers



Anisotropic structure
Longitudinal

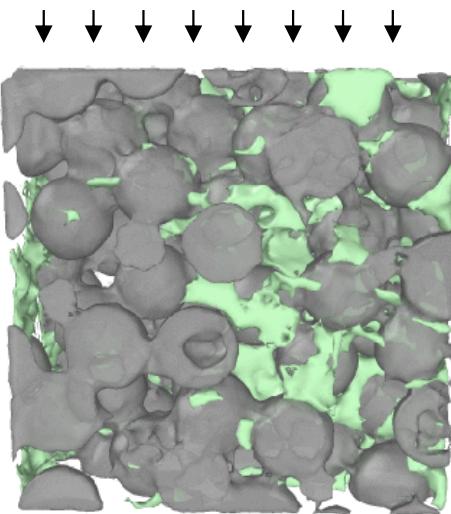


Anisotropic structure
Transverse y (weak)

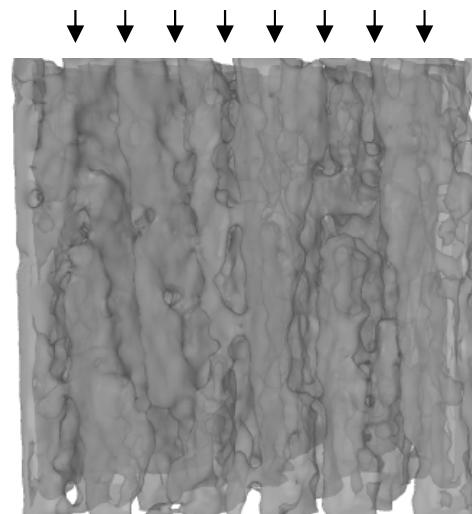


- Damage evolution

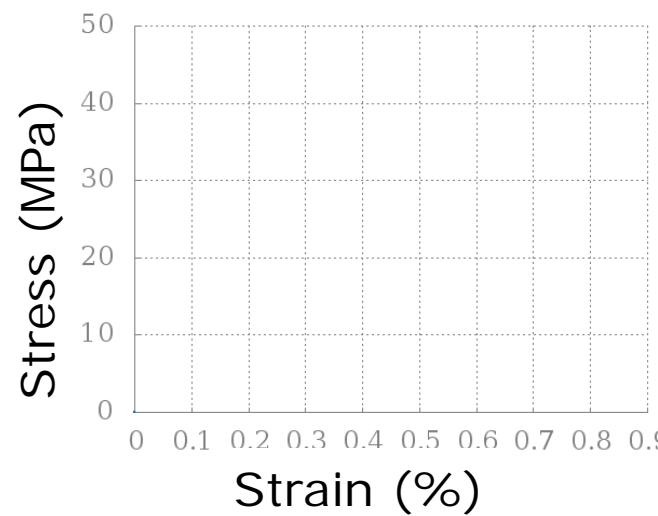
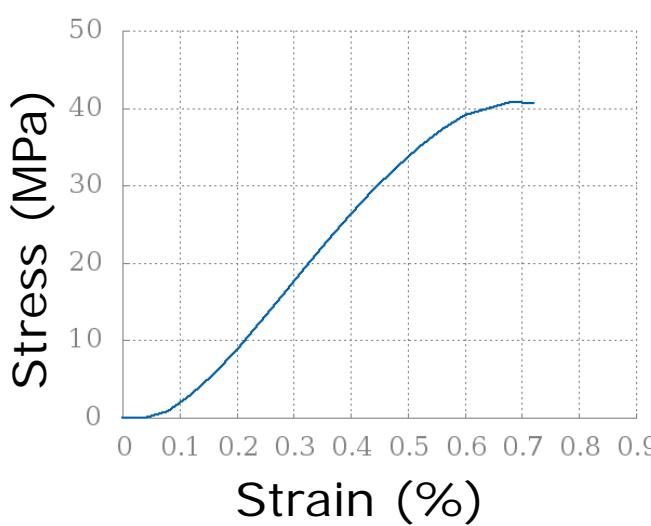
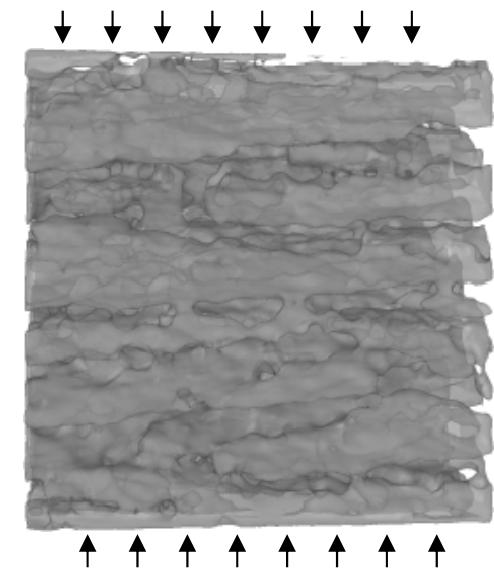
Isotropic structure
Pore formers



Anisotropic structure
Longitudinal

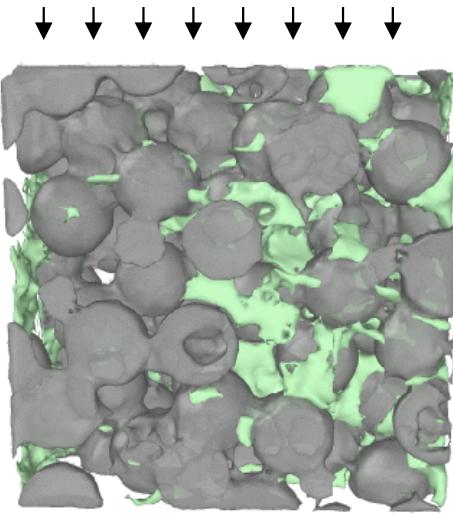


Anisotropic structure
Transverse y (weak)

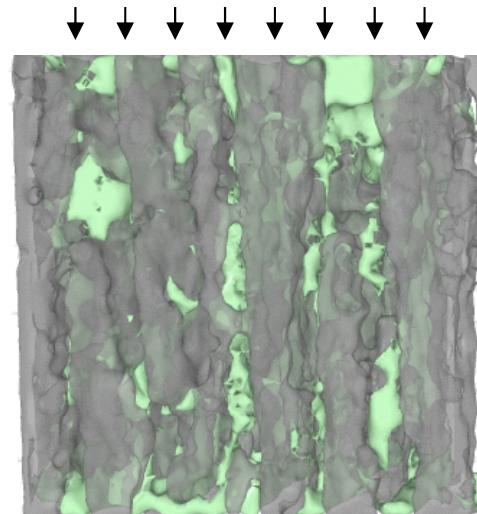


- Damage evolution

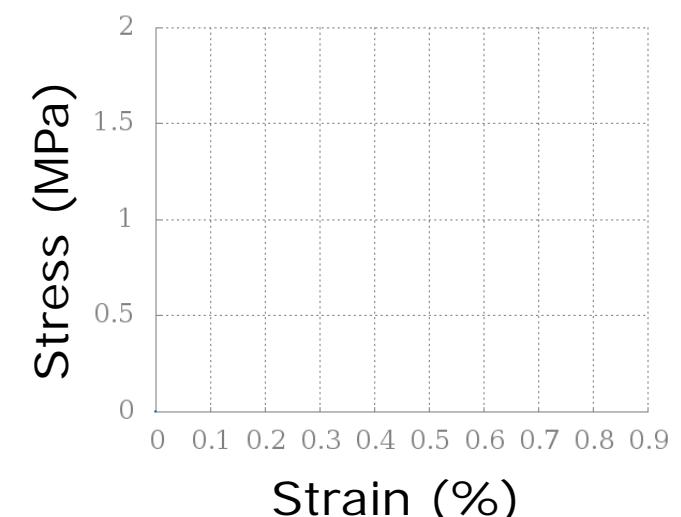
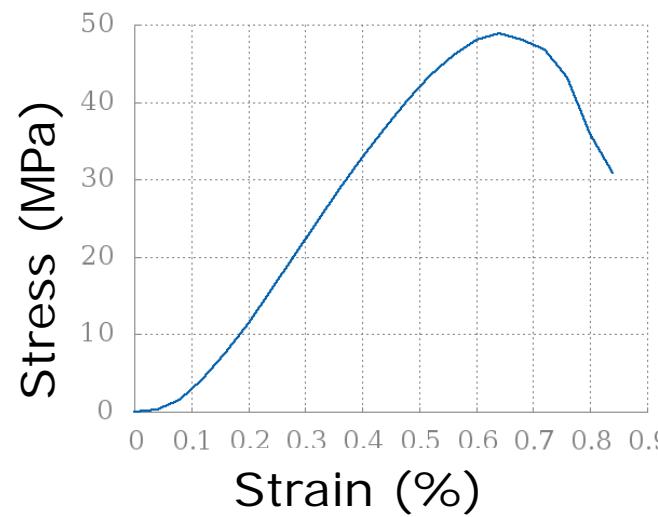
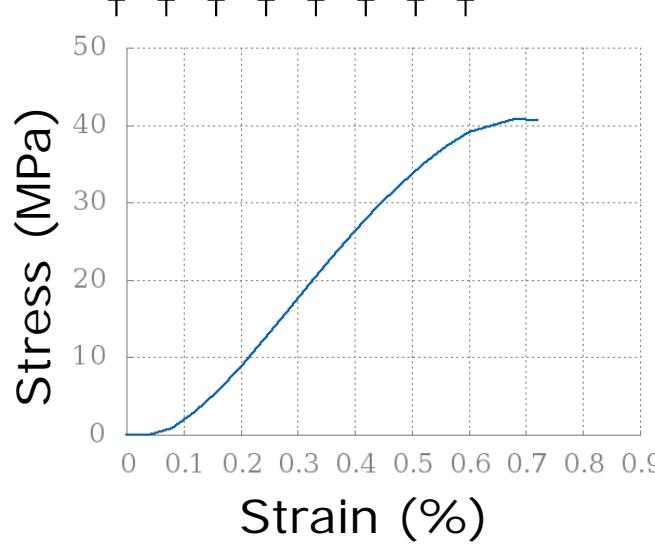
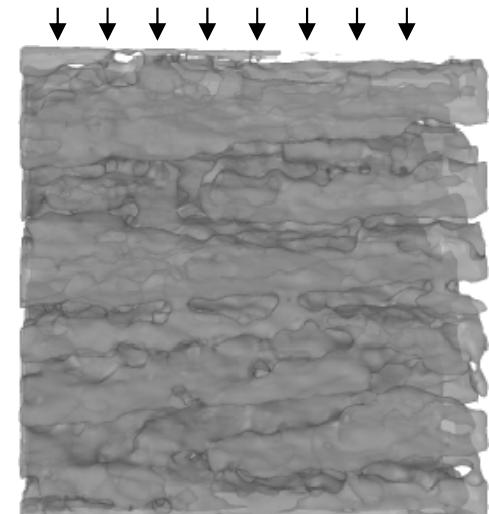
Isotropic structure
Pore formers



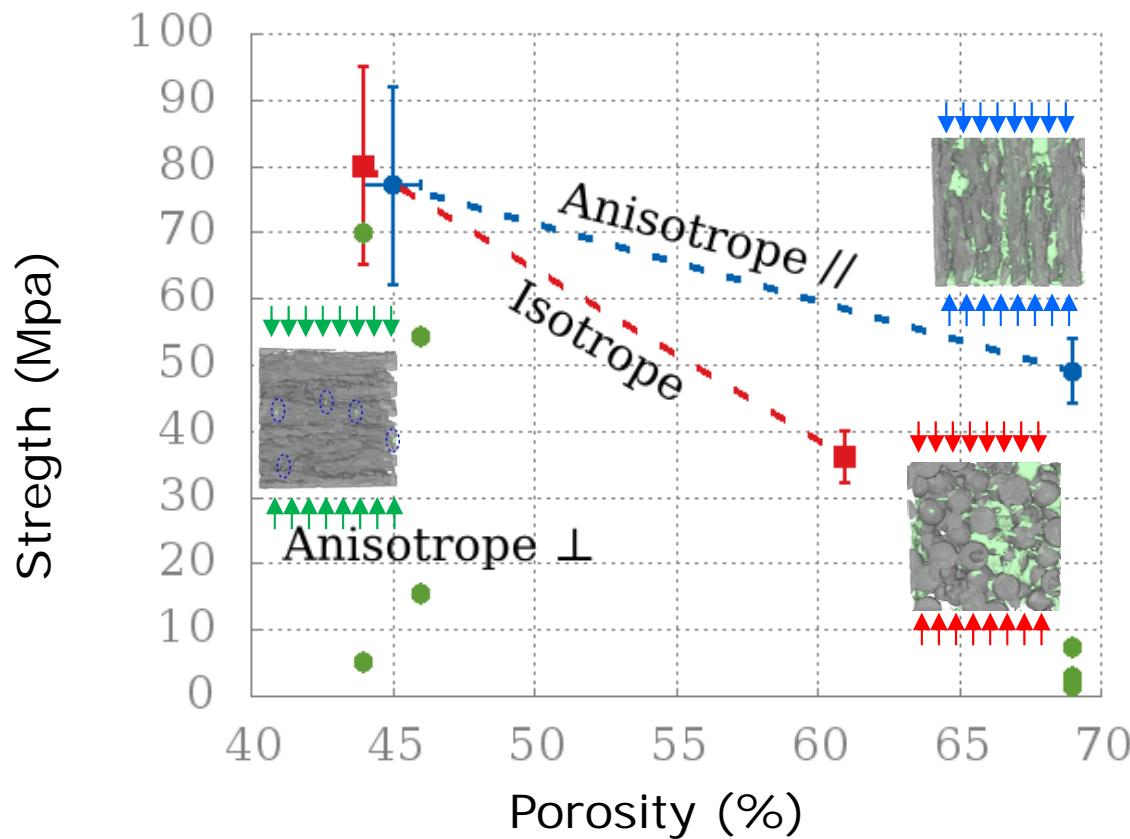
Anisotropic structure
Longitudinal



Anisotropic structure
Transverse y (weak)

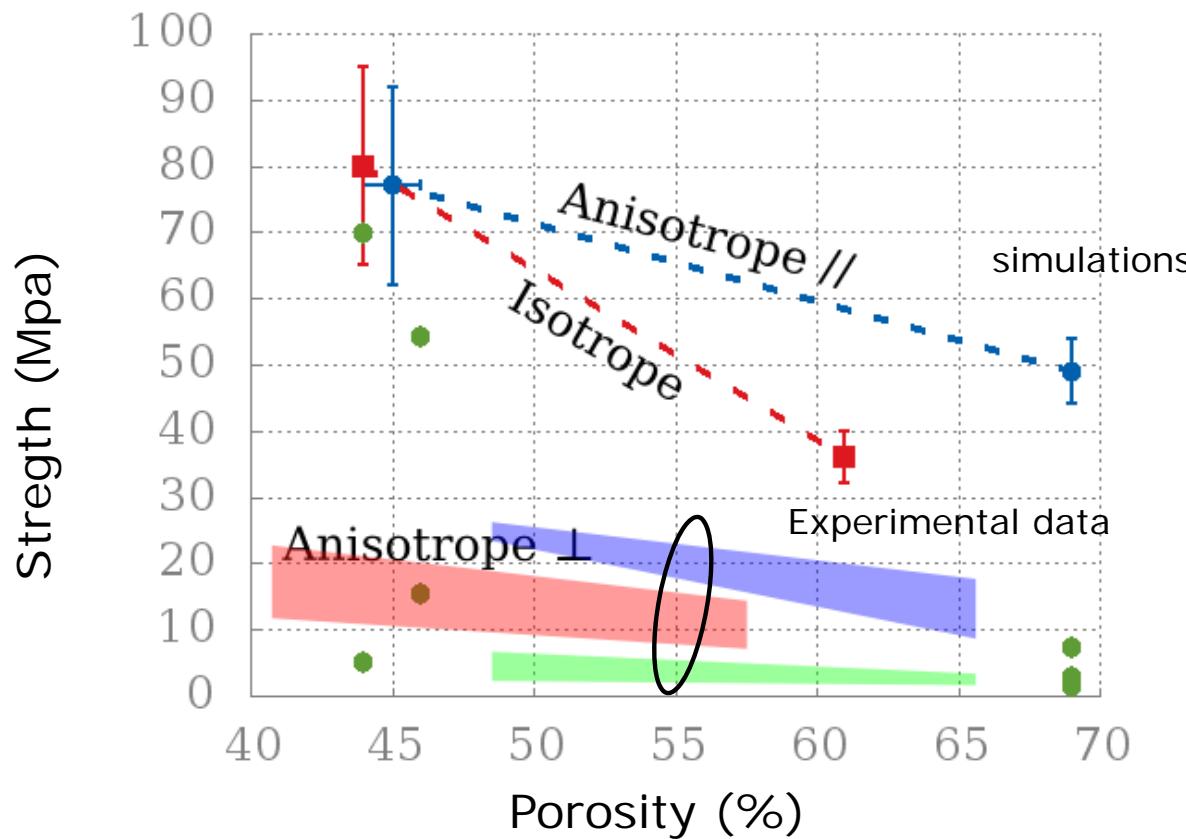


- Comparison with experiment



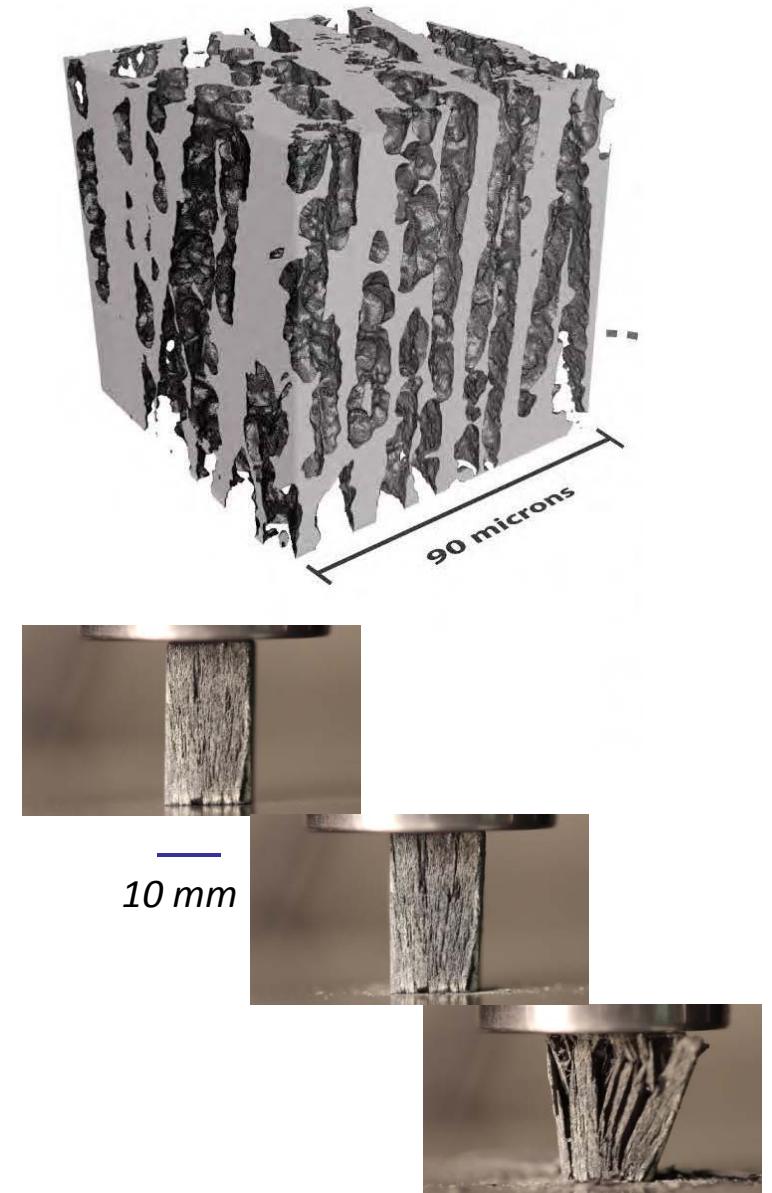
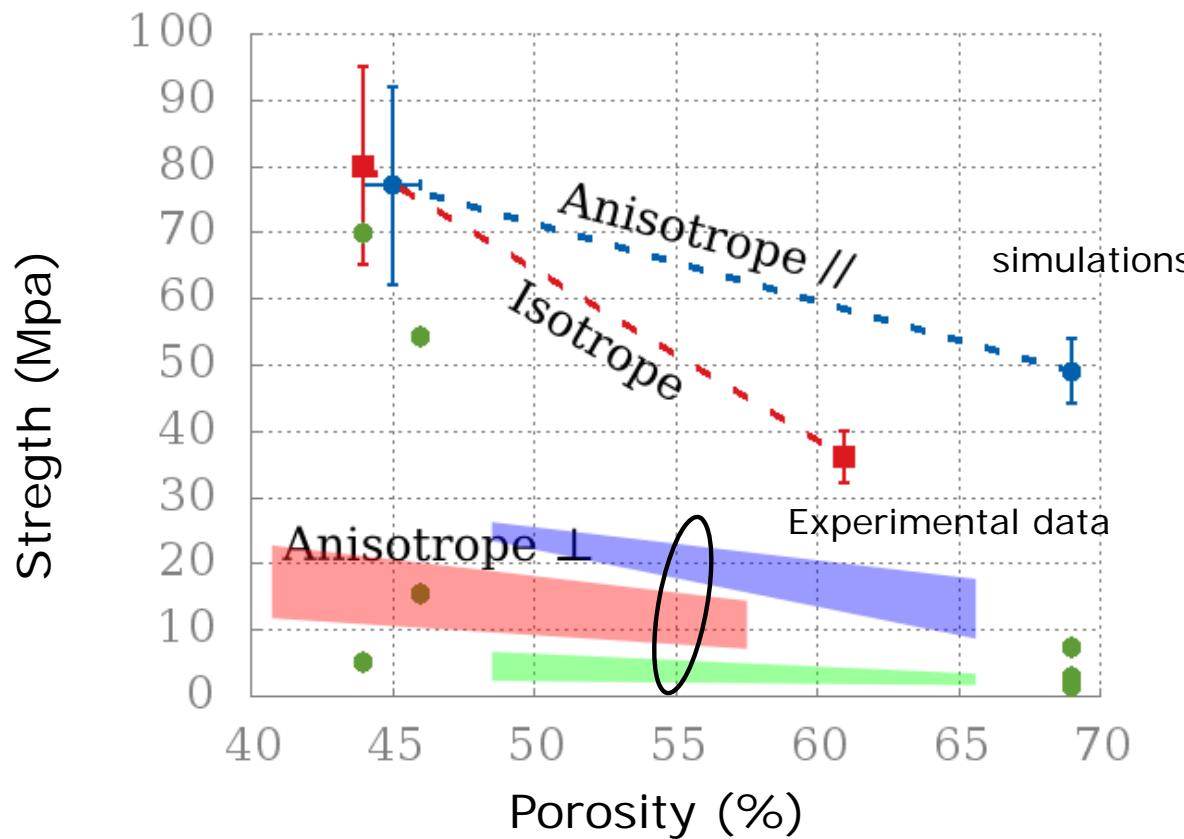
D. Roussel, et al., Scr. Mater., 113 250–253 (2016)

- Comparison with experiment



D. Roussel, et al., Scr. Mater., 113 250–253 (2016)

- Comparison with experiment

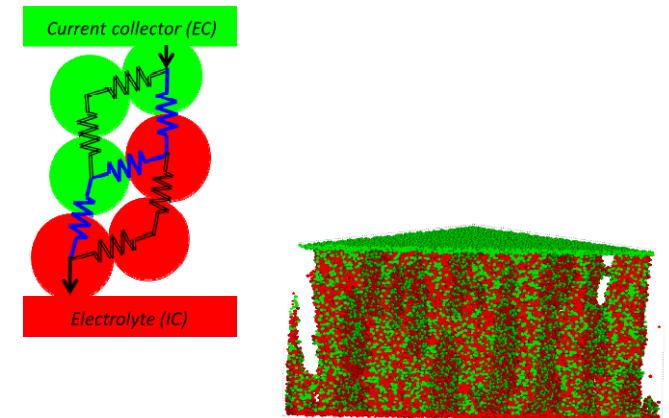


- Simulation overestimates fracture strength
- No fitting parameters
- Sample volume matters for fracture
- Weibull-like law $V_1\sigma_1^m = V_2\sigma_2^m \Rightarrow m \sim 9$

Keleş, Ö. et al., Acta Mater. 61, 2853–2862 (2013).

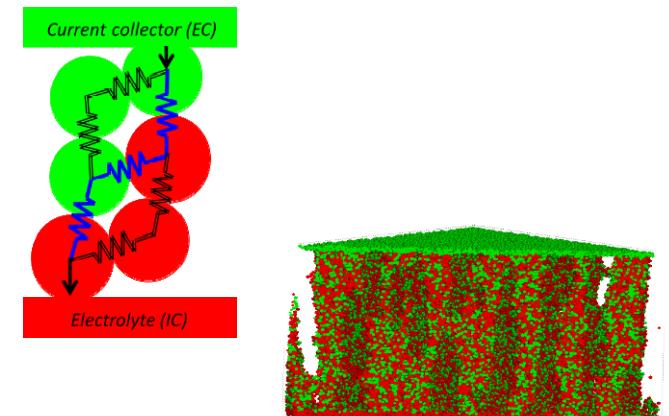
- Electrochemical simulations

- ✓ Model: resistance network with charge transfer resistance
- ✓ Comparison with FFT model on FIB-SEM 3D image
- ✓ Influence of macroporosity morphology on performance
- ✓ Prospects: comparison with experiment, coupling with gas transport model



- Electrochemical simulations

- ✓ Model: **resistance network** with **charge transfer resistance**
- ✓ Comparison with FFT model on FIB-SEM 3D image
- ✓ Influence of macroporosity morphology on performance
- ✓ Prospects: **comparison with experiment, coupling with gas transport model**



- Mechanical simulations

- ✓ Model: elastic bond + fracture criteria, **no fitting parameters**
- ✓ Validation by comparison with experimental data (elasticity, toughness)
- ✓ Strength of hierarchical porous materials: **volume matters**
- ✓ Prospect: modeling nacre-like ceramics using FIB-SEM images

