Stanford University

Surface-Modified Electrodes: Enhancing Performance Guided by In-situ Spectroscopy and Microscopy

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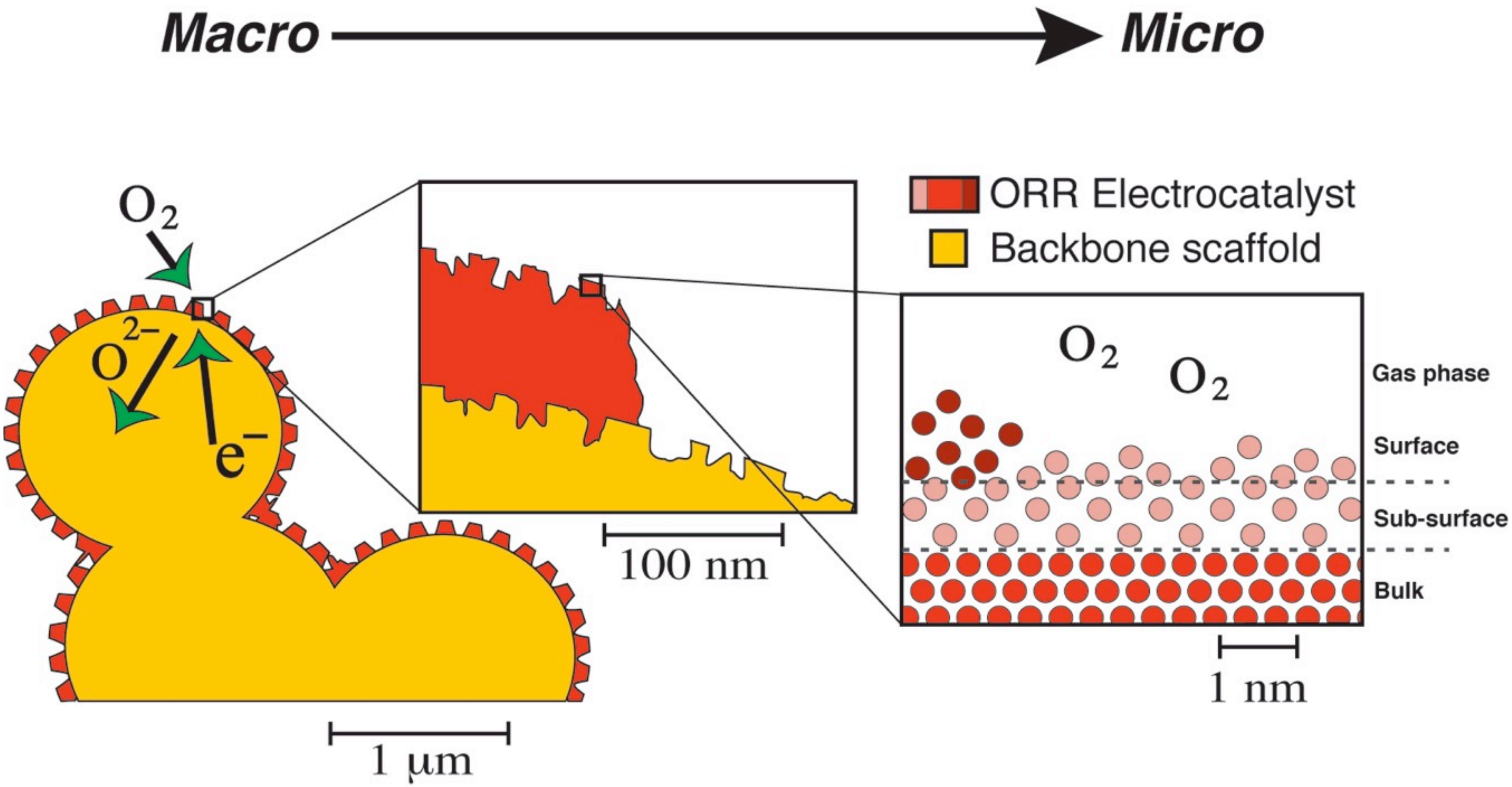
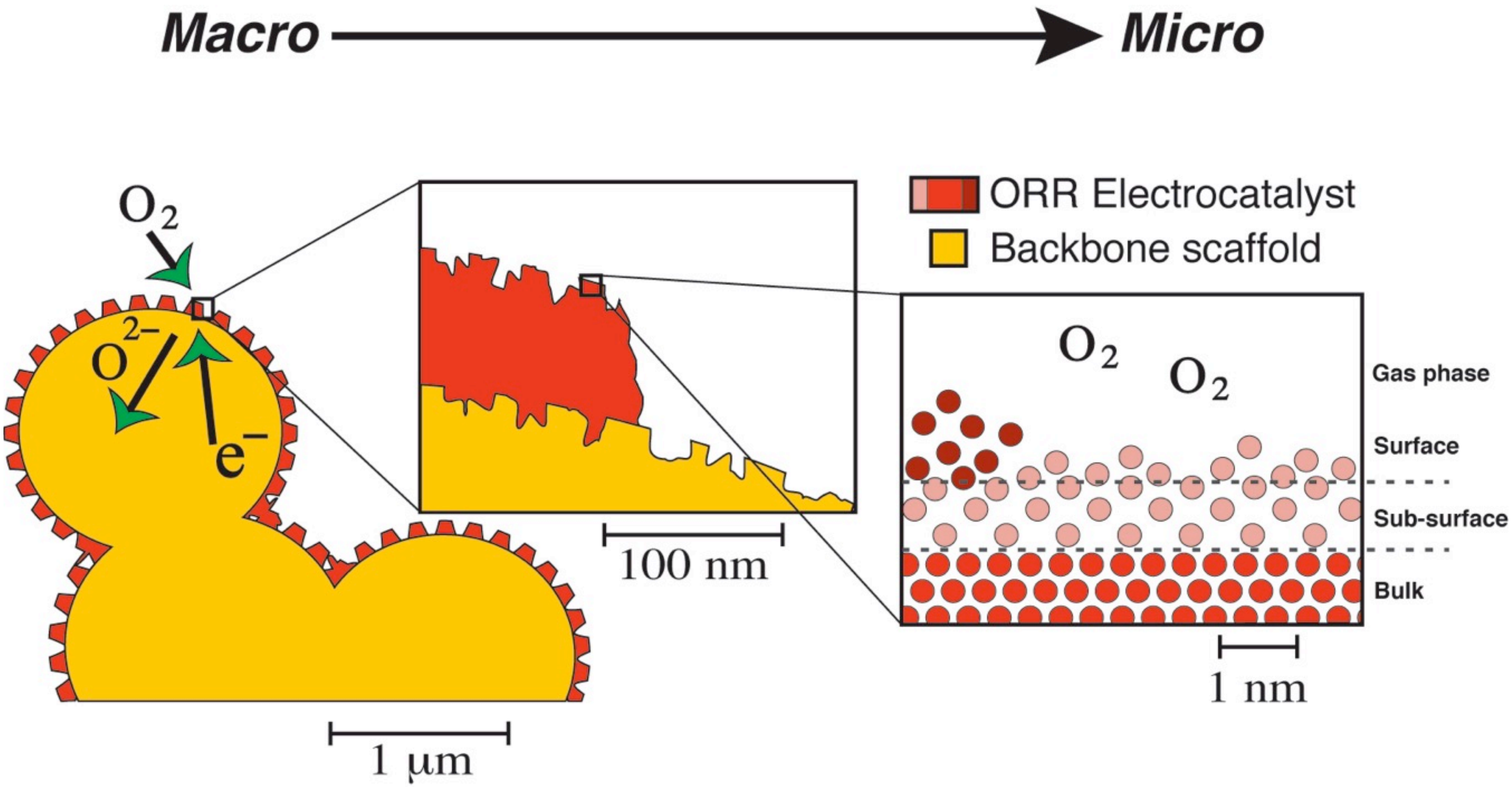


Macro
Micro
ORR Electrocatalyst
Backbone scaffold
O2
O2−
e−
1 μm
100 nm
O2
O2
Gas phase
Surface
Sub-surface
Bulk
1 nm



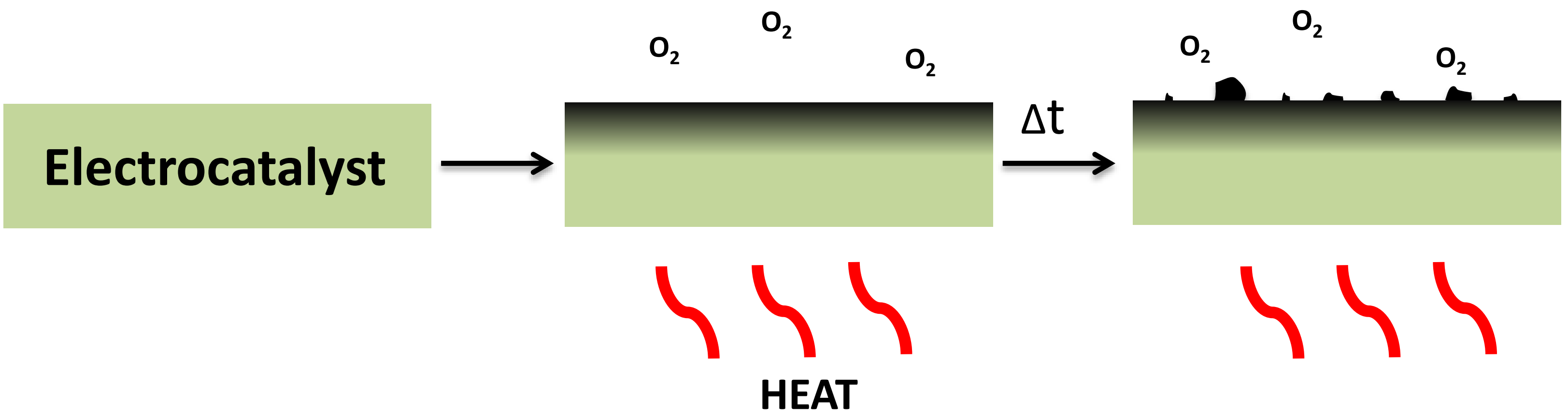
What's the nature of the active site?

What controls ORR activity and stability?

Unintentional surface rearrangement

Intrinsic

natural segregation of cations and precipitation of secondary phase



Szot, K.; Speier, W. *Phys. Rev. B* **60** (1999) 5909

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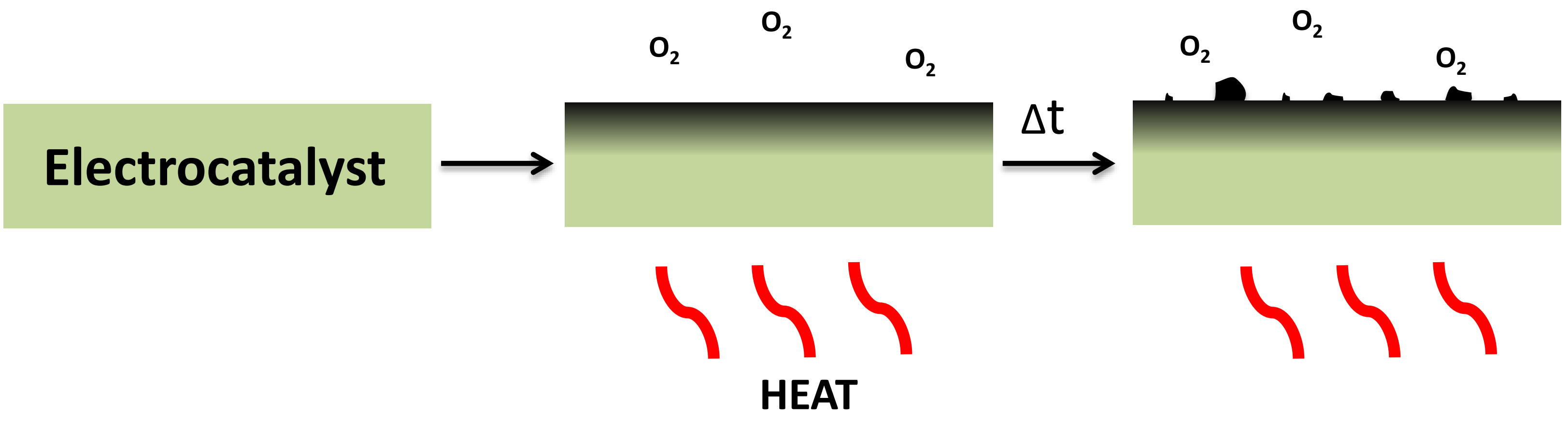

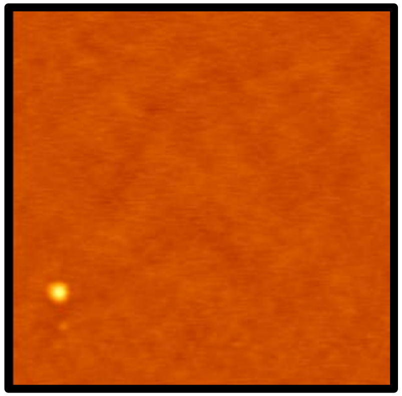

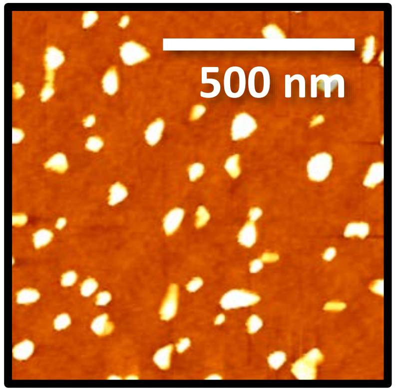

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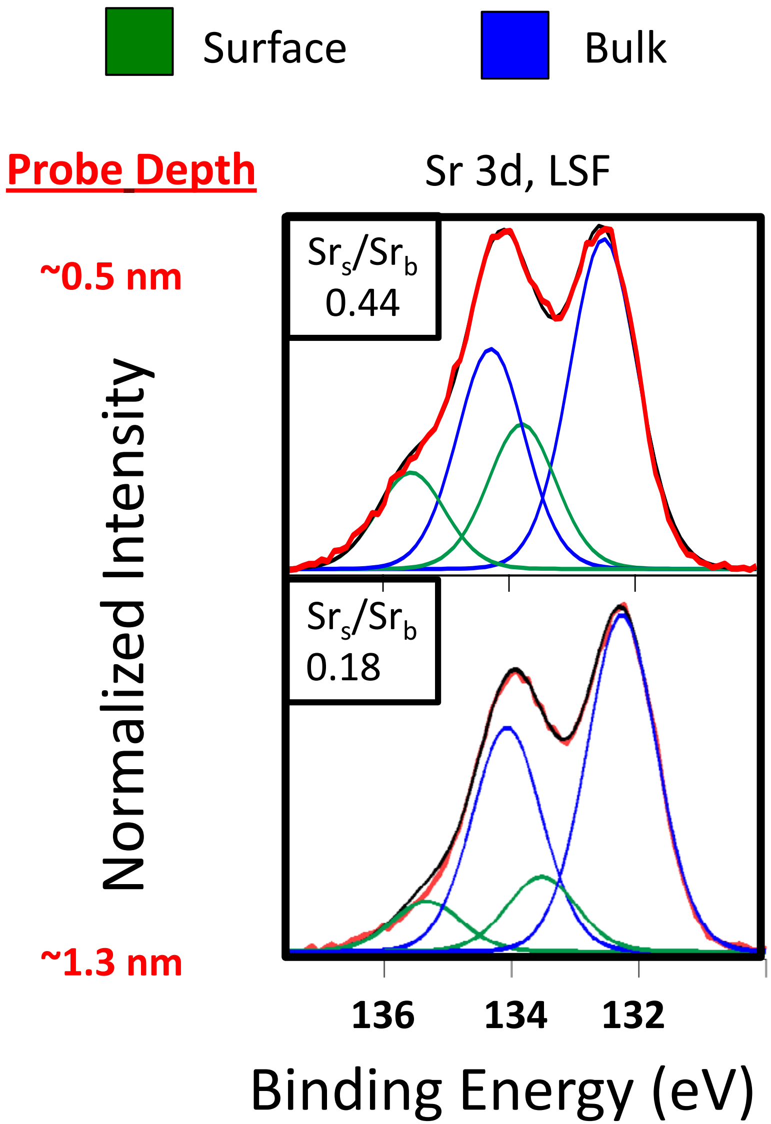
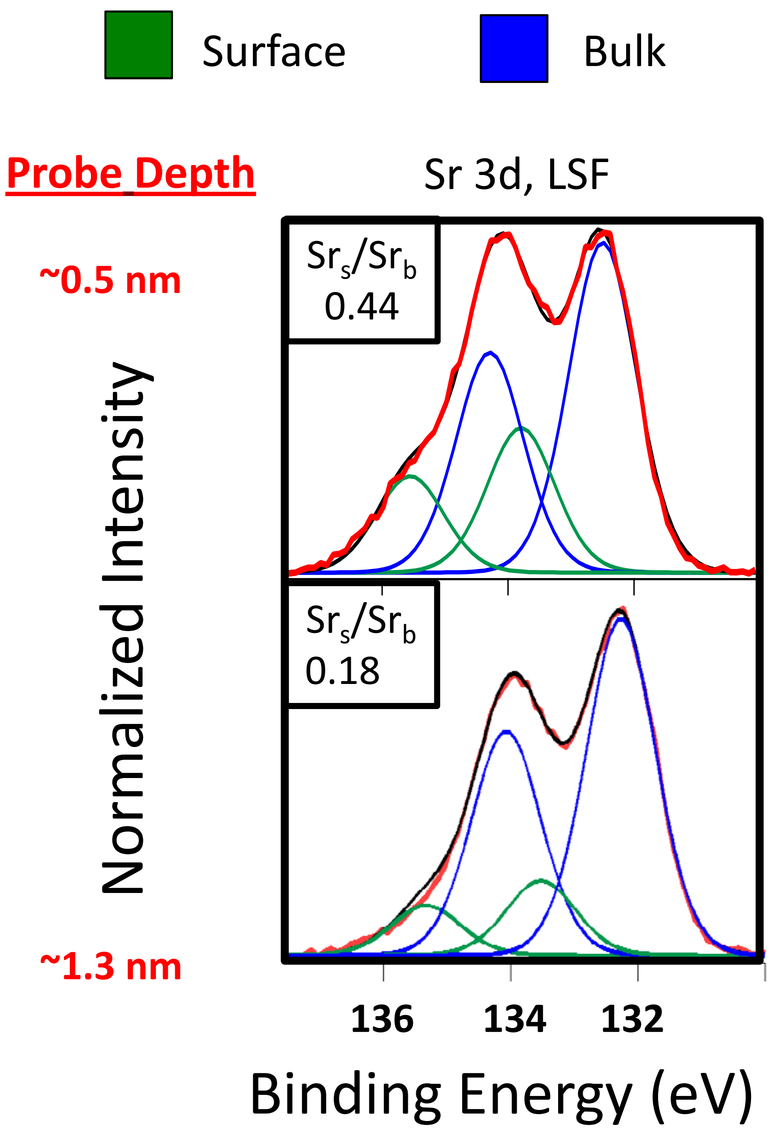
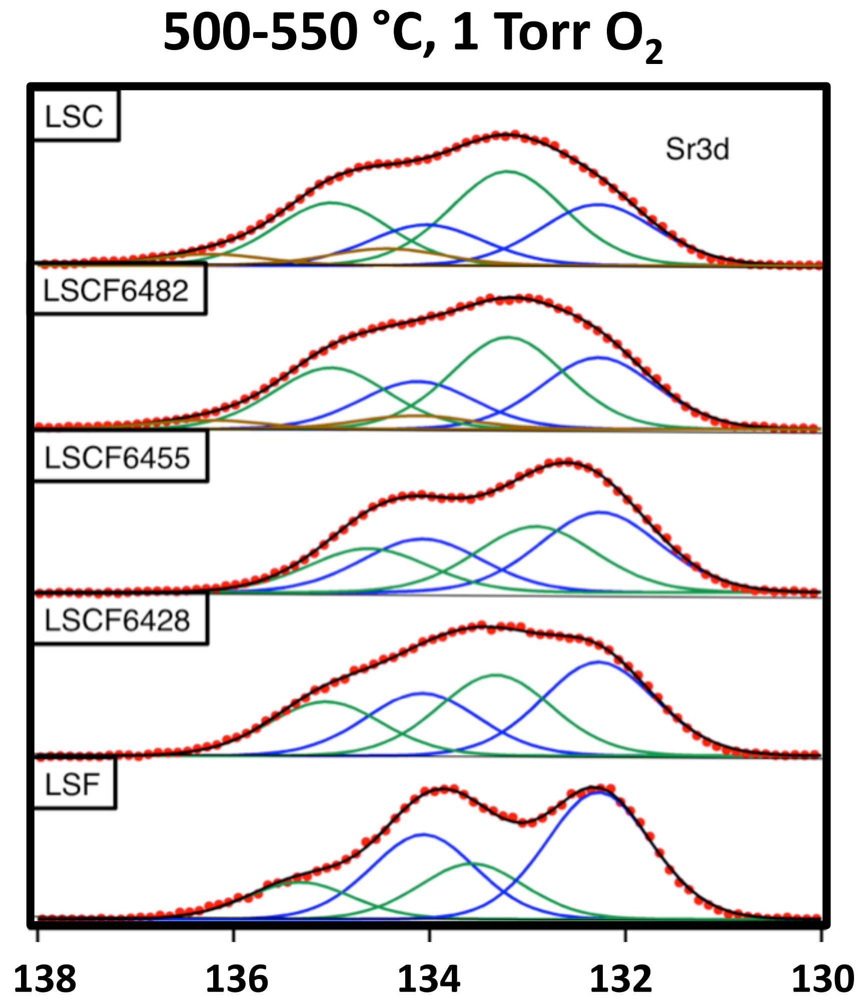
Ambient Pressure XPS: presence of surface strontium species



D.N. Mueller, M.L. Machala, H. Bluhm, W.C. Chueh, *Nat. Comm.* **6** (2015) 6097

Ambient Pressure XPS: increased Sr presence in LSCF series





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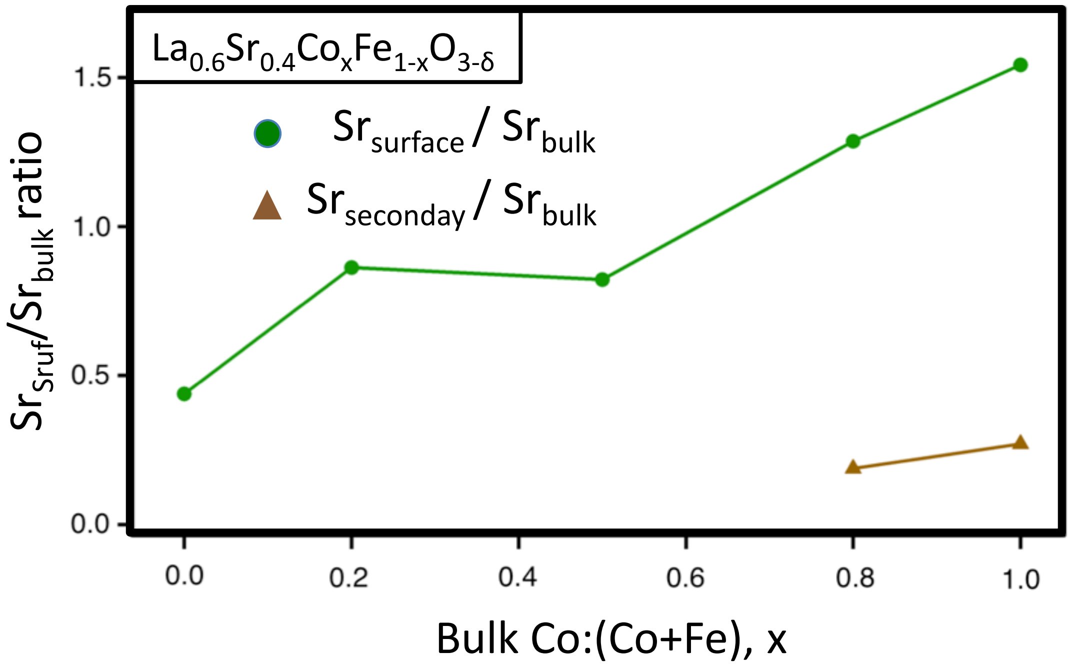
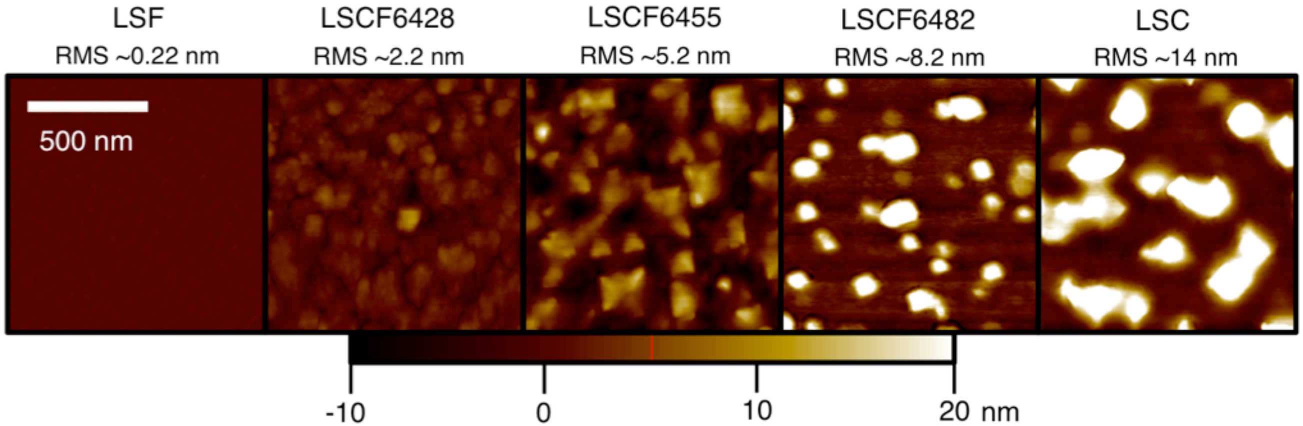
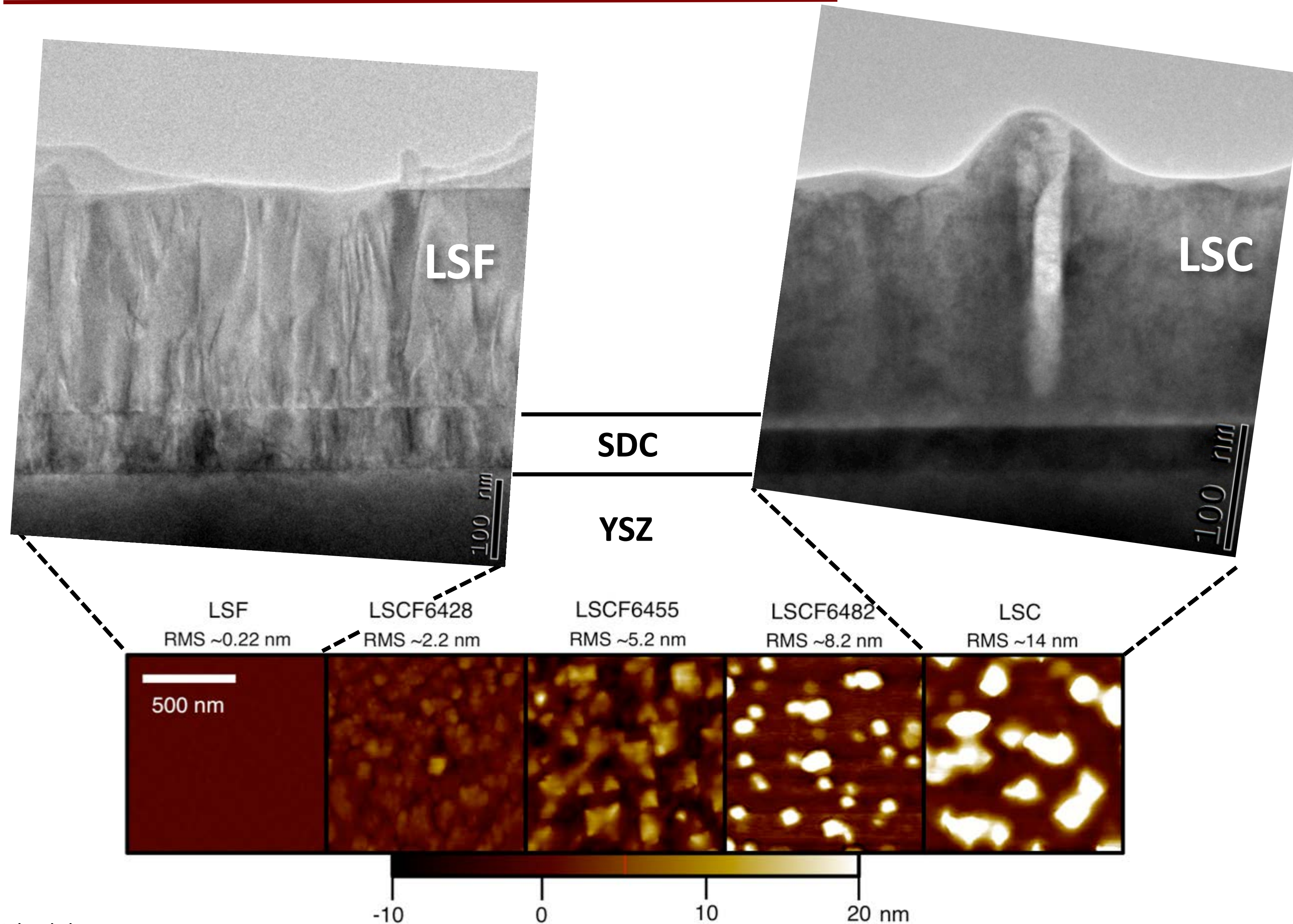
Ambient Pressure XPS: increased Sr presence in LSCF series





unpublished data

Morphological and composition instability



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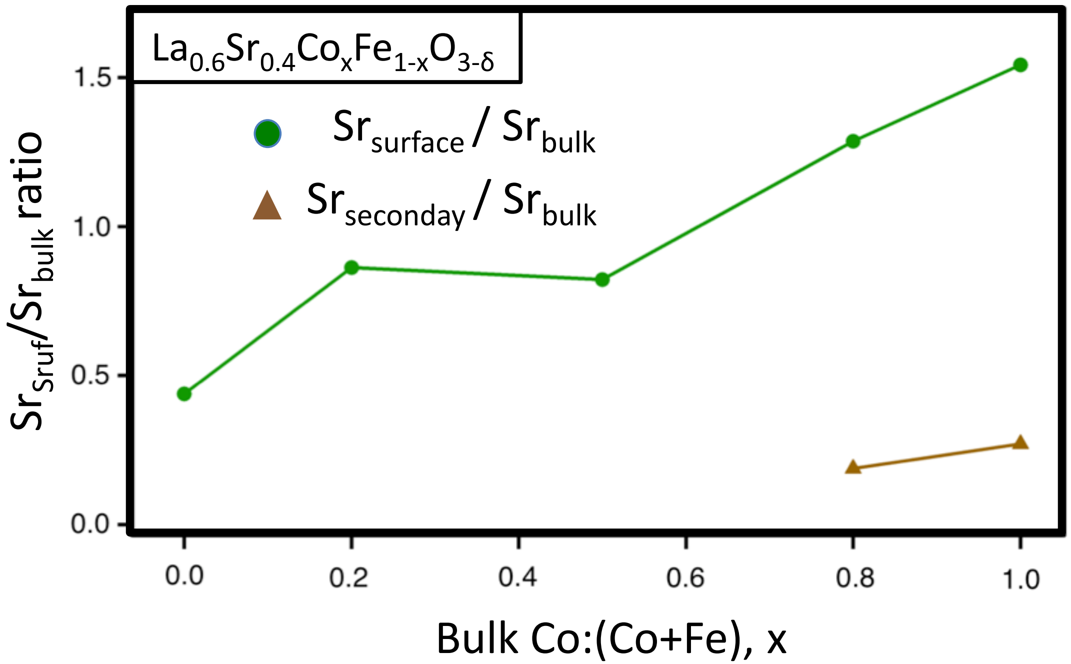
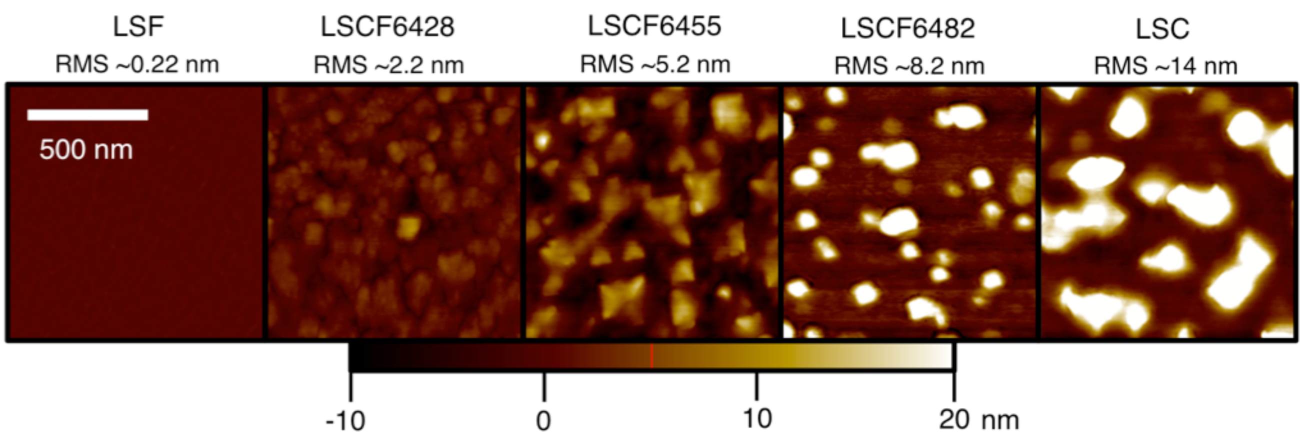
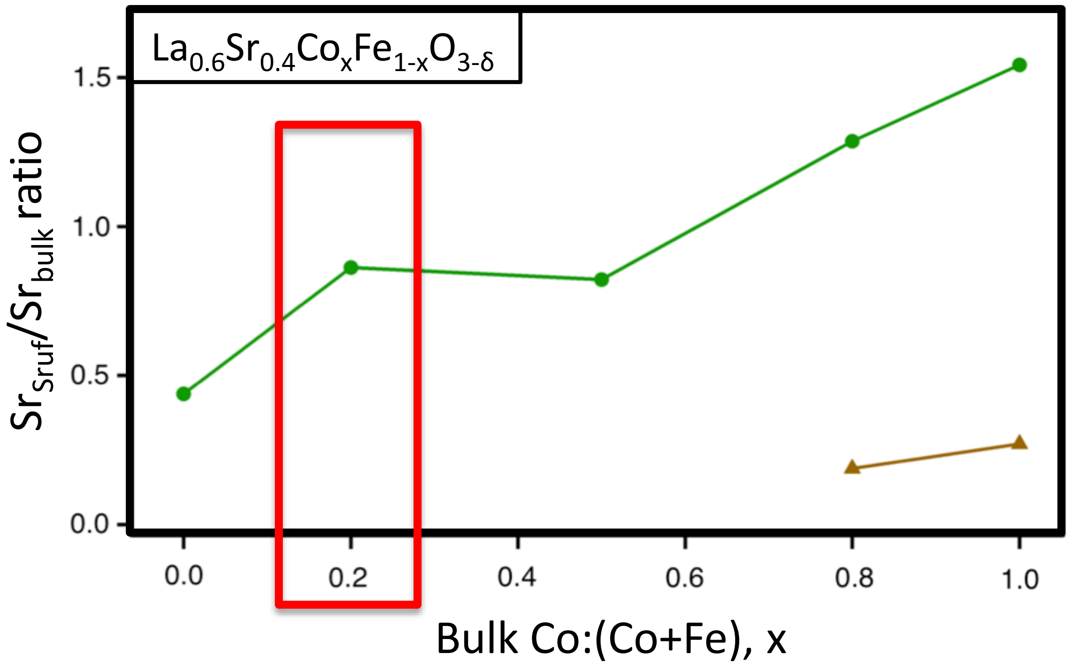
Ambient Pressure XPS: increased Sr presence in LSCF series

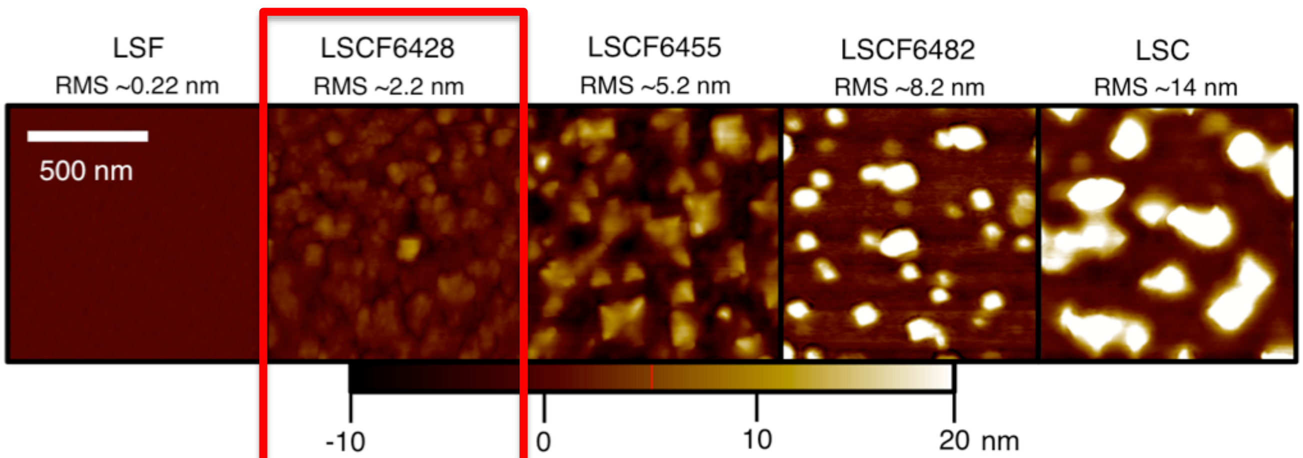




unpublished data

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ attractive / commercially relevant





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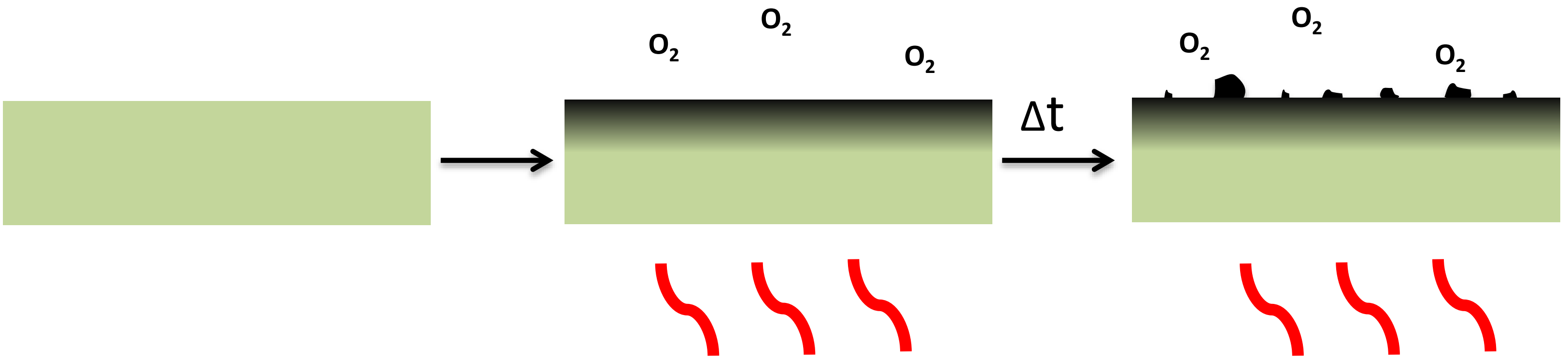
Unintentional surface rearrangement

Intrinsic

natural segregation of cations and precipitation of secondary phase

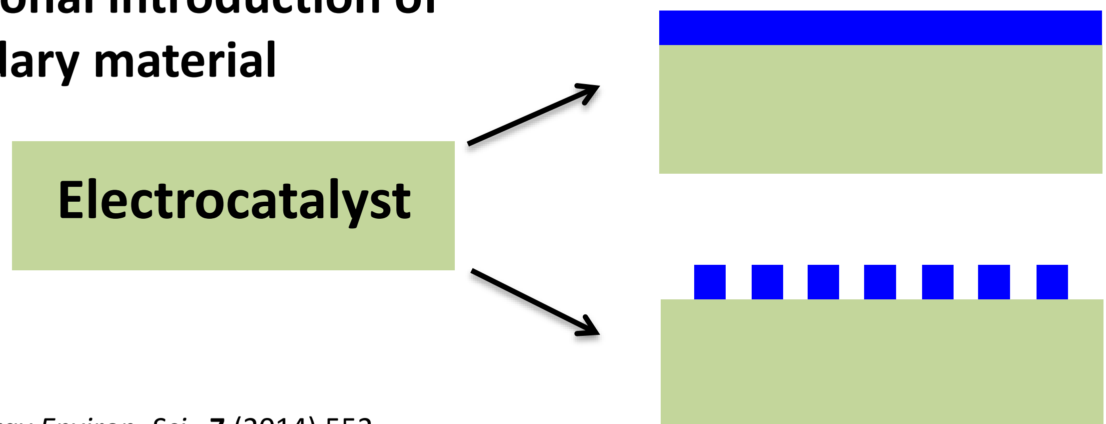


Szot, K.; Speier, W. *Phys. Rev. B* **60** (1999) 5909

Intentional surface modification

Extrinsic

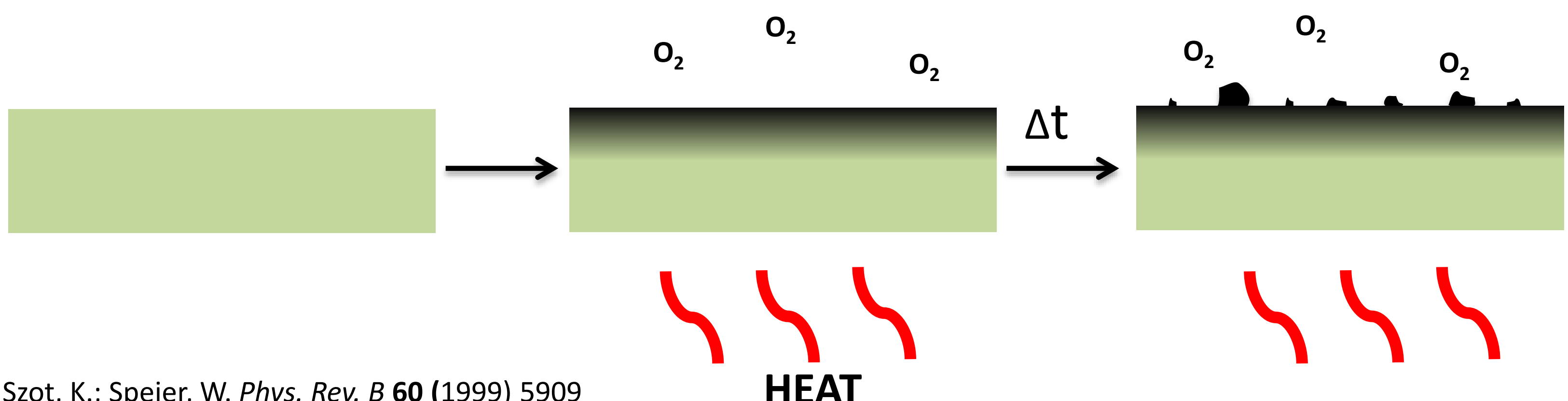
intentional introduction of secondary material



Ding and Liu et al. *Energy Environ. Sci.*, **7** (2014) 552

Intrinsic

natural segregation of cations and precipitation of secondary phase



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Surface modification can give improvements but why?

Infiltrate	Cathode backbone	Electrolyte	Cell configuration	Performance	
				Infiltrated	Baseline
$Gd_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Asymmetrical cell	R_p: 0.21 Ω cm^{-2} at 700 °C	11.8 Ω cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Symmetrical cells	R_p: 0.23 Ω cm^{-2} at 700 °C	5.3 Ω cm^{-2}
$Gd_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Asymmetrical cell	R_p: 0.60 Ω cm^{-2} at 750 °C	8.19 Ω cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Symmetrical cells	R_p: 1.13 Ω cm^{-2} at 600 °C	n/a
			Full cells	P_{max}: 0.14 W cm^{-2} at 600 °C	n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Full cells	P_{max}: 0.20 W cm^{-2} at 600 °C	0.17^a W cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Symmetrical cells	R_p: 0.19 Ω cm^{-2} at 700 °C	10^b Ω cm^{-2}
			Full cells	P_{max}: 0.53 W cm^{-2} at 750 °C	n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Symmetrical cells	R_p: 0.048 Ω cm^{-2} at 800 °C	n/a
			Full cells	P_{max}: 1.10 W cm^{-2} at 800 °C	n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Full cells	P_{max}: 1.25 W cm^{-2} at 800 °C	1.10^b W cm^{-2}

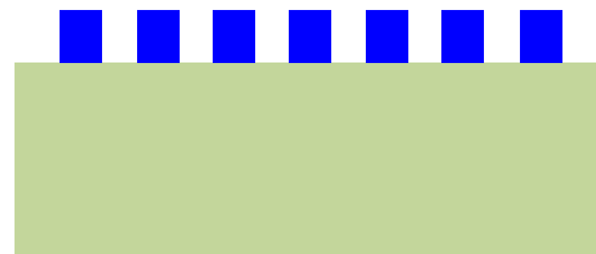
Table 1 – Performance and promotion factors of various nano-structured electrode systems.

Impregnated nanoparticles	Scaffold/skeleton	Performance	Promotion factor, f_P	Ref
Cathode of SOFC				
GDC (5.8 mg cm^{-2})	LSM	R_E = 0.21 Ωcm^2 @ 700 °C	56 for O_2 reduction	[81]
Pd (1.8 mg cm^{-2})	LSM/YSZ	R_E = 0.9 Ωcm^2 @ 600 °C	78 for O_2 reduction	[92]
Pd (1.2 mg cm^{-2})	LSCF	R_E = 2.9 Ωcm^2 @ 600 °C	1.9 for O_2 reduction	[90]
GDC (1.5 mg cm^{-2})	LSCF	R_E = 1.6 Ωcm^2 @ 600 °C	3.4 for O_2 reduction	[90]
LSM (~2 mg cm^{-2})	YSZ	R_E = 1.6 Ωcm^2 @ 600 °C	44 for O_2 reduction[a]	[92]
LSCF (1.1 mg cm^{-2})	YSZ	R_E = 0.54 Ωcm^2 @ 600 °C		[86]
LSCF (12.5 vol%)	GDC	R_E = 0.25 Ωcm^2 @ 600 °C	14 for O_2 reduction	[96]
$La_{0.6}Sr_{0.4}CoO_3$ (30 vol%)	YSZ	P = 2.1 W cm^{-2} @ 800 °C in H_2/air		[97]
$La_{0.6}Sr_{0.4}CoO_3$ (55 wt%)	SDC	R_E = 0.36 Ωcm^2 @ 600 °C		[93]

Ding and Liu et al. *Energy Environ. Sci.*, **7** (2014) 552
Jiang, *Int J Hydrogen Energ* ***37*** (2012) 449

Surface modification can give improvements but why?

Infiltrate	Cathode backbone	Electrolyte	Cell configuration	Performance: Infiltrated	Performance: Baseline
$Gd_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Asymmetrical cell	R_p: 0.21 Ω cm^{-2} at 700 °C	11.8 Ω cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Symmetrical cells	R_p: 0.23 Ω cm^{-2} at 700 °C	5.3 Ω cm^{-2}
$Gd_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Asymmetrical cell	R_p: 0.60 Ω cm^{-2} at 750 °C	8.19 Ω cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Symmetrical cells	R_p: 1.13 Ω cm^{-2} at 600 °C	n/a
			Full cells	P_{max}: 0.14 W cm^{-2} at 600 °C	n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	SDC	Full cells	P_{max}: 0.20 W cm^{-2} at 600 °C	0.17^{a} W cm^{-2}
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Symmetrical cells	R_p: 0.19 Ω cm^{-2} at 700 °C	10^{b} Ω cm^{-2}
			Full cells	P_{max}: 0.53 W cm^{-2} at 750 °C	n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Syn		n/a
			Ful		n/a
$Sm_{0.2}Ce_{0.8}O_{2-\delta}$	LSM	YSZ	Ful		1.10^{b} W cm^{-2}



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Impregnated nanoparticles	Scaffold/skeleton		f_P	Ref
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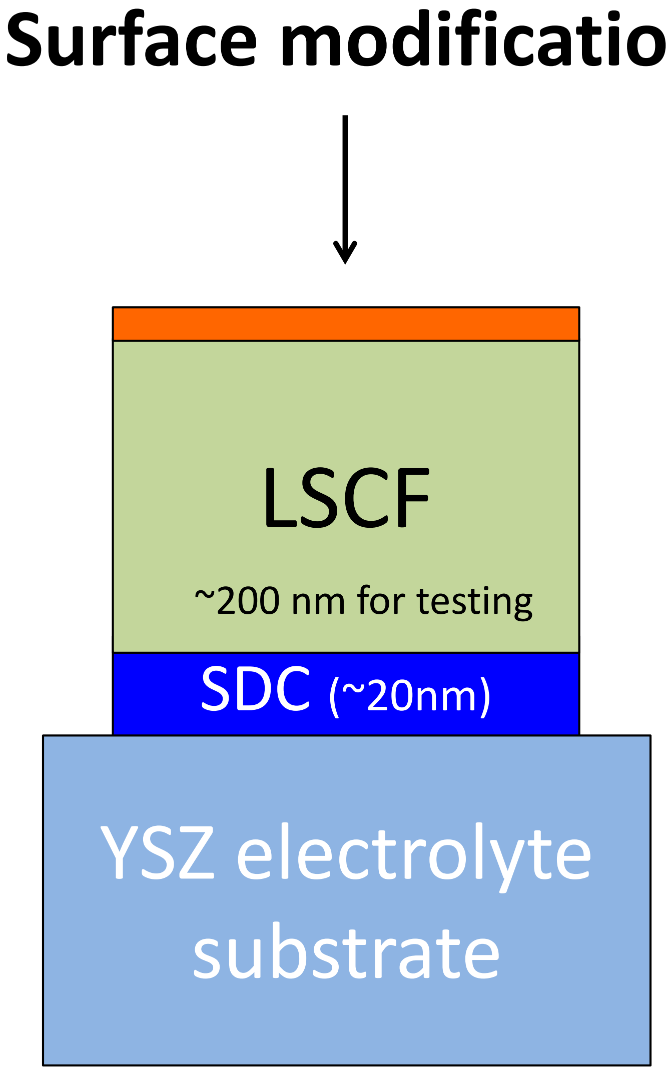
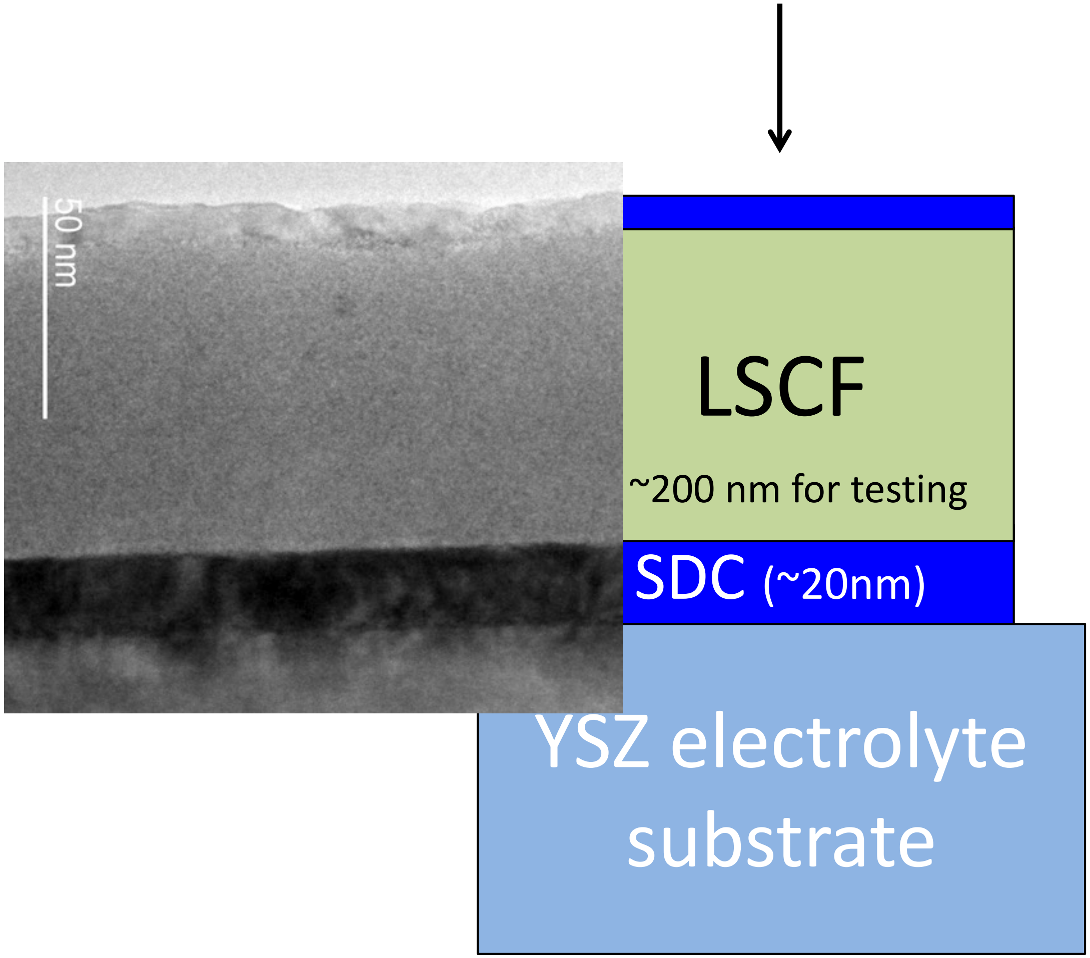
Controlled coverage by Pulsed Laser Deposition (PLD)



Controlled coverage by Pulsed Laser Deposition (PLD)

Surface modification



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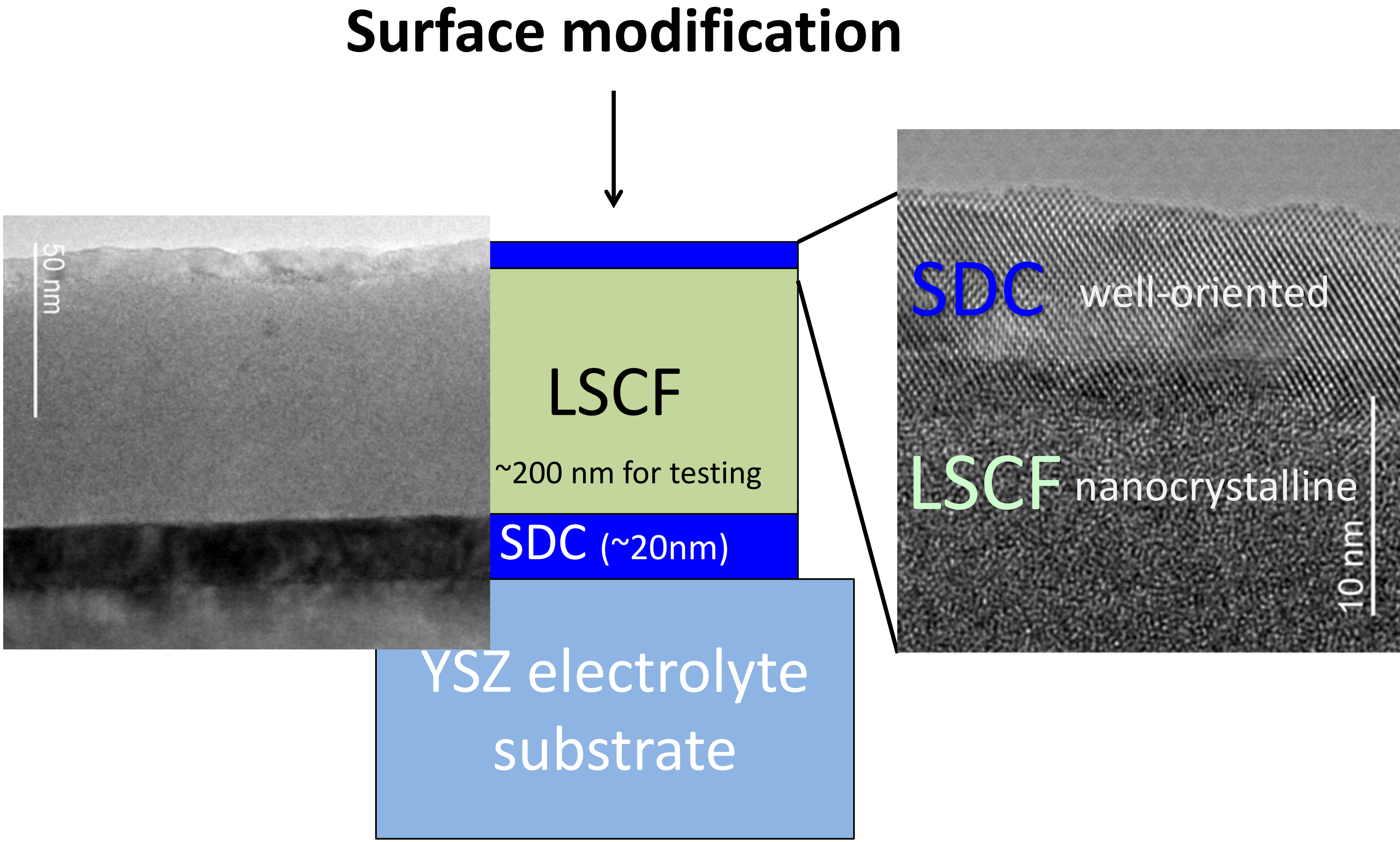
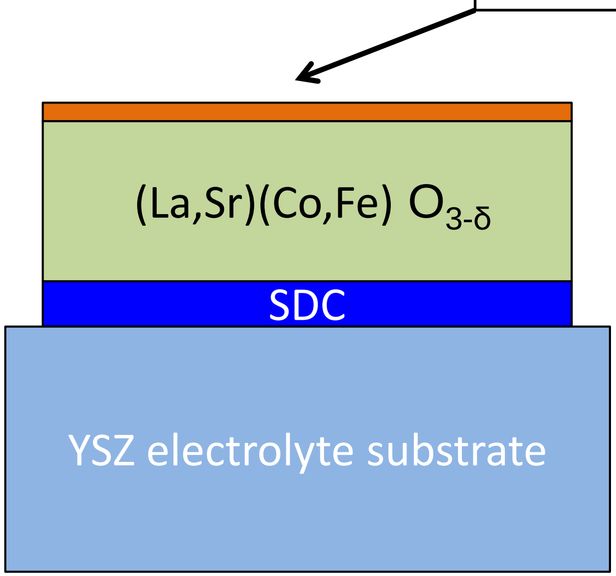


Surface modification layers on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Surface Modification	SDC	YSZ
σ_{ion} / S cm^{-1} *	0.03 [1]	0.03 [2]
σ_{eon} / S cm^{-1} *	~6 × 10^{-8} [1]	?
Lattice Constant (Å)	~5.42	~5.14
Strain % wrt. LSCF @ RT [3]	-3%	-8%

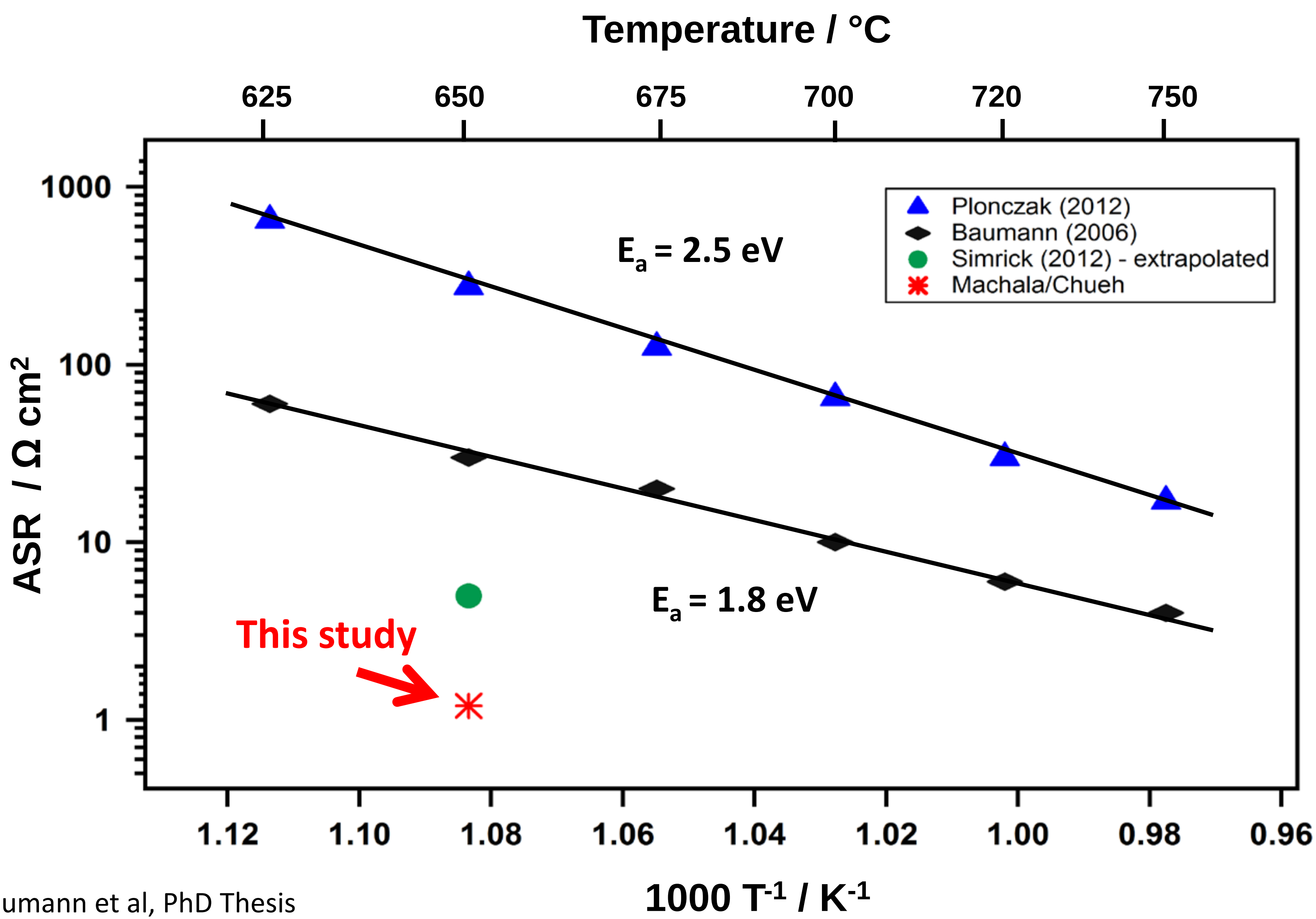


*at 650 °C, 21% O_2

[1] Lei, Haile, J. Am. Ceram. Soc. **88** (2005) 2979
[2] Kumar et al, J. Power Sources **140** (2005) 12
[3] https://icsd.fiz-karlsruhe.de

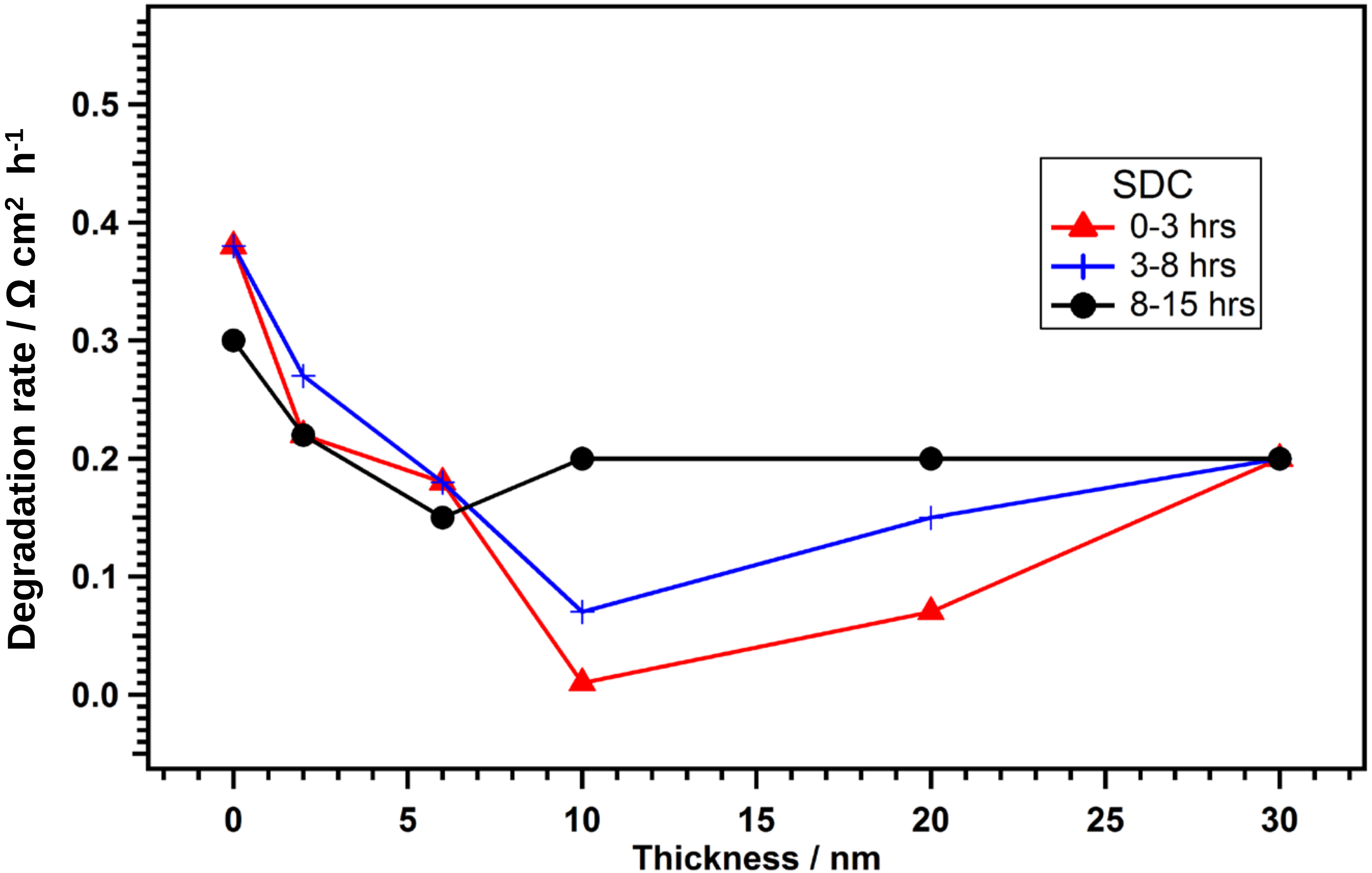
Dense LSCF deposition-dependent

Tested in 21% O_2, OCV

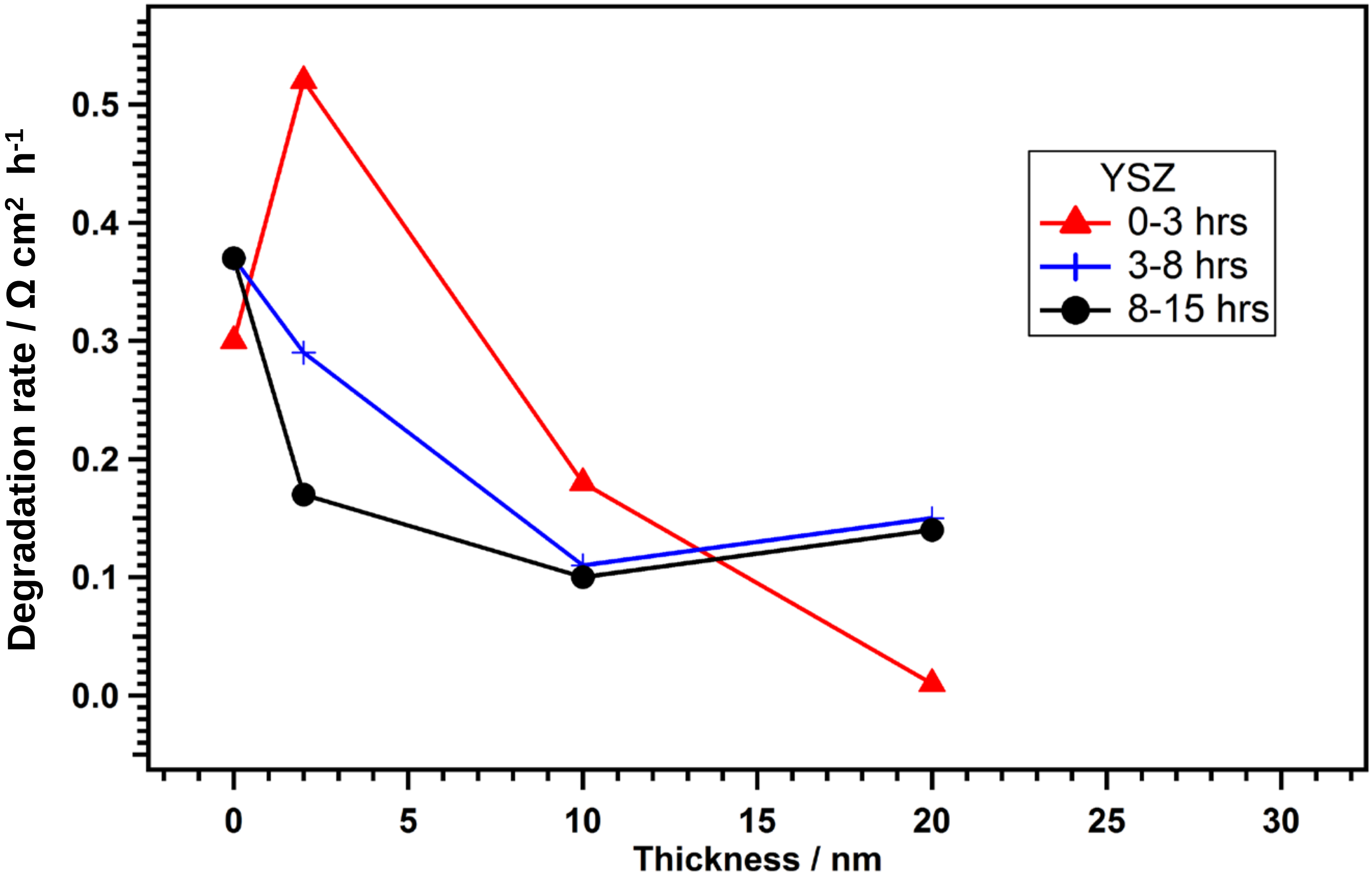


Baumann et al, PhD Thesis
Ponczak et al, J. Electrochem. Soc. **159** (2012) 471
Simrick et al, Solid State Ionics, **206** (2012) 7

SDC lowers degradation rate

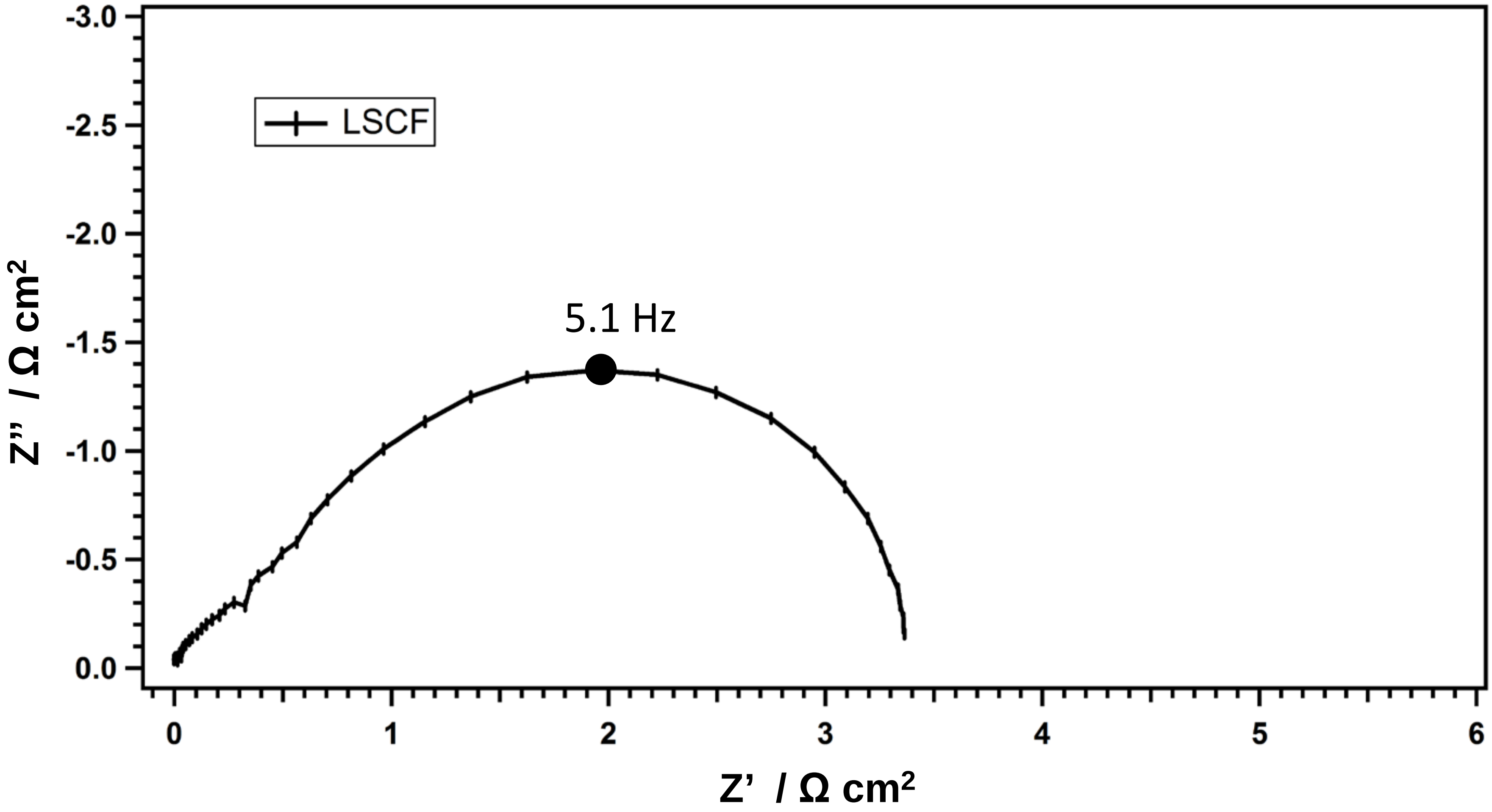


YSZ lowers degradation rate



Low-frequency arc change with surface modification

Conditions: 650 °C at 21% O_2, OCV after 3 hrs



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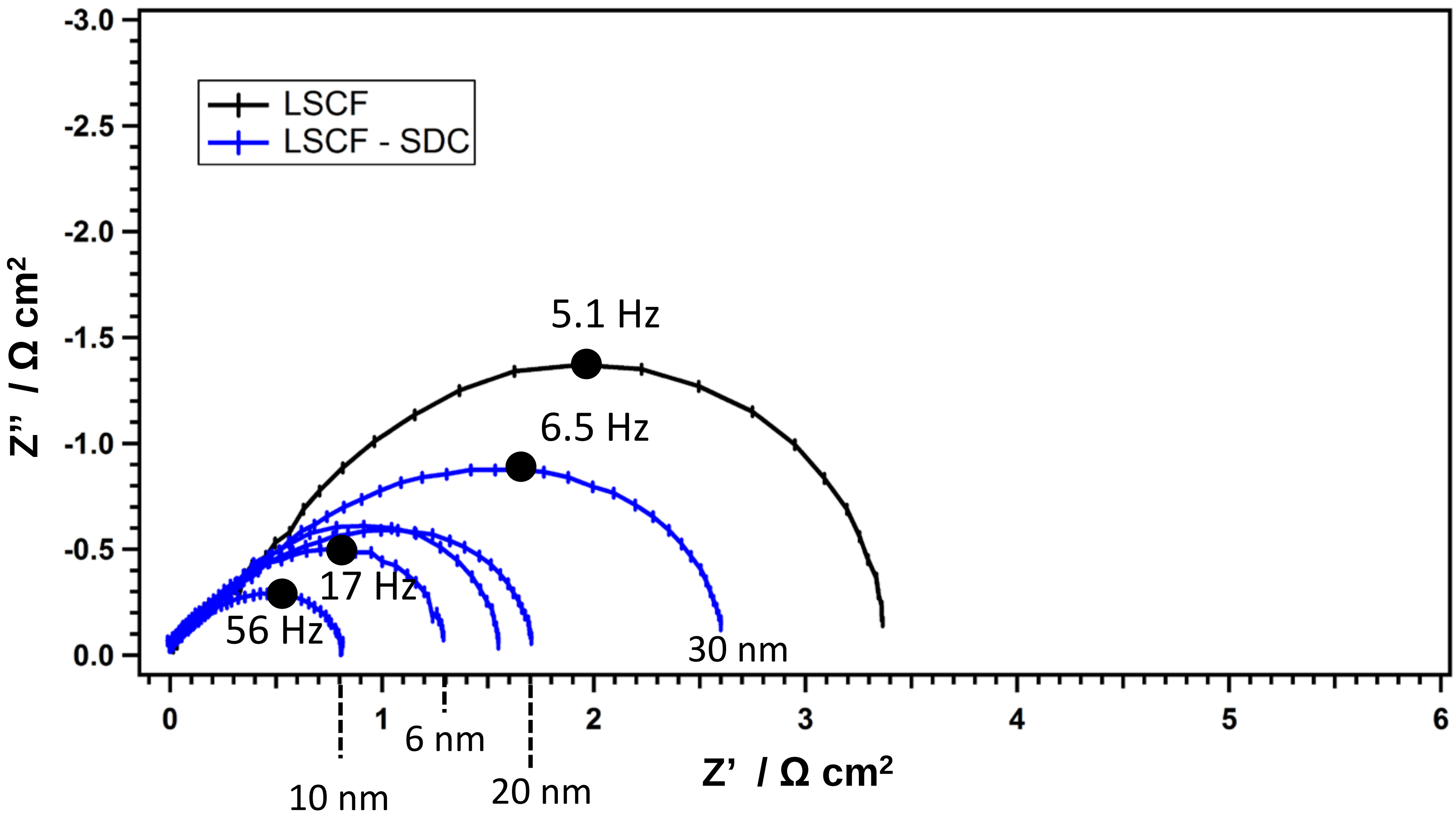

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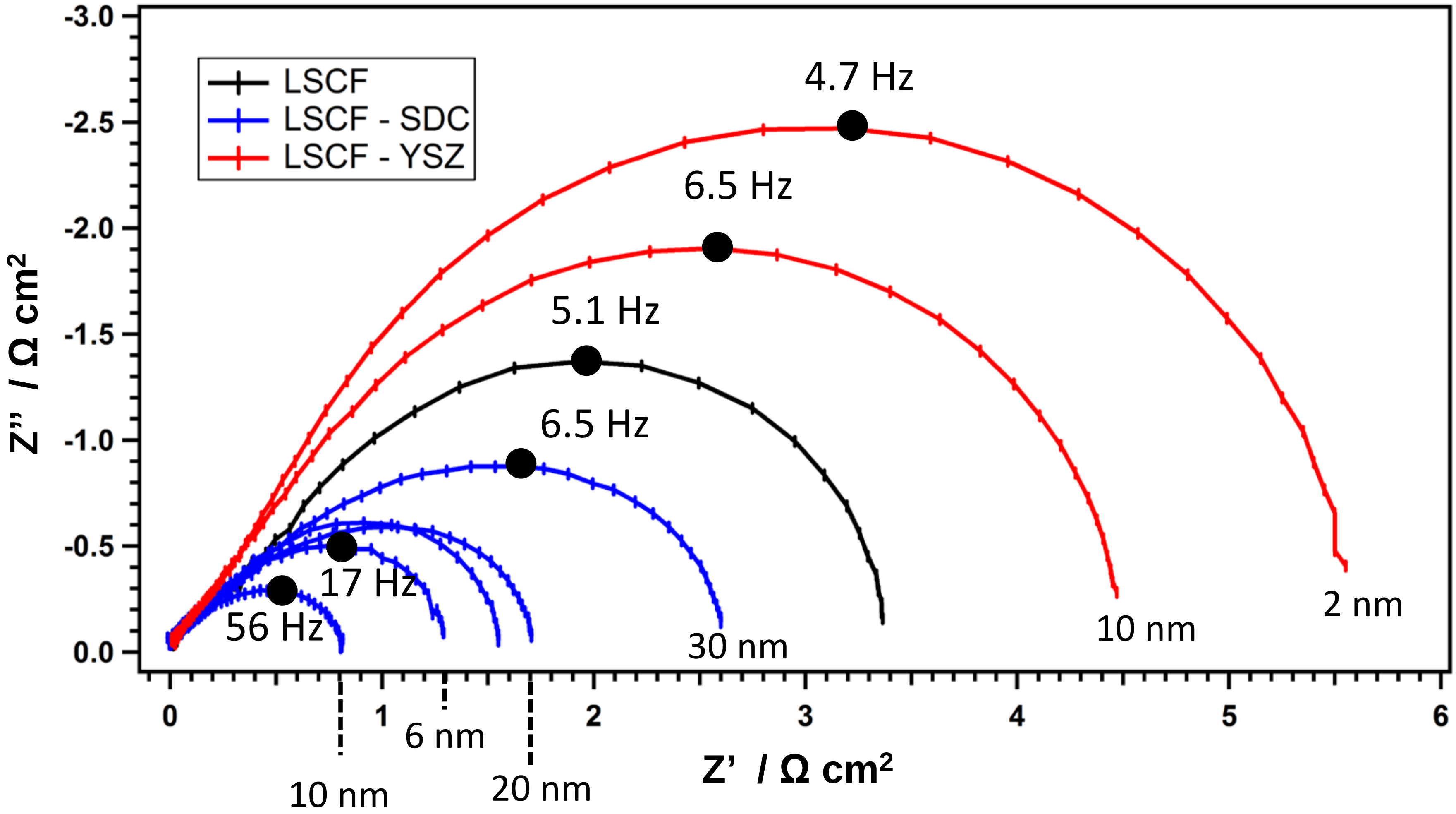
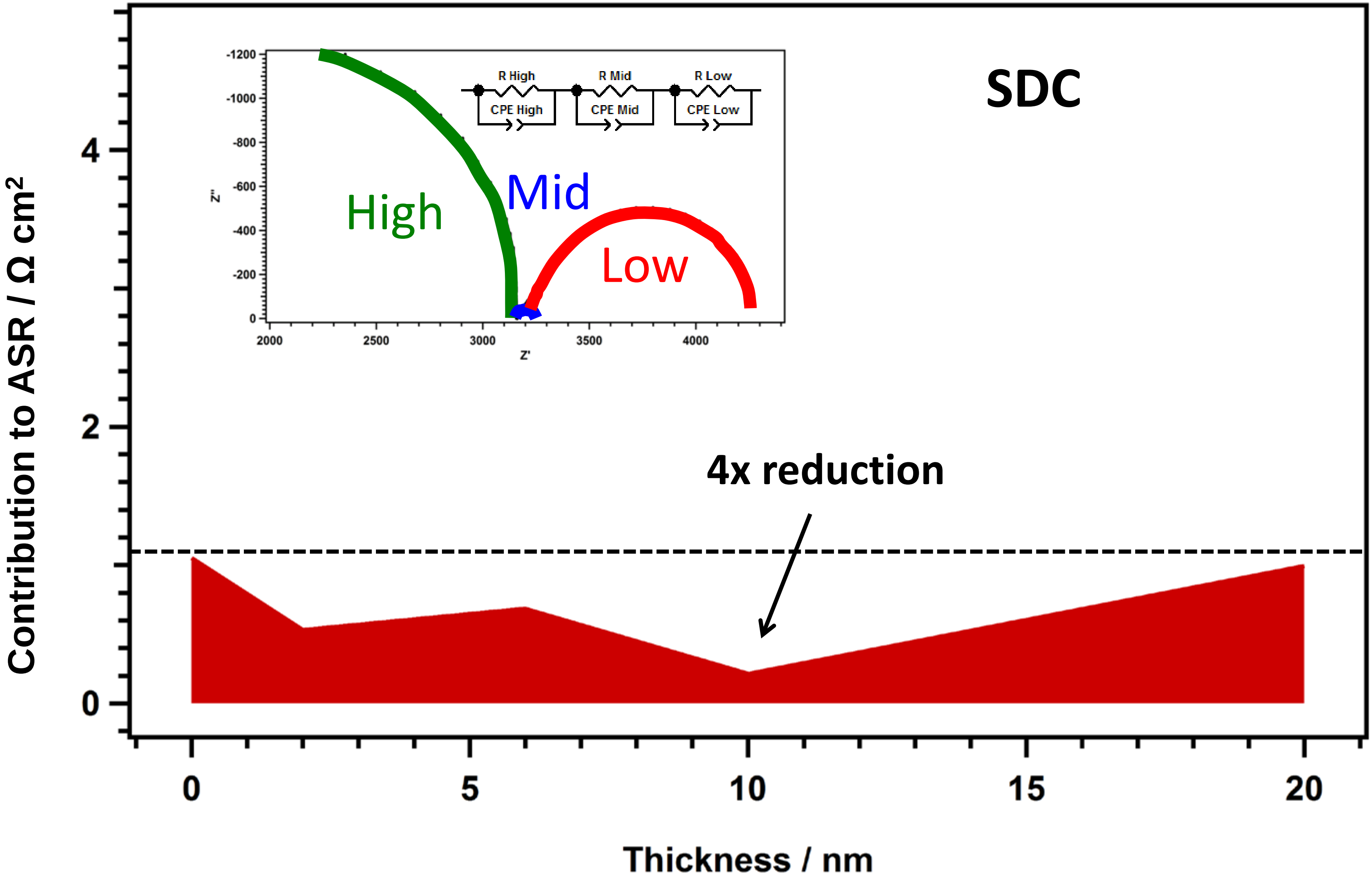
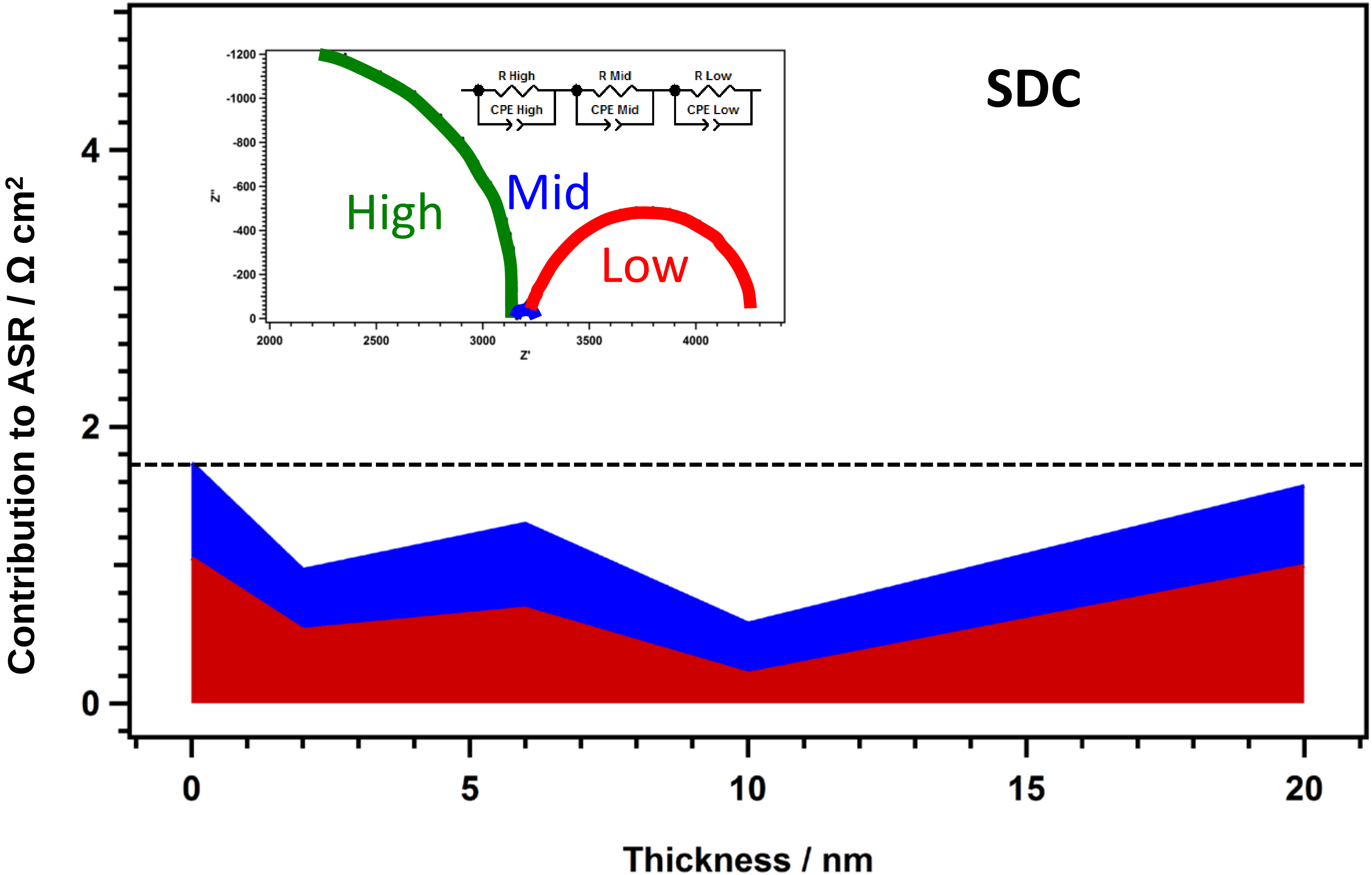


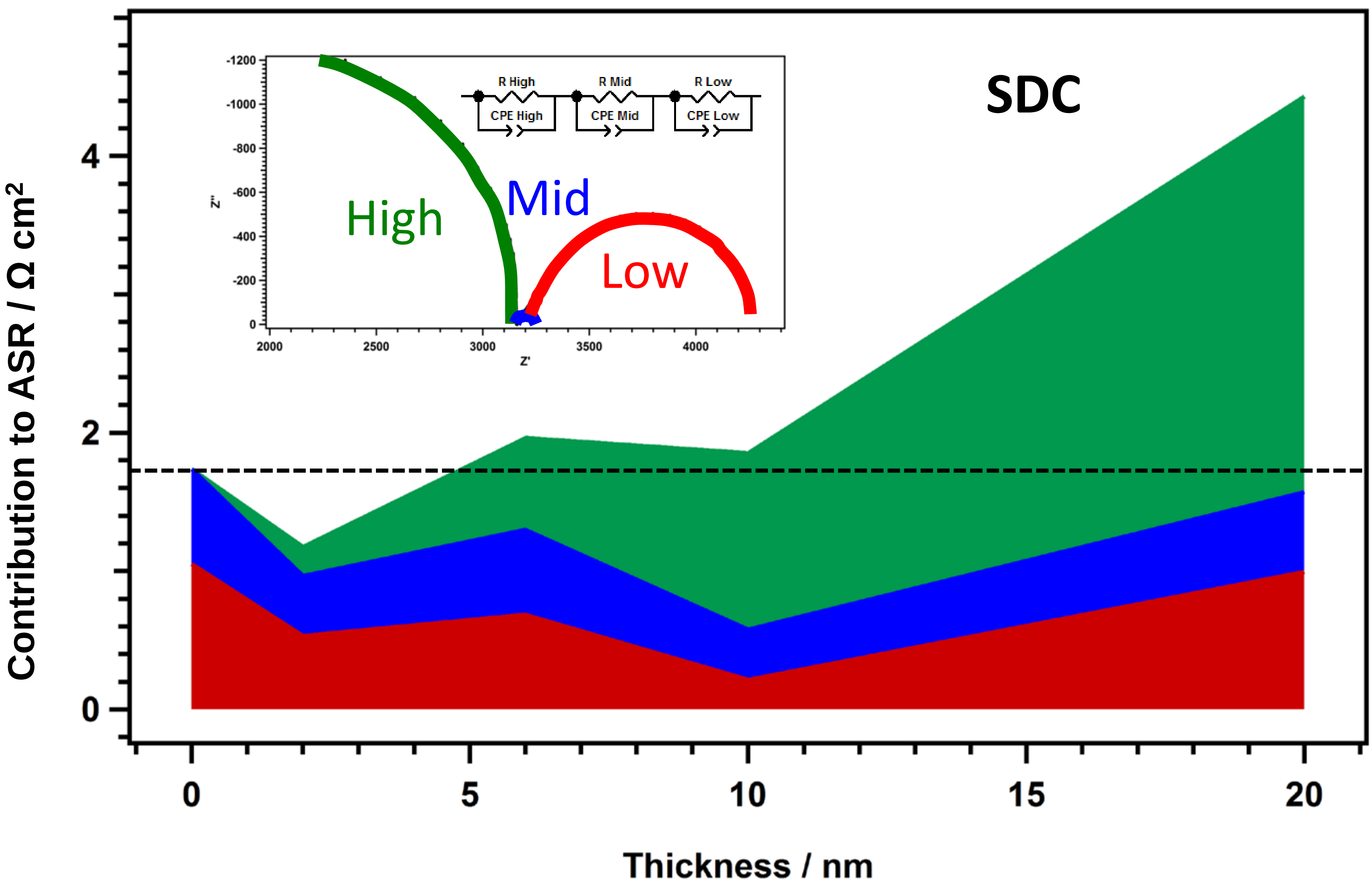
SDC overlayer: 4x reduction in oxygen exchange kinetics



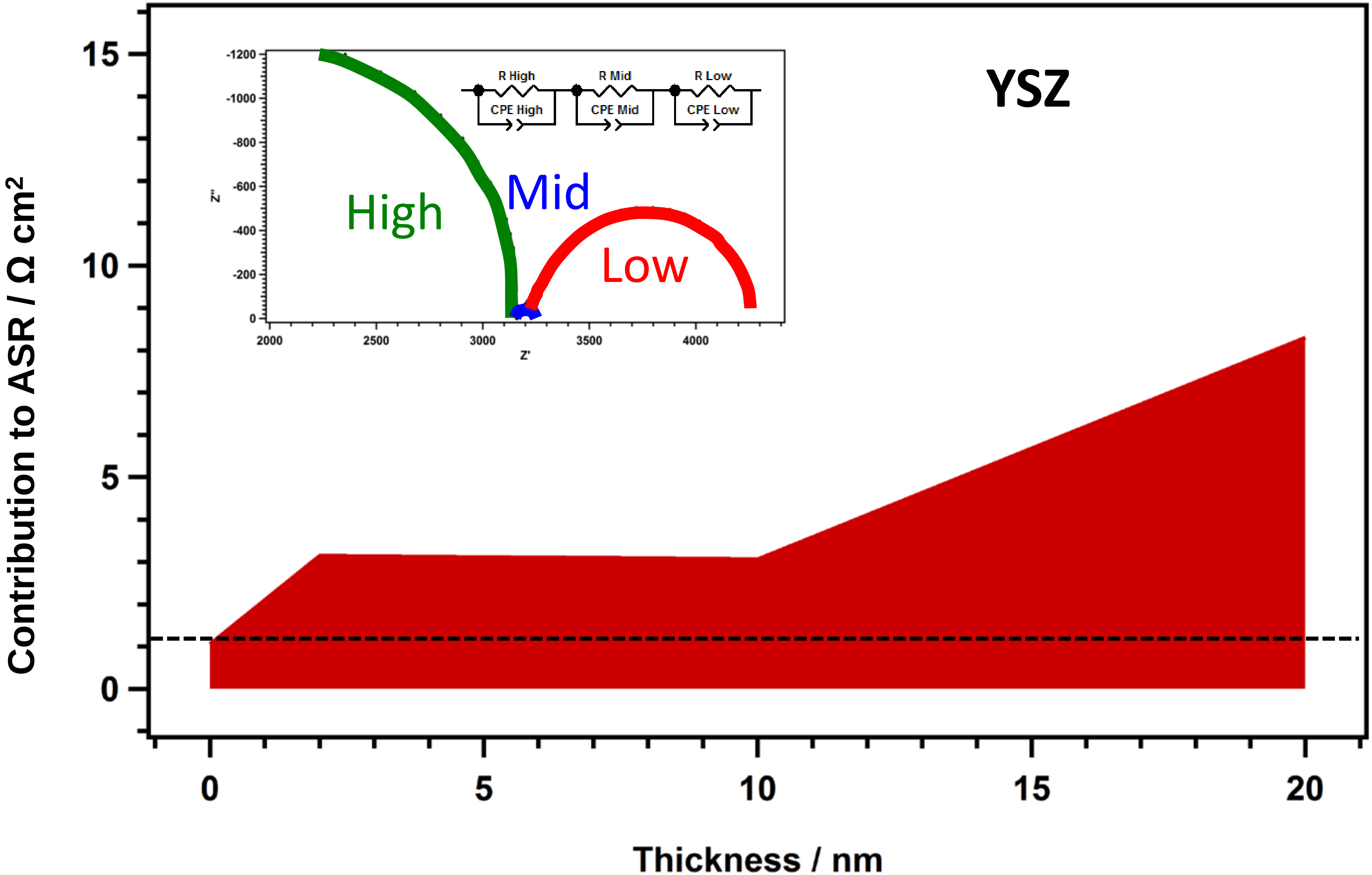
SDC overlayer: MF is constant



SDC overlayer: HF contribution increase



Area Specific Resistance contributions: YSZ overlayer



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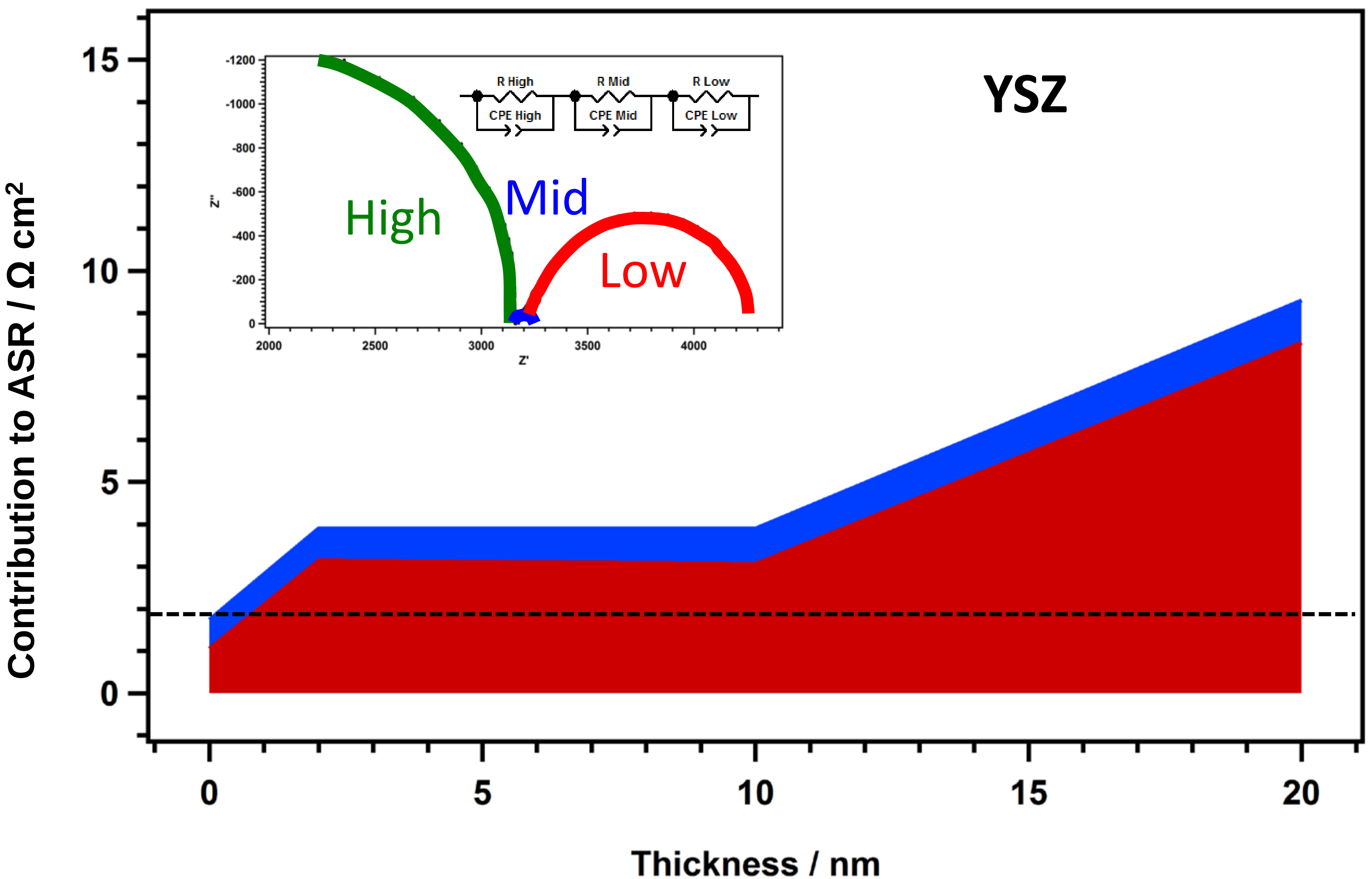
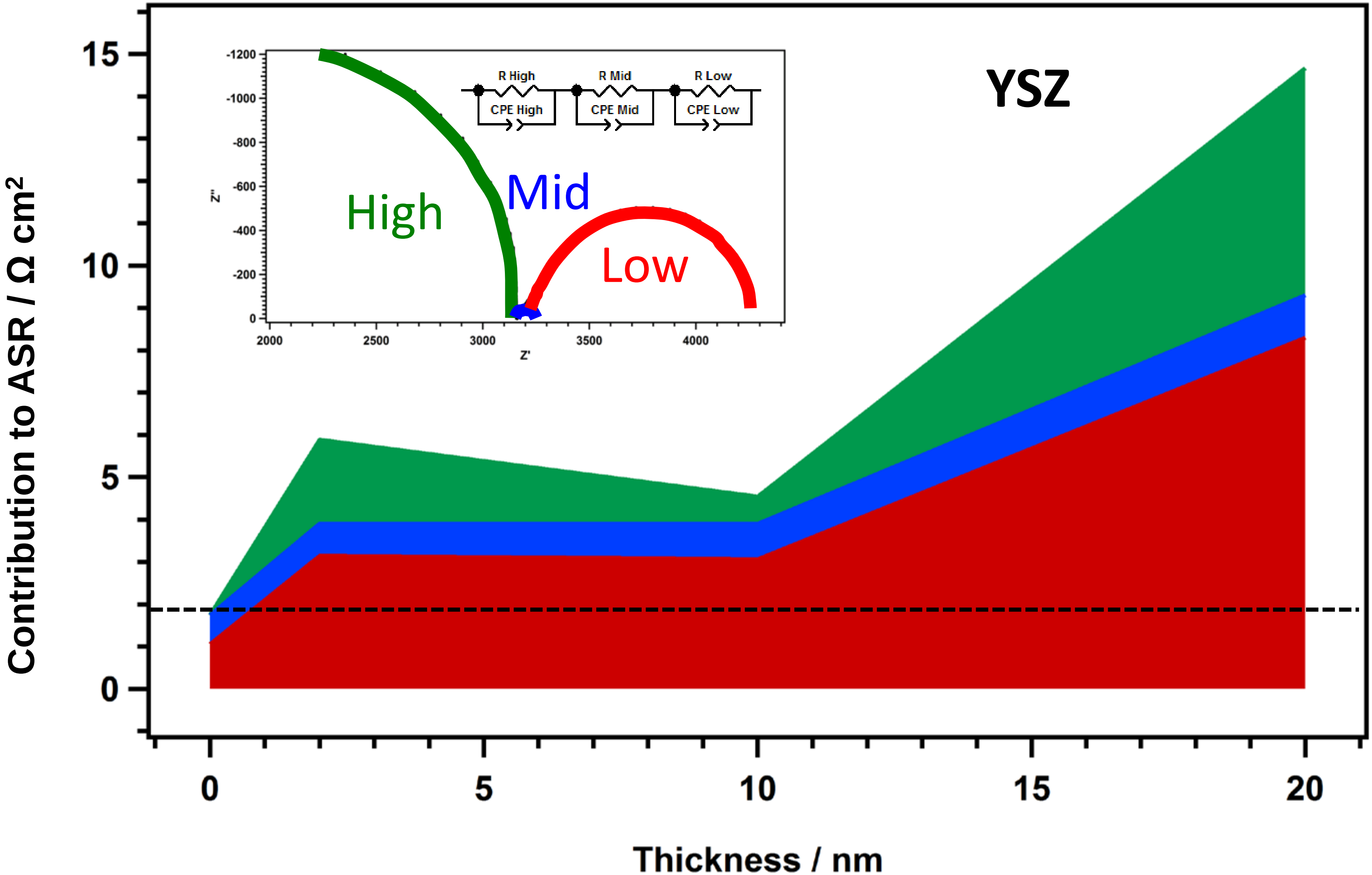
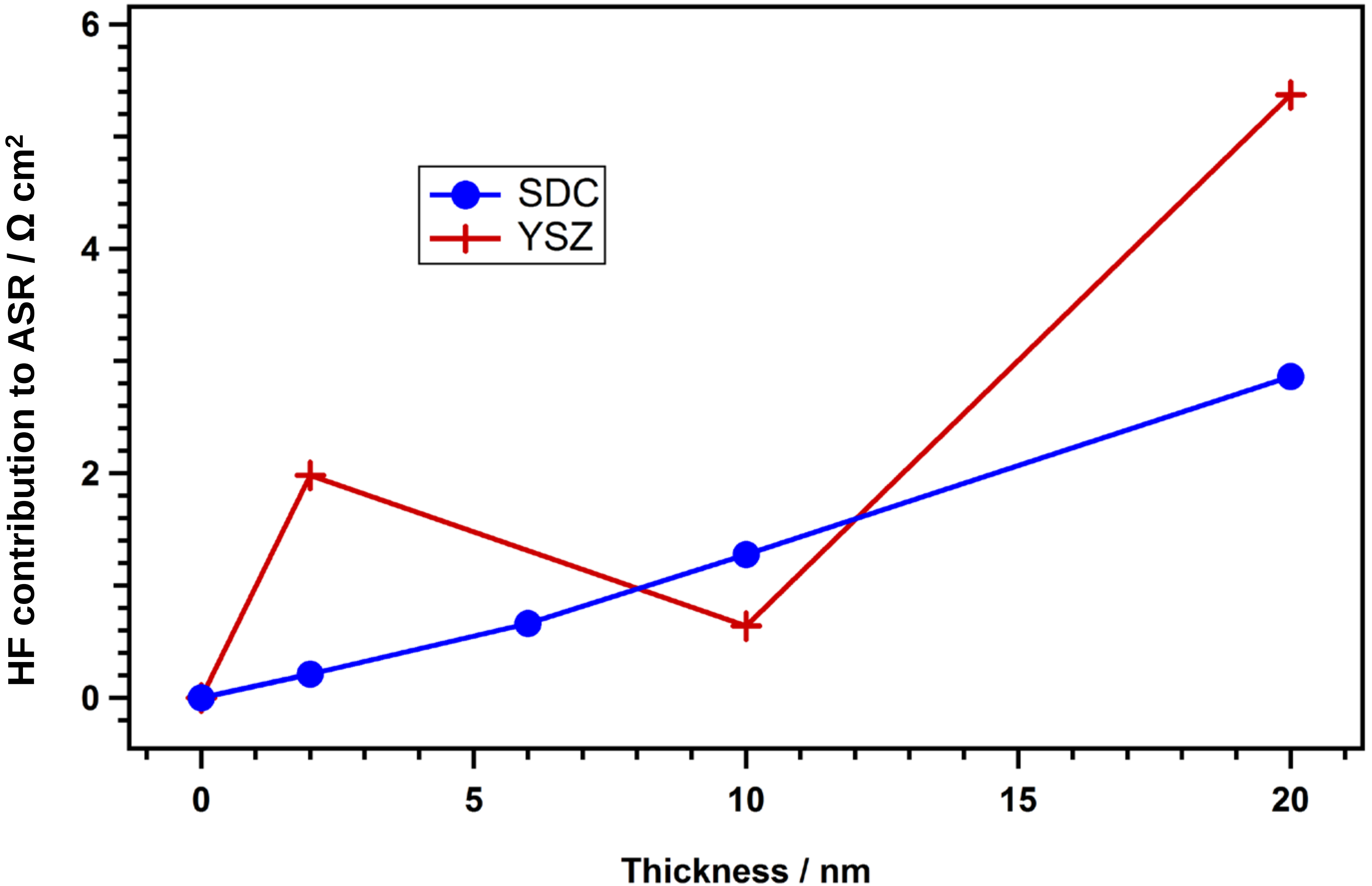


Area Specific Resistance contributions: YSZ overlayer



Electronic transport limited



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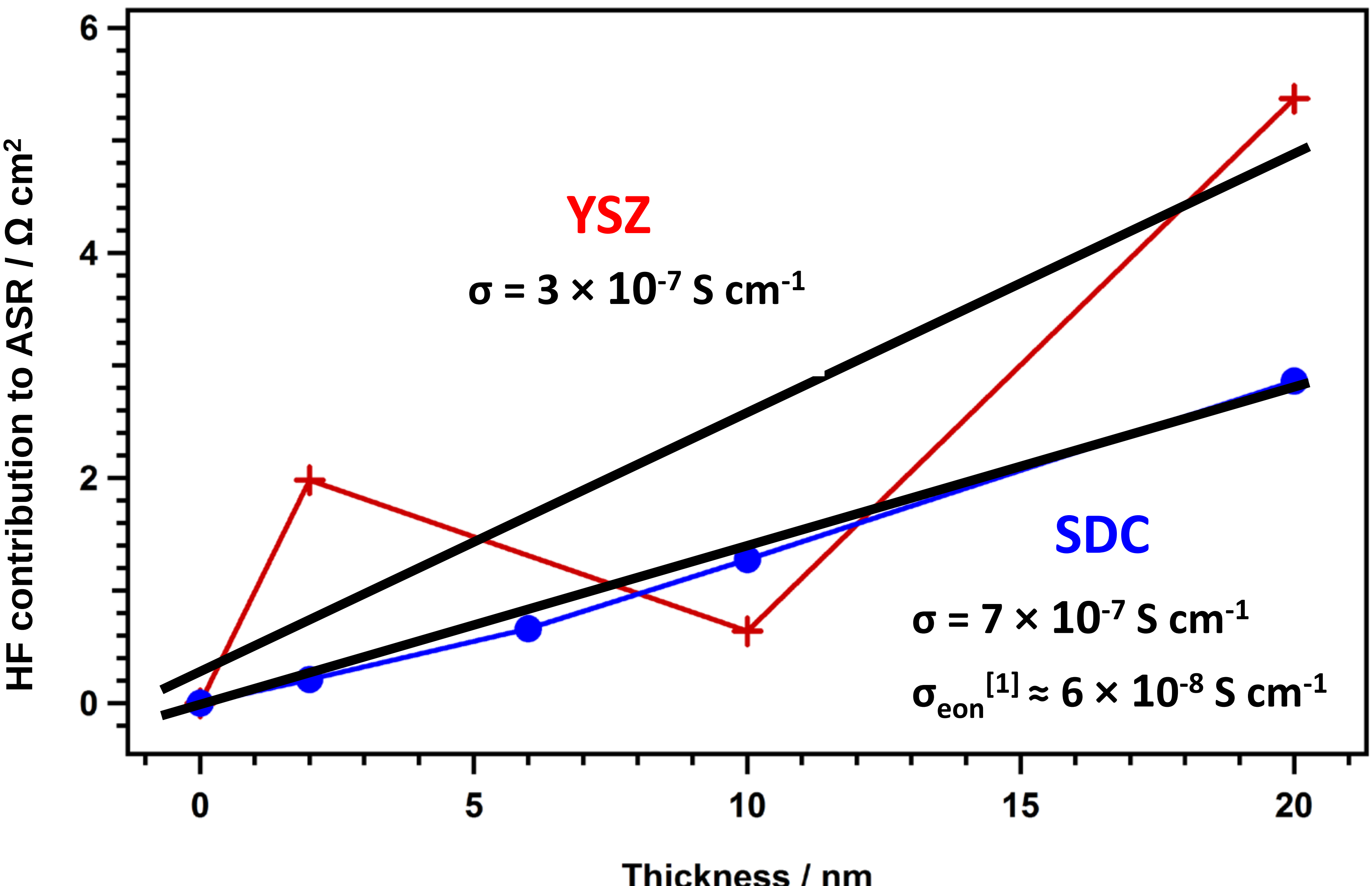
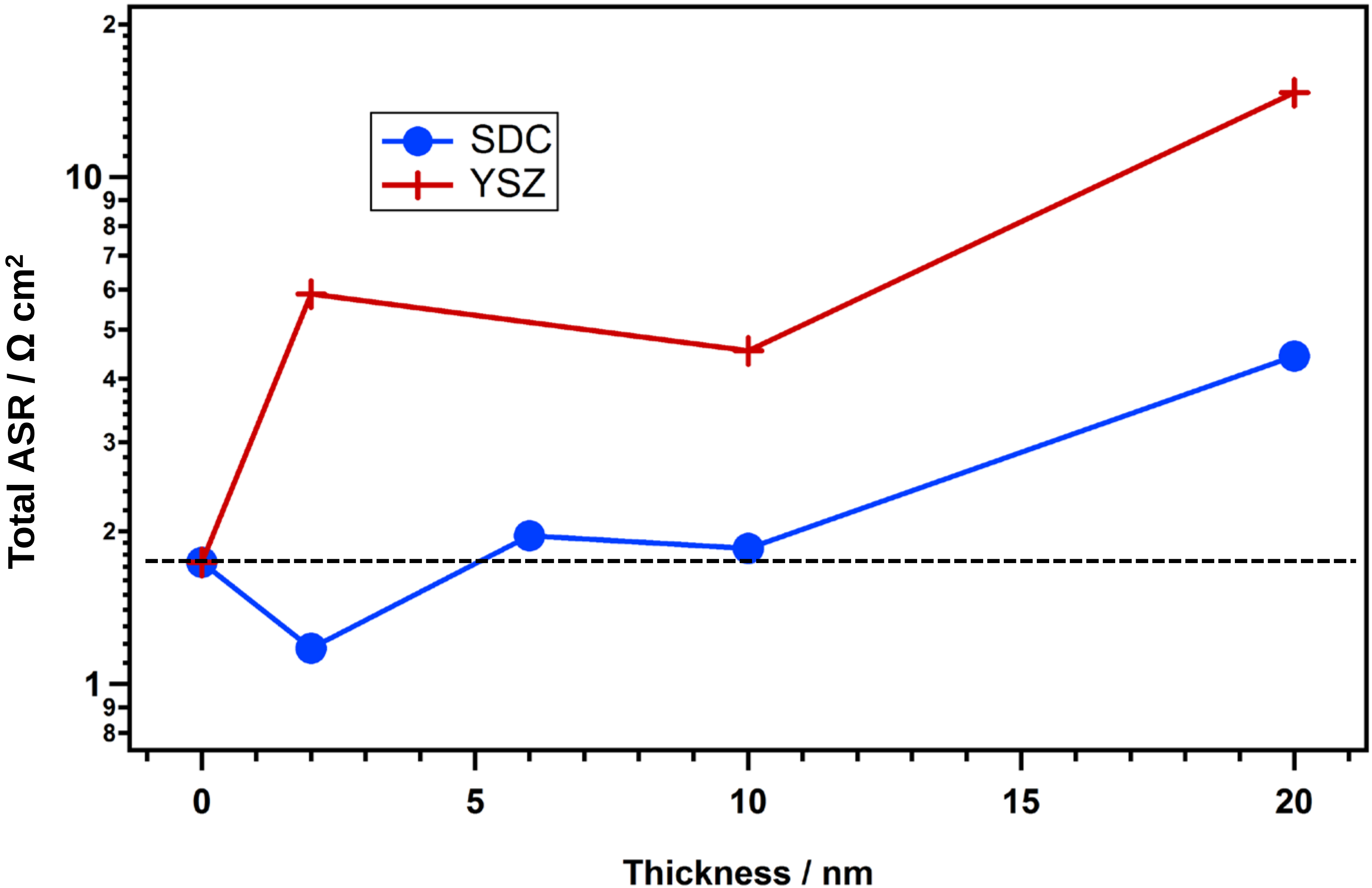


[1] Lei, Haile, J. Am. Ceram. Soc. **88** (2005) 2979

SDC less resistive than YSZ and more active



Diffusion of Co and Fe into the overlayer

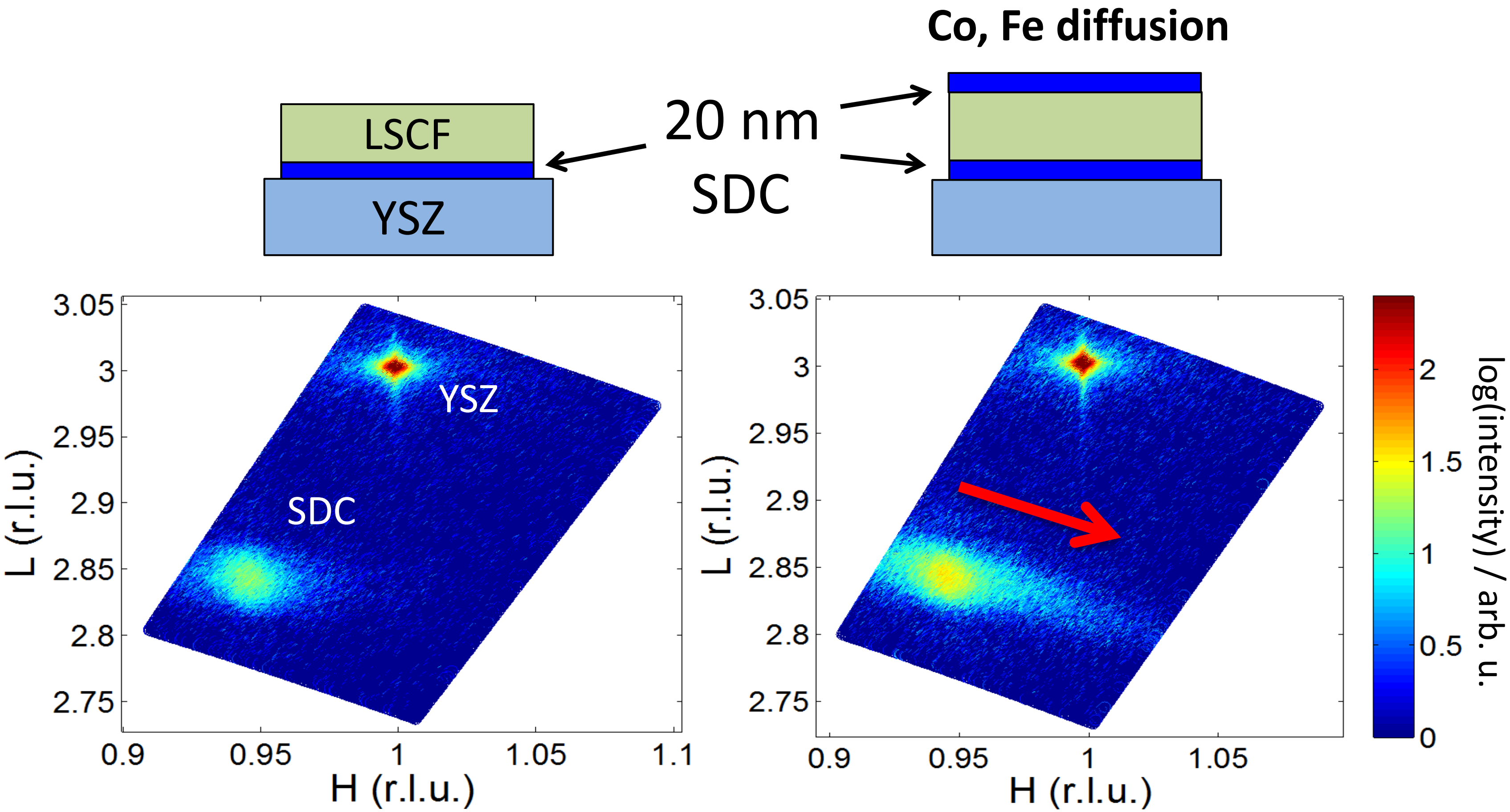
SDC : 10 nm

Element	As Deposited	Annealed	Theoretical
La	0%	0%	0%
Sr	0%	0%	0%
Co	12%	9%	0%
Fe	1%	7%	0%
Ce	66%	62%	80%
Sm	21%	21%	20%

YSZ : 10 nm

Element	As Deposited	Annealed	Theoretical
La	0%	0%	0%
Sr	1%	1%	0%
Co	1%	2%	0%
Fe	0%	0%	0%
Zr	85%	85%	84%
Y	13%	12%	16%

TM diffusion not only along grain boundaries in SDC



Sample as-deposited

Conclusions

	Oxygen exchange rate	Overall Resistance	Degradation rate	Optimal Thickness
SDC	increases	decreases*	decreases	2-10 nm
YSZ	decreases	increases	decreases	2-10 nm

*at small thicknesses

- **Nominally pure ionic conductors (YSZ & SDC) are effective surface coatings for LSCF cathodes.**
- **SDC exhibits superior oxygen exchange kinetics, ~ 4x lower ASR than LSCF. 10-nm layer gives negligible increase in the electronic transport resistance.**
- **YSZ lowered oxygen exchange kinetics on LSCF.**
- **Both SDC and YSZ improve the stability of LSCF significantly, possibly related to the absence of Sr diffusion to the surface.**
- **Significant diffusion of Co and Fe from LSCF to SDC/YSZ likely explains the higher than expected electronic conductivity, which is needed for the electrode to function.**

Acknowledgements

Briggs White, Steve Markovich,
Joe Stoffa

Core Technology Program

Graduate
Research
Fellowship
Program

Surface roughening with annealing