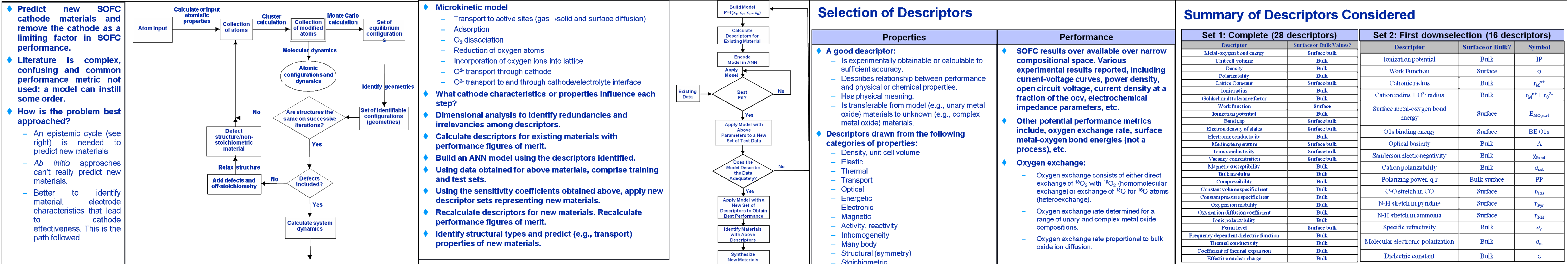


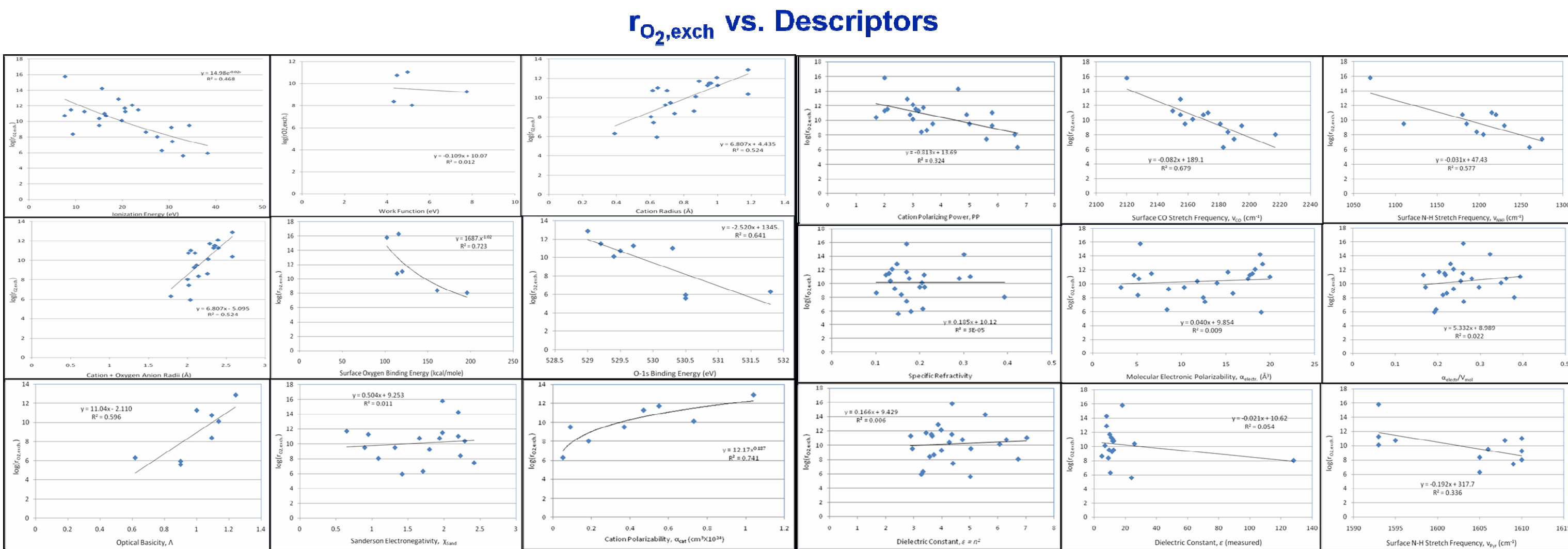
FIRST PRINCIPLES IDENTIFICATION OF NEW CATHODE ELECTROCATALYSTS FOR FUEL CELLS

Erick J. Schutte and James H. White

PURPOSE AND APPROACH

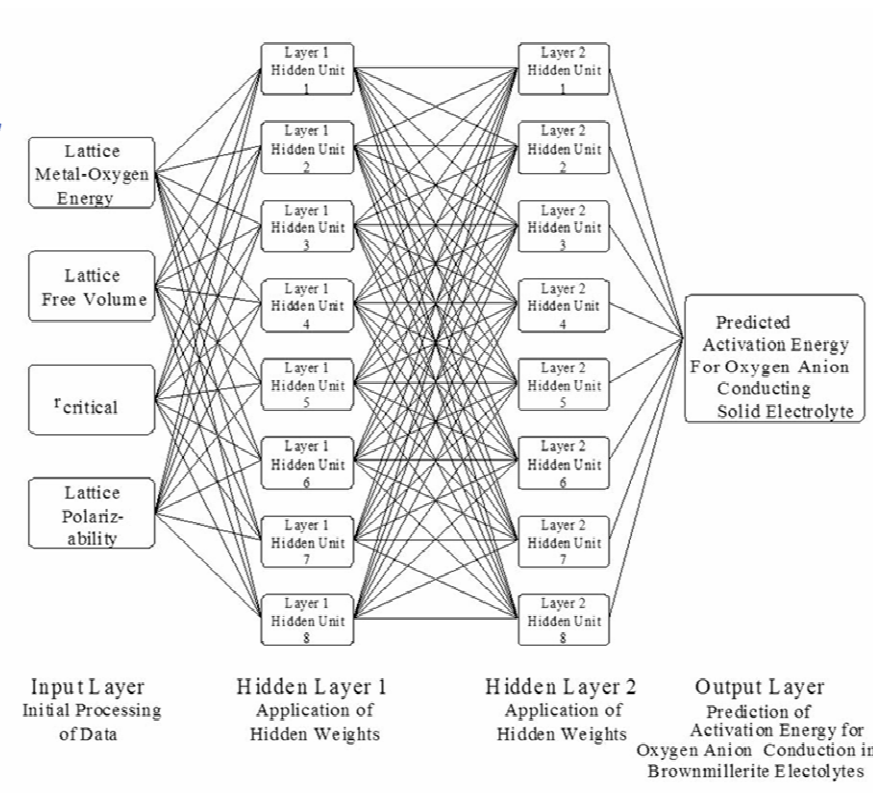


RESULTS



Artificial Neural Network (ANN)

- ANN serves as function approximator and regression system**
- Use of ANNs to fit data to model**
 - Apply training sets to train ANN
 - Apply other data to ANNs (test sets)
 - Apply production set to obtain predictions



Encoding the Model

- A general regression neural network (GRNN) model was employed because of its function approximation abilities.**
- Employed Ward Systems NeuroShell Predictor**
- Training set (table on the right) was based on a data set (in z-scores form) which, for unaries, contained 25 input vectors and for multi-component materials, contained 1 entry per component with a dichotomous stoichiometric function being employed; i.e., the network is trained by presenting the component descriptor data with the stoichiometric factor SF = 1 and fields are left blank if SF = 0.**

Metal Oxide	IP of Element	PP	Log (Rate)
TiO ₂	-1.413	-0.819	1.699
Nb ₂ O ₅	1.988	-0.819	1.699
Al ₂ O ₃	0.914	-1.400	-1.414
Ga ₂ O ₃	1.161	-0.936	0.788
TiO ₂	0.807	-1.023	1.358
ZnO	-1.173	-0.207	-0.520
Yb ₂ O ₃	-0.877	-0.463	-0.412
SrO	1.130	-0.528	0.902
MgO	-0.555	-0.353	-0.293
ZrO ₂	1.559	-0.353	-0.421
Cr ₂ O ₃	-0.075	-0.113	-0.091
PbO	-0.556	2.327	-1.431
Cr ₂ O ₃	-0.395	-0.965	0.390
NiO	-1.366	-0.470	-0.708
Fe ₂ O ₃	-0.430	-0.900	0.902
Gd ₂ O ₃	0.058	0.929	-0.577
CuO	-0.902	1.278	-1.260
Sm ₂ O ₃	0.361	1.645	-0.634
CdO	-1.217	0.987	-1.203
Y ₂ O ₃	0.045	0.637	-0.480
Md ₂ O ₃	1.249	-0.691	0.623
La ₂ O ₃	-0.102	-0.761	0.219
Mn ₂ O ₃	-0.489	-0.761	0.219
CoO	-1.356	-0.255	-1.260
IrO ₂	-1.356	-0.877	1.187

Final Descriptor Down-Selection

Metal Oxide	IP of Element	PP	Log (Rate)
TiO ₂	33	2.04	1.699
Nb ₂ O ₅	38.531	2.04	1.699
Al ₂ O ₃	28.441	1.93	-1.414
Ga ₂ O ₃	107	2.02	0.788
TiO ₂	27.467	2.005	1.358
ZnO	9.391	2.145	-0.520
Yb ₂ O ₃	121	2.56	-0.412
SrO	30.404	2.09	0.902
MgO	15.031	2.12	-0.293
Cr ₂ O ₃	14.33	2.12	-0.421
CeO ₂	19.87	2.2	-0.293
PbO	15.028	2.08	-1.431
CuO	16.493	2.05	0.390
NiO	7.633	2.1	-0.708
Fe ₂ O ₃	16.178	2.045	0.902
Gd ₂ O ₃	20.63	2.44	-0.577
CdO	11.868	2.4	-1.260
Sm ₂ O ₃	23.1	2.46	-0.634
CuO	8.991	2.15	-0.480
Y ₂ O ₃	20.514	2.29	-0.479
NiO	2.395	2.05	0.623
La ₂ O ₃	19.166	2.46	0.219
Mn ₂ O ₃	15.636	2.05	0.219
CoO	7.24	2.13	-1.260
IrO ₂	2.03	11.8	1.187

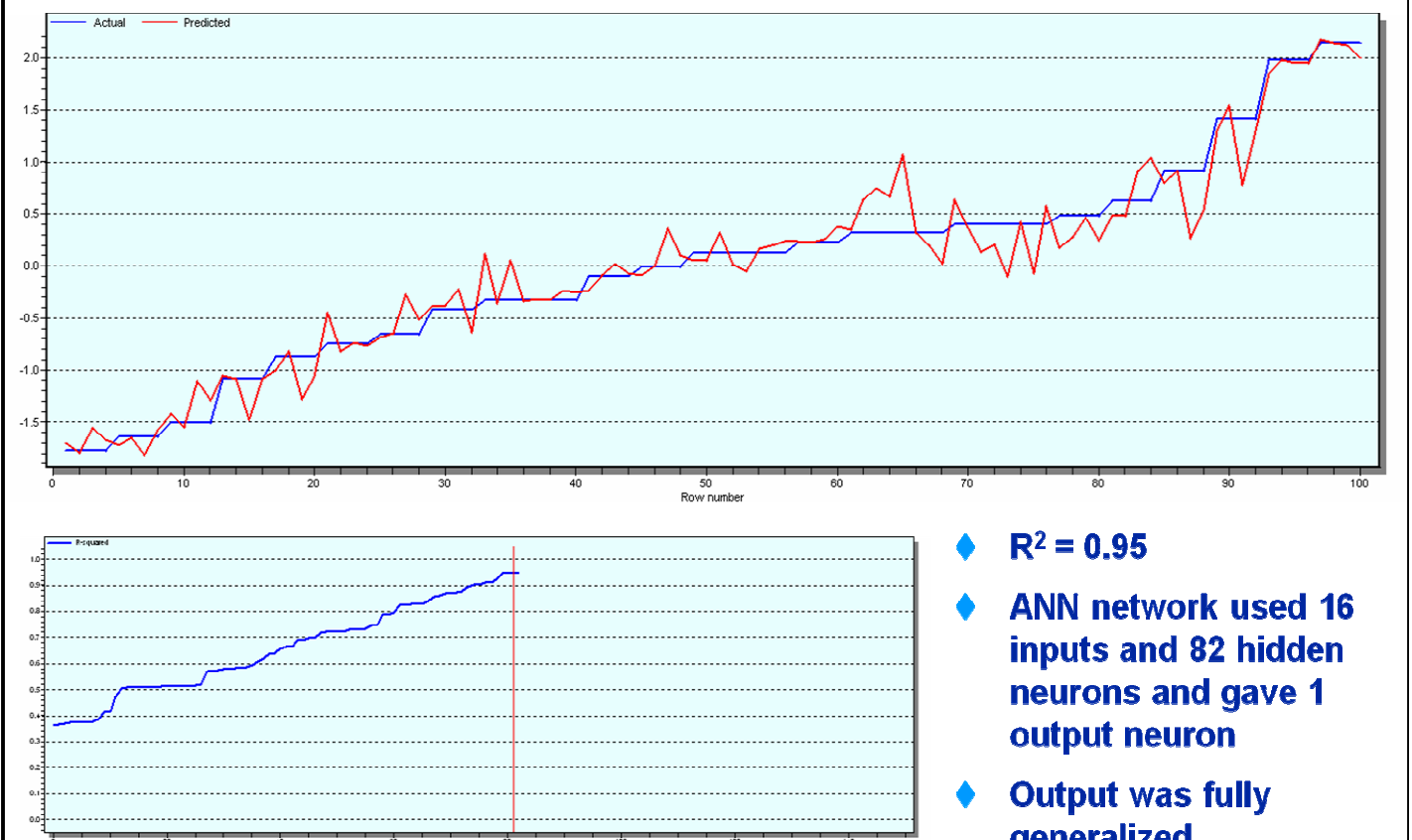
Training Set for Multi-Component Materials

Metal Oxide	IP of Element	PP	Log (Rate)
TiO ₂	1.413	-0.819	1.699
Nb ₂ O ₅	1.988	-0.819	1.699
Al ₂ O ₃	0.914	-1.400	-1.414
Ga ₂ O ₃	1.161	-0.936	0.788
TiO ₂	0.807	-1.023	1.358
ZnO	-1.173	-0.207	-0.520
Yb ₂ O ₃	-0.877	-0.463	-0.412
SrO	1.130	-0.528	0.902
MgO	-0.555	-0.353	-0.293
ZrO ₂	1.559	-0.353	-0.421
Cr ₂ O ₃	-0.075	-0.113	-0.091
PbO	-0.556	2.327	-1.431
Cr ₂ O ₃	-0.395	-0.965	0.390
NiO	-1.366	-0.470	-0.708
Fe ₂ O ₃	-0.430	-0.900	0.902
Gd ₂ O ₃	0.058	0.929	-0.577
CuO	-0.902	1.278	-1.260
Sm ₂ O ₃	0.361	1.645	-0.634
CdO	-1.217	0.987	-1.203
Y ₂ O ₃	0.045	0.637	-0.480
Md ₂ O ₃	1.249	-0.691	0.623
La ₂ O ₃	-0.102	-0.761	0.219
Mn ₂ O ₃	-0.489	-0.761	0.219
CoO	-1.356	-0.255	-1.260
IrO ₂	-1.356	-0.877	1.187

Mechanism and Model Employed

- Mechanism**
- 1) Gas diffusion in electrode pores:
 - O₂ (in bulk) → O₂ (in pores)
 - 2) Adsorption of O₂ on electrode surface (Lewis acid-base interaction):
 - O₂ (in pores) → O₂ (on surface)
 - 3) Surface diffusion of adsorbed O₂ to vicinity of three phase boundary (tpb):
 - O₂ (on surface) → O₂ (near tpb)
 - 4) Dissociation of adsorbed O₂ (surface structure, M-O bond strength):
 - O₂ (near tpb) → 2O₂ (near tpb)
 - 5) Diffusion of adsorbed oxygen atom to electrochemical reaction site (ers):
 - 2O₂ (near tpb) → 2O₂ (ers)
 - 6) Electrochemical reaction of adsorbed oxygen (redox chemistry):
 - 2O₂ (ers) + 2e⁻ → 2O₂ + 4h⁺
 - 7) Neutralization of electron holes (surface electronic properties):
 - 4h⁺ + 4e⁻ → 0
- Model**
- Using a set of assumptions, including transferability and superposability of descriptors, the following model was proposed:
 - $P = f(\Gamma_{O_2,exch}, \text{multiplier})$
 - $\Gamma_{O_2,exch, \text{multiplier}} = f(\Gamma_{O_2,exch, \text{unary}}, \Gamma_{O_2,exch, \text{unary}, 2}, \dots, \Gamma_{O_2,exch, \text{unary}, n})$
 - i.e., cathode performance is a function or functional of the oxygen exchange rate, which in turn can be expressed as a function of materials descriptors (even bulk descriptors), and finally, the exchange rate for the multiple component material is a function of that for unary oxides.

Training the ANN



SUMMARY

- Work to be Done**
- Extend model to hydrodynamic (transport) and macroscopic levels of description.
 - Predict structures and properties of predicted materials.
 - Complete experimental validation of predictions.

Surface Techniques for Obtaining Descriptors

Descriptor	Symbol	Surface Technique(s)
Work Function	ϕ	PES, Kelvin probe
Cation radius + C^{2+} radius	$r_{cat}^{ion} + r_{c2+}^{ion}$	SENAFES (also gives cation coordination number)
Surface metal-oxygen bond energy	$E_{M-O,surf}$	TPD
O1s binding energy	BE O1s	XPS
C-O stretch in CO	ν_{CO}	Surface IR
N-H stretch in pyridine	ν_{pyr}	Surface IR
N-H stretch in ammonia	ν_{am}	Surface IR
Band gap	JV_{g}	UPS
Electron Density of States	$g(E)$	UPS
Surface vacancy concentration	$C_{vac,surf}$	Surface conductivity

- Other Applications**
- Identification of new ceramic membrane materials
 - Selection of solid electrolytes
 - Selection of SOFC anode electrocatalysts
 - Design of chemical looping O₂ carriers
 - Design of selective oxidation catalysts
 - Design of deep oxidation catalysts

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