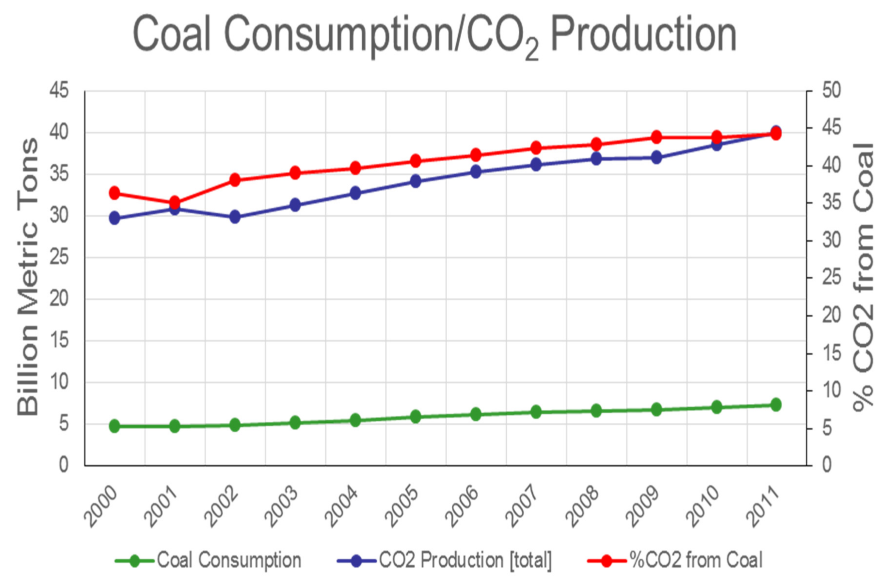
Rational Design of Mixed Oxides for Chemical Looping Combustion of Coal via Coupled Experimental-Computational Studies

Nathan Galinsky, Arya Shafie-Farhood, Amit Mishra, Erik Santiso, and Fanxing Li*

Department of Chemical and Biomolecular Engineering, North Carolina State University, U.S.A

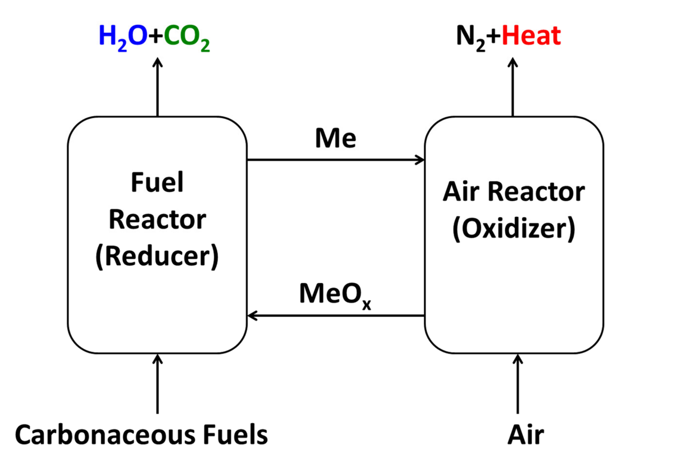
CO_2 Production from Coal



- CO_2 is identified as a leading anthropogenic greenhouse gas
- Significant portion of CO_2 is emitted from coal combustion
- Chemical looping combustion (CLC) is a potential solution

http://www.eia.gov/

Chemical Looping Combustion



Challenges:

1. Oxygen carrier performance
   - Intrinsic redox activity
   - Physical and chemical stability
   - Reaction with solid fuels
2. Reactor design

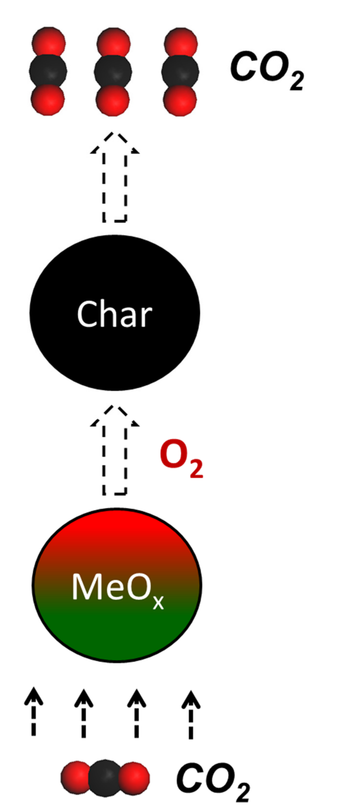
Reactions:

MeO_y + Fuel → Me + H_2O + CO_2 (reducer)

Me + 1/2O_2 (Air) → MeO_y (oxidizer)

Fan, L.-S. Chemical Looping Systems for Fossil Energy Conversions, 2010

Chemical Looping with Oxygen Uncoupling (CLOU)



Key Concepts:

1. Gaseous oxygen released from metal oxide lattice at high T;
2. Enhanced reaction rate between gaseous oxygen and coal char/volatiles

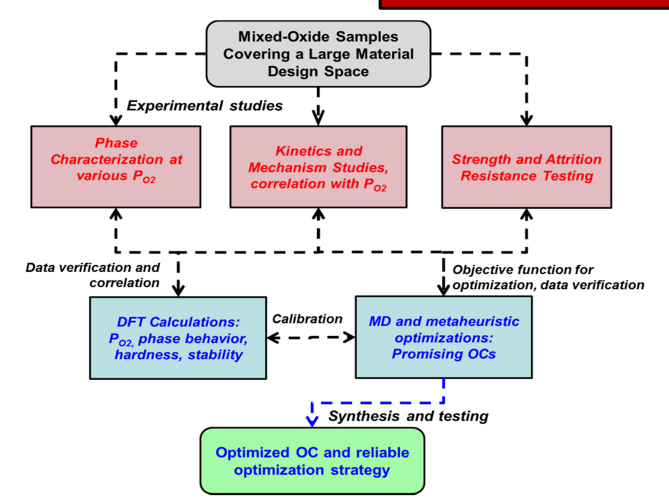
Oxygen Carriers:

- Cu, Co, and Mn oxides are known oxygen uncoupling materials

Challenges:

- Cost and environmental impacts
- Less than optimal thermal properties (Mn/Co)
- Low melting point (Cu)

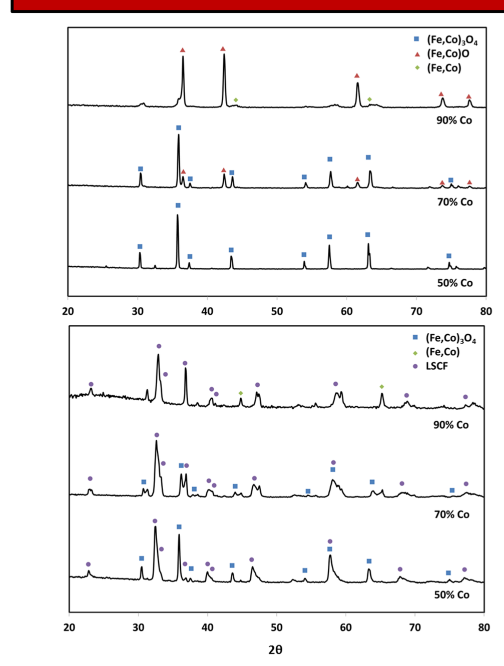
Proposed Approach

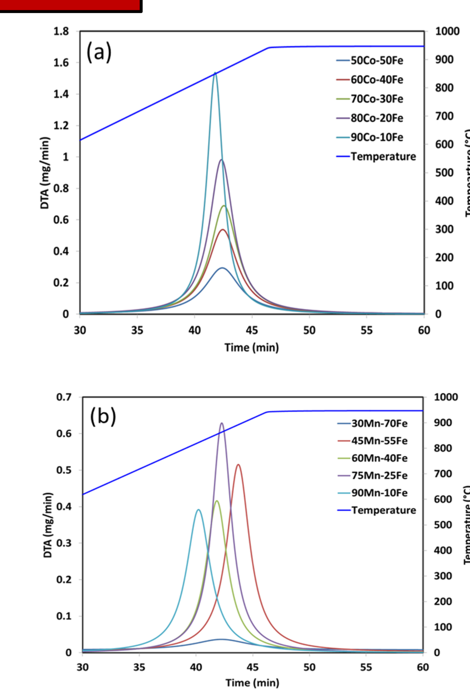


1. **Experimental:** Mixed Mn-Fe and Co-Fe oxides, perovskite, and perovskite composites
2. **Simulation:** *ab-initio*/DFT and molecular dynamics (MD) simulations, genetic algorithm for material screening

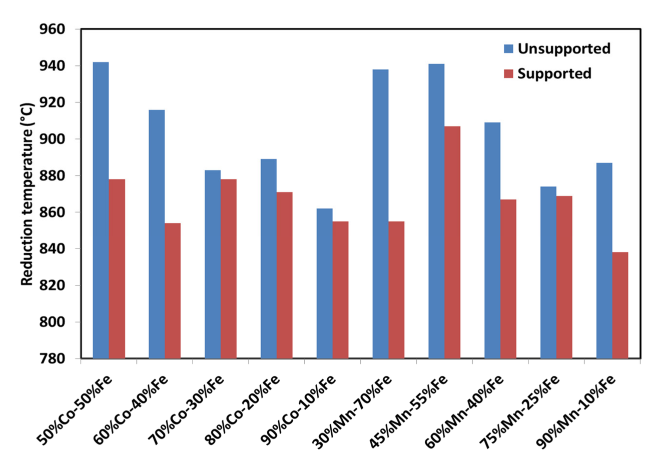
Fe-Mn and Fe-Co Oxides

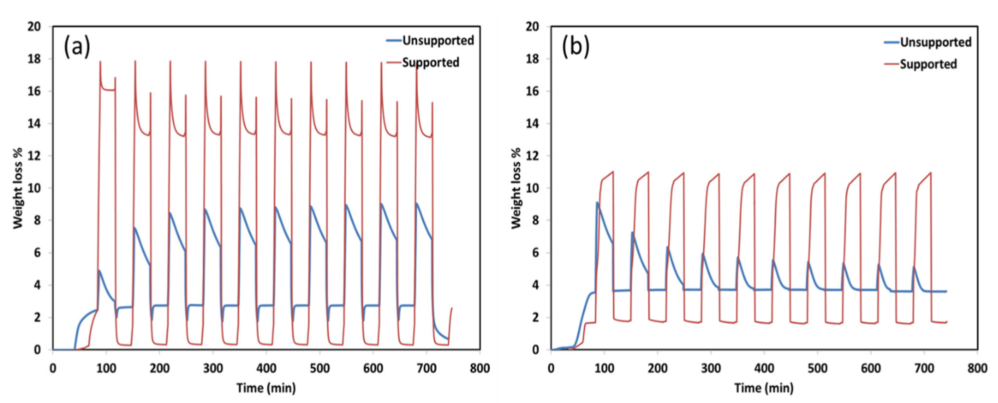
Sample #	Cation Composition
1	50%Co-50%Fe
2	60%Co-40%Fe
3	70%Co-30%Fe
4	80%Co-20%Fe
5	90%Co-10%Fe
6	30%Mn-70%Fe
7	45%Mn-55%Fe
8	60%Mn-40%Fe
9	75%Mn-25%Fe
10	90%Mn-10%Fe





Mixed oxides with desired phases formed, increasing the concentration of Co and Mn in the mixed oxides reduces their initial oxygen donation temperature



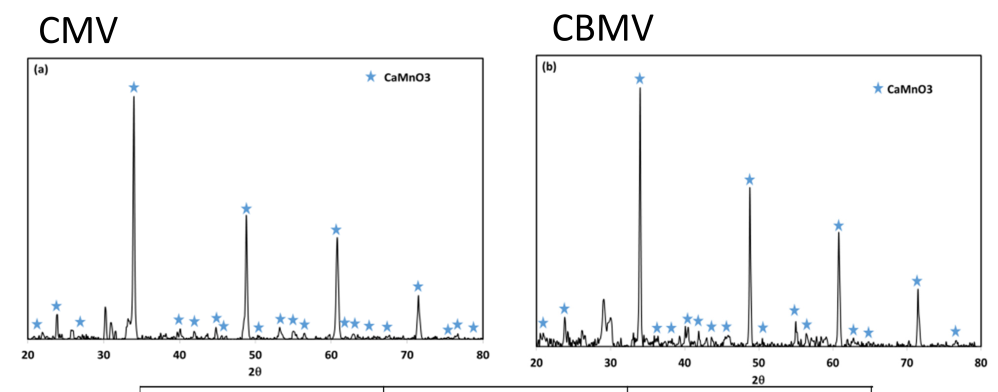


Perovskite supports decrease the oxygen donation temperature of the mixed oxides, they also affect the redox activity of the oxygen carriers

Screening of Perovskites

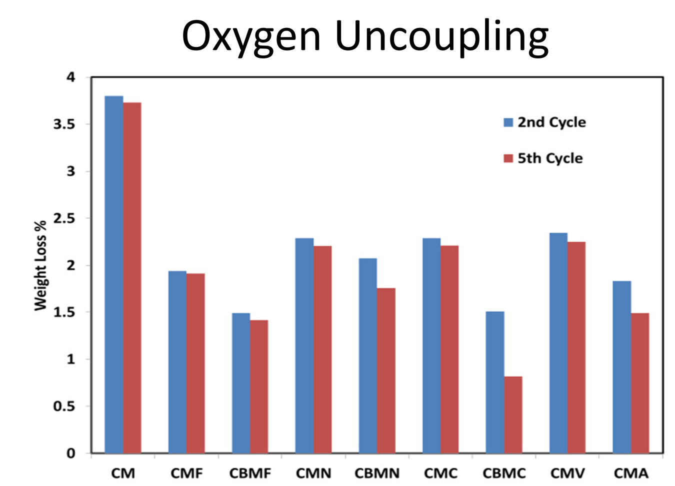
Perovskite	Synthesis	Abbreviation
$CaMnO_3$	Sol-gel	CM
$BaMnO_3$	Sol-gel	BM
$CaMn_{0.8}Fe_{0.2}O_3$	Sol-gel	CMF
$Ca_{0.8}Ba_{0.2}Mn_{0.8}Fe_{0.2}O_3$	Sol-gel	CBMF
$CaMn_{0.8}Ni_{0.2}O_3$	Sol-gel	CMN
$Ca_{0.8}Ba_{0.2}Mn_{0.8}Ni_{0.2}O_3$	Sol-gel	CBMN
$CaMn_{0.8}Co_{0.2}O_3$	Sol-gel	CMC
$Ca_{0.8}Ba_{0.2}Mn_{0.8}Co_{0.2}O_3$	Sol-gel	CBMC
$CaMn_{0.8}V_{0.2}O_3$	Sol-gel	CMV
$Ca_{0.8}Ba_{0.2}Mn_{0.8}V_{0.2}O_3$	Sol-gel	CBMV
$CaMn_{0.8}Al_{0.2}O_3$	Sol-gel	CMA
$Ca_{0.8}Ba_{0.2}Mn_{0.8}Al_{0.2}O_3$	Sol-gel	CBMA

Lattice parameters can be refined to confirm A and B-site dopants



Lattice Parameter	Database	CMV
a (Å)	5.279	5.33
b (Å)	7.4438	7.45
c (Å)	5.2583	5.23
Volume (10^6 pm^3)	206.63	207.78

Perovskite Characterizations



$CaMnO_3$ perovskite exhibits 40% or more uncoupling weight loss at 900 °C

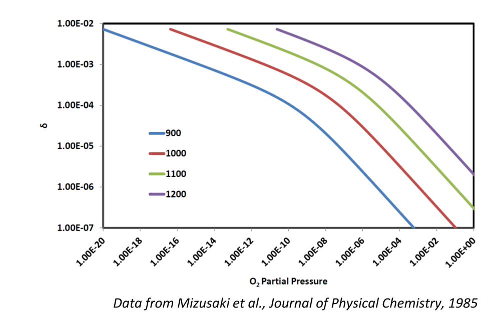
B site dopants, e.g. Fe, enhances the recyclability of the oxygen carriers

Ba addition stabilizes the perovskite structure

Simulation Studies

Ab-initio Calculation Values	Data Interpretation
Vacancy formation energy	Expected oxygen vacancy concentrations at various T and P_{O2}
DFT energy difference between two phases	P_{O2} at phase boundary
Lattice parameter change after vacancy creation	Stability of the oxide material in redox reactions and (potentially) attrition resistance
Energy barrier for vacancy migration	Ease for O^{2-} and electron migrations
Bond population and volume	Material hardness and attrition resistance

Case Study with $LaFeO_{3-\delta}$



Data from Mizusaki et al., Journal of Physical Chemistry, 1985

Significant information can be obtained from DFT simulations. When DFT is used to calibrate MD, efficient algorithms can be developed

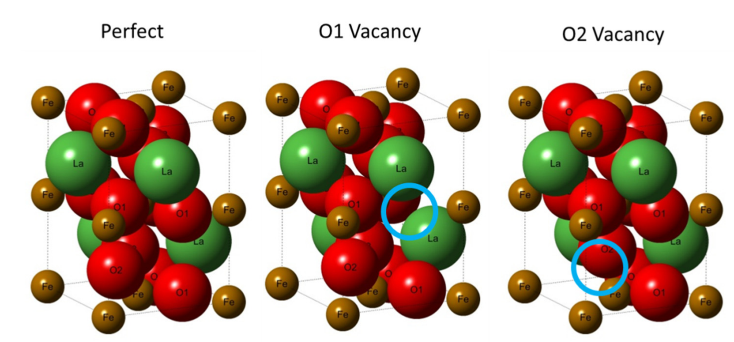
$$\frac{1}{\delta}LaFeO_3 \rightleftharpoons \frac{1}{\delta}LaFeO_{3-\delta} + \frac{1}{2}O_2$$

$$\Delta G = E_{defected} - E_{perfect} + \delta\mu_O$$

$$\mu_{O_2}(P_{O_2},T) = \mu_{O_2}(P^0,T^0) + G(P^0,T) - G(P^0,T^0) + kT\ln\left(\frac{P_{O_2}}{P^0}\right)$$

Structure	DFT energy (eV)	DFT energy without entropy (eV)
Perfect $LaFeO_3$	-159.81278	-159.820515
$LaFeO_{2.75}$ with O1 defect	-151.316723	-151.338344
$LaFeO_{2.75}$ with O2 defect	-151.392715	-151.394119

Perfect O1 Vacancy O2 Vacancy



Temperature (°C)	DFT-estimated P_{O2} (atm)	P_{O2} extrapolated from experiments (atm)
900	4.75E-31	2.87E-31
1000	1.21E-27	1.22E-27
1100	8.74E-25	1.55E-24
Lattice parameters	DFT Calculated	Experimentally determined
a	5.535	5.557
b	5.599	5.652
c	7.888	7.854

DFT predicts equilibrium oxygen partial pressure with reasonable accuracy

Conclusions

- **Co and Mn containing mixed oxides of various structures are prepared;**
- **Perovskite supports can notably affect the CLOU properties of Co/Mn containing spinel and bixbyites;**
- **Dopants can stabilize $CaMnO_3$ parent perovskite;**
- **DFT can be effective to predict material properties using first principle.**

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