

# **Outline–Draft JCP format for: Reactive Force Field for Perovskite–Based Solid Oxides and Its Application to Solid Oxide Electrolysis Cells**

Franz Martinez\*

*Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada*

E-mail: [franzmichel.martinez@ucalgary.ca](mailto:franzmichel.martinez@ucalgary.ca)

## Abstract

Conversion of CO<sub>2</sub> to syngas can be achieved in solid oxide electrolysis cells at high temperatures ( 1000 K) by using Perovskite-based solid oxides as electrocatalysts. This process is projected to be a viable way of generating fuels by converting, and therefore reducing, CO<sub>2</sub> from industrial emissions. However, full understanding of the mechanism involved in CO<sub>2</sub> conversion on these electrocatalysts is far from complete. In this work, we perform DFT calculations and reactive molecular dynamics to understand the electronic structure and stability of perovskite-based solid oxides used as electrocatalysts for CO<sub>2</sub> conversion. To this end, our study involves firstly, generation of a dataset from DFT calculations, which include optimized geometries, equations of state, surface energies, and slab—CO<sub>2</sub> interactions from a set of ABO<sub>3</sub>-type perovskites. Secondly, we parametrize the reactive force field, ReaxFF, using an annealing Monte Carlo optimizer and a covariance matrix adaptation evolution strategy. Finally, we explore bulk dynamics of the perovskites at high temperature and the time evolution of reactions involving CO<sub>2</sub> on the surface of slabs from the perovskites. Of interest, our results demonstrate the modes in which the CO<sub>2</sub> is chemisorbed at high temperature; the consequent formation of intermediates; and their role in further conversion of the CO<sub>2</sub>. This study serves as a base to elucidate the elementary steps involved in the mechanism of CO<sub>2</sub> conversion on perovskites at high temperature, which will allow us to understand the most favorable conditions for the reaction to occur and, consequently, provide us of a way to improve the design of perovskite-based solid oxide electrocatalysts.

## 1 Introduction

CO<sub>2</sub>, electrocatalysts, and solid oxide fuels.<sup>1–16</sup>

DFT studies.<sup>17–26</sup>

Molecular dynamics studies.<sup>27</sup>

## 2 Computational Methods

### 2.1 ReaxFF and Parameterization Strategy

ReaxFF is a force field based on the dynamical computation of the bond-order, which dictates the connectivity between atoms on the fly. This approach allows ReaxFF to consider bond breaking and formation, and therefore the ability to follow the apparition of intermediates involved in the reaction mechanism in complex systems containing thousands of atoms.<sup>28–39</sup>

Its use bridges the advantages of classical molecular dynamics simulation with those of quantum-mechanical approaches.

Parametrization of ReaxFF involves generation of a dataset, generally from quantum mechanical calculations, and subsequent fitting of the force field parameters with respect to the dataset by minimizing the error function,  $E_f$ ,

$$E_f = \frac{(x_i - x_{ReaxFF,i})^2}{w_i}. \quad (1)$$

Where  $x_i$  is the value of a property  $x$  (e.g. heat of formation, geometries, energetic differences, etc.);  $x_{ReaxFF,i}$  is such property calculated using ReaxFF; and  $w_i$  is the weight, or accuracy, associated to the desired deviation between both  $x_i$  and  $x_{ReaxFF,i}$ . In this work the Monte Carlo Force Field Optimizer,<sup>40</sup> part of the ADF package, has been used to fit the various parameters of the force field, mostly because the method has been shown to give good results independent of the initial guess for the force fields parameters.

The parametrization of the force field was performed using various stages, and it started with known parameters for C, H, O, S, Fe, and Cr from a previous study of hydrocarbon oxidation on pyrite-covered  $\text{Cr}_2\text{O}_3$ ,<sup>31</sup> and for Ca from a previous study of calcium oxyde hydration.<sup>41</sup>

With starting parameters for most elements except for La, the first stage of the parametrization involved fitting the La–La parameters of the force field to the following: quantum me-

chanically calculated equations of state corresponding to three solid phases of La, i.e. double hexagonal close packed (dhcp,  $\alpha$ -La), face centered cubic (fcc,  $\gamma$ -La), and body centered cubic (bcc,  $\beta$ -La); and data from the electronic structure calculation of the  $\text{La}_2$  molecule was added. This stage was carried out while keeping parameters for other interactions unchanged. The following stage involved further fitting of the La–La parameters, namely those related to the electrostatic interaction (EEM shielding, EEM electronegativity, and EMM hardness), and the La–O parameters by adding to the dataset Mulliken charges and geometrical information obtained from the optimized structures of the  $\text{La}_2\text{O}_3$  cluster, three  $\text{La}_4\text{O}_6$  clusters, and one  $\text{La}_6\text{O}_9$  cluster. Also, the equations of state corresponding to two solid structures of  $\text{La}_2\text{O}_3$  were computed and added.

## 2.2 Electronic Structure Calculations for Dataset Generation

DFT calculations are carried out using Quantum Espresso,<sup>42</sup> for all solid oxides in bulk or slab form. Calculations were performed using the pseudo-potentials from the PSlibrary with scalar-relativistic effects due to the presence of Lanthanum **put references**. A value of 75.0 Ry was used for the kinetic energy cutoff, which were tested for convergence ensuring that  $\Delta E_{tot}/\Delta E_{cut} < 0.01$  eV per atom. Monkhorst-Pack k-point sampling of the Brillouin zone was chosen to be  $4 \times 4 \times 4$  for most calculations using cells of approximately  $5.5 \text{ \AA} \times 7.6 \text{ \AA} \times 5.5 \text{ \AA}$ , due to the variable size of the cells after variable cell relaxation. The k-point grid used was also tested using the same criterion to ensure convergence.

Because the transition metals present localized electronic density on their d-orbitals with strong correlation, the Hubbard correction is employed to take into account these effects.**put references** Values used for the Hubbard term, U, were taken from **put values, and justify about not determining their values from linear response theory**

The convergence criterion used for all calculations was of 0.02 eV for the total energy, and in the case of relaxations the maximum force component on each atom had to satisfy being smaller than 0.01 eV/Å

Some energetic and geometric parameters were also obtained from clusters and molecules in the gas phase using the ADF package. Here, for consistency with other parameters obtained previously for ReaxFF, the B3LYP functional has been used with TZP STO-basis functions. Scalar relativistic effects were introduced using the ZORA correction.

## 2.3 Molecular Dynamics Trajectories Using ReaxFF

For the molecular dynamics simulations using ReaxFF, the system **specify details for bulk simulations and slabs** ... first is equilibrated using classical molecular dynamics with the UFF force field. From the equilibrated trajectory at the conditions required **double check temperature and pressure and change this part**, several points are selected randomly as starting points for the simulation. This ensures that the system starts from a correct point in equilibrium of the ensemble for the ReaxFF dynamics.

# 3 Results and Discussion

## 3.1 Equations of State

Equations of state for hexagonal La, LaFeO<sub>3</sub>, LaCrO<sub>3</sub>, ... were calculated using DFT, and the ReaxFF force field was parametrized to reproduce this curve to the best possible fit. Because the relationship between energy and volume in solids allow to capture the stability of the phase, fitting of these curves give ReaxFF the ability to model accurately the bulk phase of the perovskite.

The bulk modulus for  $\alpha$ -La was obtained by fitting the calculated points to the Birch-Murnaghan equation of state<sup>43</sup>, and the value obtained of 25.6 GPa agrees with an approximate 8% of error compared to the reported experimental bulk modulus value of 27.9 GPa.<sup>44</sup>

## 3.2 Surface Energies

Given the differences, in structure and energetics, of the surface compared to the bulk, it is necessary to introduce this behaviour to the force field. To this end, slabs of various perovskites were constructed from their bulk counterparts to extend the ReaxFF force field.

**Calculations currently going on**

## 3.3 Oxygen Vacancy Formation Energies

Introduction of Ca and Sr in the A-site of the perovskites favours the formation of oxygen vacancies due to the change in ionic size compared to La and the different charges of these cations. **cite** Also, this changes allows for oxygen ionic diffusion through the solid. The existence of oxygen vacancies in the system needs to be captured by ReaxFF in the form of correctly capturing changes in the chemical environment and in the relative stability of the perovskite unit cell in the absence of one oxygen. For various perovskites, the oxygen vacancy formation energy is calculated and incorporated into the dataset used to fit ReaxFF.

# 4 Applications and Discussion

## 4.1 Oxygen Diffusion through the Perovskites

To exemplify the dynamics on the bulk, diffusion of  $\text{O}_2^{-2}$  is followed through the perovskite in bulk phase.

Also, to account for the accuracy of the force field, the expansion coefficient is computed for LCFCr and LSFCr. This value is compared to experimental results ...

## 4.2 $\text{CO}_2$ Interactions on the Surface

Using a slab of a representative portion **fill in details of the real size** of the surface of the LCFCr, various mixtures of gases are fed into one of the surfaces ...

Formation of intermediates is observed at 1073 K **double check temperature**

## 5 Concluding Remarks

## Acknowledgement

This work has been enabled by the use of computing resources provided by Compute Canada.

## References

- (1) Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. Photocatalytic Reduction of CO<sub>2</sub> on TiO<sub>2</sub> and Other Semiconductors. *Angewandte Chemie International Edition* **2013**, *52*, 7372–7408.
- (2) E. Benson, E.; P. Kubiak, C.; J. Sathrum, A.; M. Smieja, J. Electrocatalytic and homogeneous approaches to conversion of CO<sub>2</sub> to liquid fuels. *Chemical Society Reviews* **2009**, *38*, 89–99.
- (3) Pradeep Indrakanti, V.; D. Kubicki, J.; H. Schobert, H. Photoinduced activation of CO<sub>2</sub> on Ti-based heterogeneous catalysts : Current state, chemical physics-based insights and outlook. *Energy & Environmental Science* **2009**, *2*, 745–758.
- (4) Indrakanti, V. P.; Schobert, H. H.; Kubicki, J. D. Quantum Mechanical Modeling of CO<sub>2</sub> Interactions with Irradiated Stoichiometric and Oxygen-Deficient Anatase TiO<sub>2</sub> Surfaces: Implications for the Photocatalytic Reduction of CO<sub>2</sub>. *Energy & Fuels* **2009**, *23*, 5247–5256.
- (5) Zeng, S.; Kar, P.; Thakur, U. K.; Shankar, K. A review on photocatalytic CO<sub>2</sub> reduction using perovskite oxide nanomaterials. *Nanotechnology* **2018**, *29*, 052001.
- (6) Yamada, I.; Takamatsu, A.; Asai, K.; Shirakawa, T.; Ohzuku, H.; Seno, A.; Uchimura, T.; Fujii, H.; Kawaguchi, S.; Wada, K. et al. Systematic Study of Descriptors for Oxygen Evolution Reaction Catalysis in Perovskite Oxides. *The Journal of Physical Chemistry C* **2018**, *122*, 27885–27892.
- (7) Kar, P.; Farsinezhad, S.; Mahdi, N.; Zhang, Y.; Obuekwe, U.; Sharma, H.; Shen, J.; Semagina, N.; Shankar, K. Enhanced CH<sub>4</sub> yield by photocatalytic CO<sub>2</sub> reduction using TiO<sub>2</sub> nanotube arrays grafted with Au, Ru, and ZnPd nanoparticles. *Nano Research* **2016**, *9*, 3478–3493.



- (8) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y.-L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nature Communications* **2013**, *4*, 2439.
- (9) Ni, M. An electrochemical model for syngas production by co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub>. *Journal of Power Sources* **2012**, *202*, 209–216.
- (10) Tan, S.; Zhao, Y.; Zhao, J.; Wang, Z.; Ma, C.; Zhao, A.; Wang, B.; Luo, Y.; Yang, J.; Hou, J. CO<sub>2</sub> dissociation activated through electron attachment on the reduced rutile TiO<sub>2</sub>(110)-1 $\times$ 1 surface. *Physical Review B* **2011**, *84*, 155418.
- (11) Baniecki, J. D.; Ishii, M.; Kurihara, K.; Yamanaka, K.; Yano, T.; Shinozaki, K.; Imada, T.; Nozaki, K.; Kin, N. Photoemission and quantum chemical study of SrTiO<sub>3</sub>(001) surfaces and their interaction with CO<sub>2</sub>. *Physical Review B* **2008**, *78*, 195415.
- (12) Jia, J.; Qian, C.; Dong, Y.; Li, Y. F.; Wang, H.; Ghossoub, M.; Butler, K. T.; Walsh, A.; Ozin, G. A. Heterogeneous catalytic hydrogenation of CO<sub>2</sub> by metal oxides: defect engineering – perfecting imperfection. *Chemical Society Reviews* **2017**, *46*, 4631–4644.
- (13) Yin, W.; Weng, B.; Ge, J.; sun, d. q.; Li, Z.; Yan, Y. Oxide Perovskites, Double Perovskites and Derivatives for Electrocatalysis, Photocatalysis, and Photovoltaics. *Energy Environ Sci* **2018**,
- (14) Zheng, Y.; Wang, J.; Yu, B.; Zhang, W.; Chen, J.; Qiao, J.; Zhang, J. A review of high temperature co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology. *Chem Soc Rev* **2017**, *46*, 1427–1463.

- (15) Andersson, M. Review on modeling development for multiscale chemical reactions coupled transport phenomena in solid oxide fuel cells. *Appl Energy* **2010**, *87*, 1461–1476.
- (16) Beatriz, M.-S.; Jesús, P.-G.; David, Á.-B.; Birss, V.; Morán, E. Microwave-assisted synthesis and characterization of new cathodic material for solid oxide fuel cells:  $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ . *Ceram Int* **2015**, *41*, 8411–8416.
- (17) Tian, X.; Wang, T.; Fan, L.; Wang, Y.; Lu, H.; Mu, Y. A DFT based method for calculating the surface energies of asymmetric MoP facets. *Applied Surface Science* **2018**, *427*, 357–362.
- (18) Mayeshiba, T.; Morgan, D. Strain effects on oxygen vacancy formation energy in perovskites. *Solid State Ionics* **2017**, *311*, 105–117.
- (19) Wang, L.; Maxisch, T.; Ceder, G. Oxidation energies of transition metal oxides within the  $\text{GGA}+\text{U}$  framework. *Physical Review B* **2006**, *73*, 195107.
- (20) Li, W.; Walther, C. F. J.; Kuc, A.; Heine, T. Density Functional Theory and Beyond for Band-Gap Screening: Performance for Transition-Metal Oxides and Dichalcogenides. *Journal of Chemical Theory and Computation* **2013**, *9*, 2950–2958.
- (21) Liu, R.; Fang, L.; Hao, Y.; Chi, Y. Influence of Oxygen Vacancy Density on the Polaronic Configuration in Rutile. *Materials* **2018**, *11*, 2156.
- (22) Seo, M.; Park, H.; Lee, D.; Park, M.; Chen, Z. Design of highly active perovskite oxides for oxygen evolution reaction by combining experimental and ab initio studies. **2015**, *5*, 4337–4344.
- (23) Evarestov, R.; Bandura, A.; Alexandrov, V. Adsorption of water on (0 0 1) surface of  $\text{SrTiO}_3$  and  $\text{SrZrO}_3$  cubic perovskites: hybrid HF-DFT LCAO calculations. **2007**, *601*, 1844–1856.

- (24) Pilania, G.; Gao, P.-X.; Ramprasad, R. Establishing the LaMnO<sub>3</sub> Surface Phase Diagram in an Oxygen Environment: An ab Initio Kinetic Monte Carlo Simulation Study. *J Phys Chem C* **2012**, *116*, 26349–26357.
- (25) Pilania, G.; Ramprasad, R. Adsorption of atomic oxygen on cubic PbTiO<sub>3</sub> and LaMnO<sub>3</sub> (001) surfaces: A density functional theory study. **2010**, *604*, 1889–1893.
- (26) Zurek, E.; Grochala, W. Predicting crystal structures and properties of matter under extreme conditions via quantum mechanics: the pressure is on. **2015**, *17*, 2917–2934.
- (27) wang, y.-f. coarse-grained molecular dynamics investigation of nanostructures and thermal properties of porous anode for solid oxide fuel cell. *J Power Sources* **2014**, *254*, 209–217.
- (28) Migliorati, V.; Serva, A.; Terenzio, F.; Paola, D. Development of Lennard-Jones and Buckingham Potentials for Lanthanoid Ions in Water. *Inorg Chem* **2017**, *56*, 6214–6224.
- (29) Merinov, B. V.; Mueller, J. E.; van Duin, A. C. T.; An, Q.; Goddard, W. A. ReaxFF Reactive Force-Field Modeling of the Triple-Phase Boundary in a Solid Oxide Fuel Cell. *The Journal of Physical Chemistry Letters* **2014**, *5*, 4039–4043.
- (30) Raymand, D.; van Duin, A. C.; Baudin, M.; Hermansson, K. A reactive force field (ReaxFF) for zinc oxide. *Surface Science* **2008**, *602*, 1020–1031.
- (31) Shin, Y. K.; Kwak, H.; Vasenkov, A. V.; Sengupta, D.; van Duin, A. C. Development of a ReaxFF Reactive Force Field for Fe/Cr/O/S and Application to Oxidation of Butane over a Pyrite-Covered Cr<sub>2</sub>O<sub>3</sub> Catalyst. *ACS Catalysis* **2015**, *5*, 7226–7236.
- (32) van Duin, A. C.; Merinov, B. V.; Jang, S.; Goddard, W. A. ReaxFF reactive force field for solid oxide fuel cell systems with application to oxygen ion transport in yttria-stabilized zirconia. *J Phys Chem* **2008**, *112*, 3133–40.

- (33) Goddard, W. A.; van Duin, A.; Chenoweth, K.; Cheng, M.-J.; Pudar, S.; Oxgaard, J.; Merinov, B.; Jang, Y.; Persson, P. Development of the ReaxFF reactive force field for mechanistic studies of catalytic selective oxidation processes on BiMoOx. *Top Catal* **2006**, *38*, 93.
- (34) Hubin, P. O.; Jacquemin, D.; Leherste, L.; Vercauteren, D. P. Parameterization of the ReaxFF reactive force field for a proline-catalyzed aldol reaction. **2016**, *37*, 2564–2572.
- (35) Senftle, T. P.; Hong, S.; Islam, M.; Kylasa, S. B.; Zheng, Y.; Shin, Y.; Junkermeier, C.; Roman, E.-H.; Janik, M. J.; Aktulga, H. et al. The ReaxFF reactive force-field: development, applications and future directions. *Npj Comput Mater* **2016**, *2*, npjcomputats201511.
- (36) Chenoweth, K.; T, v. D., Adri C.; Goddard, W. A. The ReaxFF Monte Carlo Reactive Dynamics Method for Predicting Atomistic Structures of Disordered Ceramics: Application to the Mo3VOx Catalyst. **2009**, *121*, 7766–7770.
- (37) Chenoweth, K.; van Duin, A. C.; Goddard, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. **2008**, *112*, 1040–1053.
- (38) van Duin, A. C.; Merinov, B. V.; Han, S.; Dorso, C. O.; Goddard, W. A. ReaxFF reactive force field for the Y-doped BaZrO3 proton conductor with applications to diffusion rates for multigranular systems. **2008**, *112*, 11414–22.
- (39) Liu, L.; Liu, Y.; Zybin, S. V.; Sun, H.; Goddard, W. A. ReaxFF-lg: Correction of the ReaxFF Reactive Force Field for London Dispersion, with Applications to the Equations of State for Energetic Materials. **2011**, *115*, 11016–11022.
- (40) Iype, E. Parameterization of a reactive force field using a Monte Carlo algorithm. *J Comput Chem* **2013**, *34*, 1143–1154.

- (41) Manzano, H.; Pellenq, R. J. M.; Ulm, F.-J.; Buehler, M. J.; van Duin, A. C. T. Hydration of Calcium Oxide Surface Predicted by Reactive Force Field Molecular Dynamics. *Langmuir* **2012**, *28*, 4187–4197.
- (42) Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M. et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of Physics: Condensed Matter* **2017**, *29*, 465901.
- (43) Fu, C. L.; Ho, K. M. First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to Nb and Mo. *Phys. Rev. B* **1983**, *28*, 5480–5486.
- (44) Lide, D. R. *CRC handbook of chemistry and physics*; CRC press, 2003.

## Graphical TOC Entry

