# *Ab Initio Calculations of the Redox Chemistry in Alkali-Oxygen Batteries*

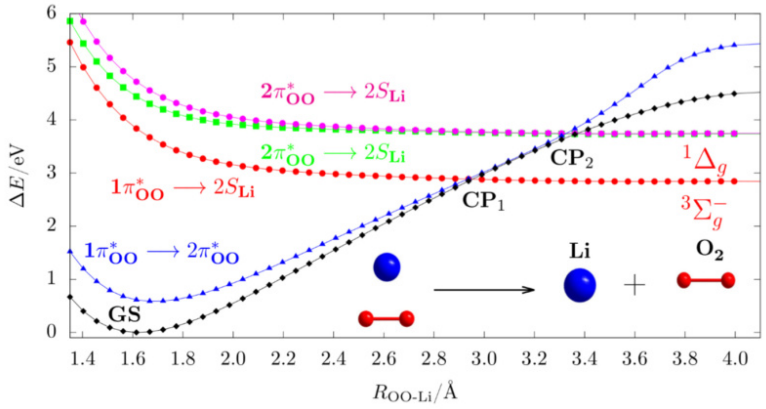


Figure 1: Dissociation curves of electronic doublet states for $LiO_2$ calculated at CASSCF(13,12)/CASPT2/cc-pV5Z level of theory.

## Introduction

Alkali metal-oxygen batteries have a particularly high energy density and therefore concepts for rechargeable batteries are currently intensively studied. Thus, a deep understanding of metal-oxygen chemistry of the alkali peroxides $Li_2O_2$, $Na_2O_2$ and superoxides $LiO_2$, $NaO_2$, $KO_2$ plays an important role [1]. We investigated the dissociation of small model systems, namely molecular superoxides and peroxides, at electronic level by using multi-reference methods.

## Methods

We applied highly correlated multi-reference wavefunction-based methods for our study. The complete active space self-consistent field (CASSCF) method allow to consider several electronic states of the system and is important to describe the reaction path of dissociation. Furthermore, the complete active space second order perturbation theory (CASPT2) approach was employed to account for dynamical electron correlation effects. The methods contain operations with large data sets and need high performance calculations.

## Results

Potential energy surfaces and curves have been calculated to consider molecular and electronic structures of the model systems. The potential energy curves contain crossing points (CP) between the groundstate (GS) of the molecular superoxides and excited states during the dissociation path. In case of alkali superoxides the dissociation preferable leads to

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Project Areas
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Clusters
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Software
MOLPRO

Additional Software
VASP, MOLCAS

Institute
Institute of Physical Chemistry

University
Justus Liebig University Giessen

molecularoxygen (singlet or triplet) and the alkali atom:

$LiO_2 \rightarrow O_2 + Li$

$NaO_2 \rightarrow O_2 + Na$

$KO_2 \rightarrow O_2 + K$

Molecular peroxides can dissociate to either superoxides as intermediates or directly to oxygen and metal dimers $Li_2$-$Na_2$. The later described dissociation path demonstrates two electron transition processes and crossing points between different electronic states, which lead to different products. The potential energy curves of lowest electronic states for the dissociation $LiO_2 \rightarrow O_2$ +Li are shown in Figure 1.

## Discussion

For a fundamental understanding of the chemical processes of the charging process in lithium oxygen batteries,we considered the reaction from molecular superoxides and peroxides to oxygen and the alkali metal. The dissociation of the superoxides leads over two different crossing points either to the thermodynamically preferred triplet oxygen or to the energetically higher lying singlet oxygen formation. The molecular peroxides dissociate directly to a metallic phase and the oxygen molecule or more probably to the superoxide intermediate.

## Outlook

The theoretical research with multi-reference methods of molecular superoxide and peroxide systems has given detailed information about the reaction mechanism, which can be used to improve the battery performance by developing avoiding strategies for side reactions.

## Publications

A. Zaichenko, D. Schröder, J. Janek, D. Mollenhauer, Manuscript to be submitted

## Reference

[1] X. Zhang, X.-G. Wang, Z. Xie, Z. Zhou “Recent progress in rechargeable alkali metal–air batteries” Green Energy & Environment 1, 1, 4–17 (2016)

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