Thermodynamic and Kinetic Limitations for Peroxide and Superoxide Formation in Na-O2 Batteries

The Na–O2 system holds great potential as a low-cost, high-energy-density battery, but under normal operating conditions, the discharge is limited to sodium superoxide (NaO₂), whereas the high-capacity peroxide state (Na₂O₂) remains elusive. Here, we apply density functional theory calculations with an improved error-correction scheme to determine equilibrium potentials and free energies as a function of temperature for the different phases of NaO₂ and Na₂O₂, identifying NaO₂ as the thermodynamically preferred discharge product up to ∼120 K, after which Na₂O₂ is thermodynamically preferred. We also investigate the reaction mechanisms and resulting electrochemical overpotentials on stepped surfaces of the NaO₂ and Na₂O₂ systems, showing low overpotentials for NaO₂ formation (η_{dis} = 0.14 V) and depletion (η_{cha} = 0.19 V), whereas the overpotentials for Na₂O₂ formation (η_{dis} = 0.69 V) and depletion (η_{cha} = 0.68 V) are found to be prohibitively high. These findings are in good agreement with experimental data on the thermodynamic properties of the NaₓO₂ species and provide a kinetic explanation for why NaO₂ is the main discharge product in Na–O₂ batteries under normal operating conditions.

General information
State: Published
Organisations: Department of Energy Conversion and Storage, Atomic Scale Materials Modelling
Contributors: Mekonnen, Y. S., Christensen, R., García-Lastra, J. M., Vegge, T.

Publication information
Journal: Journal of Physical Chemistry Letters
Volume: 9
Issue number: 15
ISSN (Print): 1948-7185
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 8.37 SJR 4.667 SNIP 1.595
Web of Science (2017): Impact factor 8.709
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 8.18 SJR 4.602 SNIP 1.651
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 8.04 SJR 4.143 SNIP 1.758
Web of Science (2015): Impact factor 8.539
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 7 SJR 3.725 SNIP 1.71
Web of Science (2014): Impact factor 7.458
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 6.61 SJR 3.529 SNIP 1.608
Web of Science (2013): Impact factor 6.687
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 6.3 SJR 3.965 SNIP 1.742
Web of Science (2012): Impact factor 6.585
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 5.95 SJR 3.283 SNIP 1.613
Web of Science (2011): Impact factor 6.213
ISI indexed (2011): ISI indexed no
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Web of Science (2010): Impact factor
Web of Science (2010): Indexed yes
Web of Science (2009): Indexed yes
Web of Science (2008): Indexed yes
Web of Science (2007): Indexed yes
Web of Science (2006): Indexed yes
Web of Science (2005): Indexed yes
Web of Science (2004): Indexed yes
Web of Science (2003): Indexed yes
Web of Science (2002): Indexed yes
Web of Science (2001): Indexed yes
Web of Science (2000): Indexed yes
Original language: English
DOIs:
10.1021/acs.jpcclett.8b01790
Source: FindIt
Source-ID: 2437852260
Research output: Research - peer-review; Journal article – Annual report year: 2018