StanleyBlack&Decker

Fast-Charging as an Enhancing Technology for New Generation of Power Tools & Outdoor Equipment

William A. Rigdon, PhD

July 11, 2019

STANLEY BLACK+DECKER DEWALT PROTO BOSTITCH FACOM PORTER CABLE MAC TOOLS Powers Vidmar LISTA STANLEY FATMAX

Stanley Black & Decker (SB&D)

STANLEY BLACK & DECKER (NYSE: SWK)

2018 Revenue: $14.0B

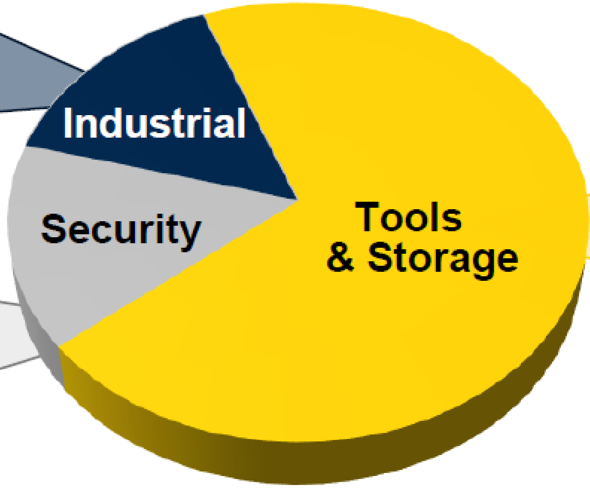
Market Cap: $21.7B

Cash Dividend Yield: 1.8%

Dividend Paid Consecutively For 143 Years; Increased For Past 51 Consecutive Years

Industrial $2.2B
- STANLEY Engineered Fastening
- Infrastructure

Security $2.0B
- Commercial Electronic Security
- Mechanical Access



1843 STANLEY is Founded

60,000+ Employees in 50 Countries

Tools & Storage $9.8B
- Power Tools & Equipment
- Hand Tools, Accessories & Storage

500,000+ Products

15,000+ Active Global Patents

Vision	**Known For Innovation**	**Continued Top Quartile Performance**	**Social Responsibility**

Global Tools & Storage Driving Growth

To Be The WORLDWIDE LEADER (#1 Or #2 Position) In Defined Market Categories In Which Our Products Compete Through:

Innovation + **Supply Chain Excellence** + **Globalization** + **Brand Building** + **World-Class Organization**

Innovation

Supply Chain Excellence

MWWS
MAKE WHERE WE SELL

MADE IN THE USA WITH GLOBAL MATERIALS

PROUDLY MADE IN THE USA WITH GLOBAL MATERIALS

MADE IN THE UK

Stanley Black & Decker SFS 2.0

Quality Always

Safety Always

Globalization

Brand Building

STANLEY
BLACK+DECKER
DEWALT
PROTO
BOSTITCH
FACOM
PORTER+CABLE
MAC TOOLS
CRAFTSMAN
LISTA
Vidmar
STANLEY FATMAX
IRWIN
LENOX

World-Class Organization

MOST INCLUSIVE
1000 | 100

MOST REPUTABLE
Forbes 2018
THE BEST EMPLOYERS for DIVERSITY

MOST SUSTAINABLE
Dow Jones Sustainability Indices
BARRON'S
AMERICA'S TOP 100 MOST SUSTAINABLE COMPANIES

MOST INNOVATIVE
PTIA 2018 AWARD WINNER
reddot award winner
The Patent Board

MOST ADMIRED
FORTUNE
WORLD'S MOST ADMIRED COMPANIES 2018

From $600M Hand Tool Company To $10B Diversified Tool Industry Leader

Fast Charging Case Study - DeWalt 40V Outdoor

DEWALT 40V MAX* Outdoor Power Equipment

A-Hr	MSRP
9.0	$3??
7.5	$289
6.0	$249
4.5	$219

Battery Packs

- ❑ Introduced in FY 2014
- ❑ Largest pack (30 of 18650)
- ❑ 10S3P cell arrangement
- ❑ Targeted for commercial use
- ❑ Gas tool power output

Limited adoption because of runtime anxiety and the cost for an adequate quantity of batteries needed to outfit entire lawn care crews.

40V MAX Fast Charger Development

40V MAX Outdoor intended for landscaping crews

10 Amp (400W) “fast charger” sequentially charges up to six battery packs was priced MSRP **$389** and could completely charge 1 battery in ~ 60-90 min

Outlets available at most jobsites

Bldg. Code (NEC):

Homes must have at least one outdoor receptacle at the front and rear of the house. They must be readily accessible from the ground positioned no more than 6’ above grade.

On Board Charging from Starter Battery

(10) **Pub. No.: US 2018/0115169 A1**
(43) **Pub. Date: Apr. 26, 2018**

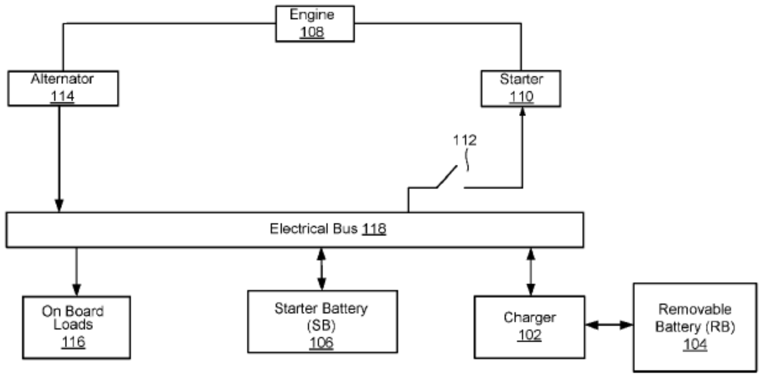
(54) **BATTERY PACK DISCHARGE AND CHARGER SYSTEM**

(71) Applicant: **Black & Decker Inc.**, New Britain, CT (US)

(72) Inventors: **Elyse Edwards**, Aberdeen, MD (US); **Matthew J. Velderman**, Baltimore, MD (US); **William A. Rigdon**, Baltimore, MD (US); **Andrew E. Seman, Jr.**, Pylesville, MD (US); **Daniel J. White**, Baltimore, MD (US)

(21) Appl. No.: **15/794,808**

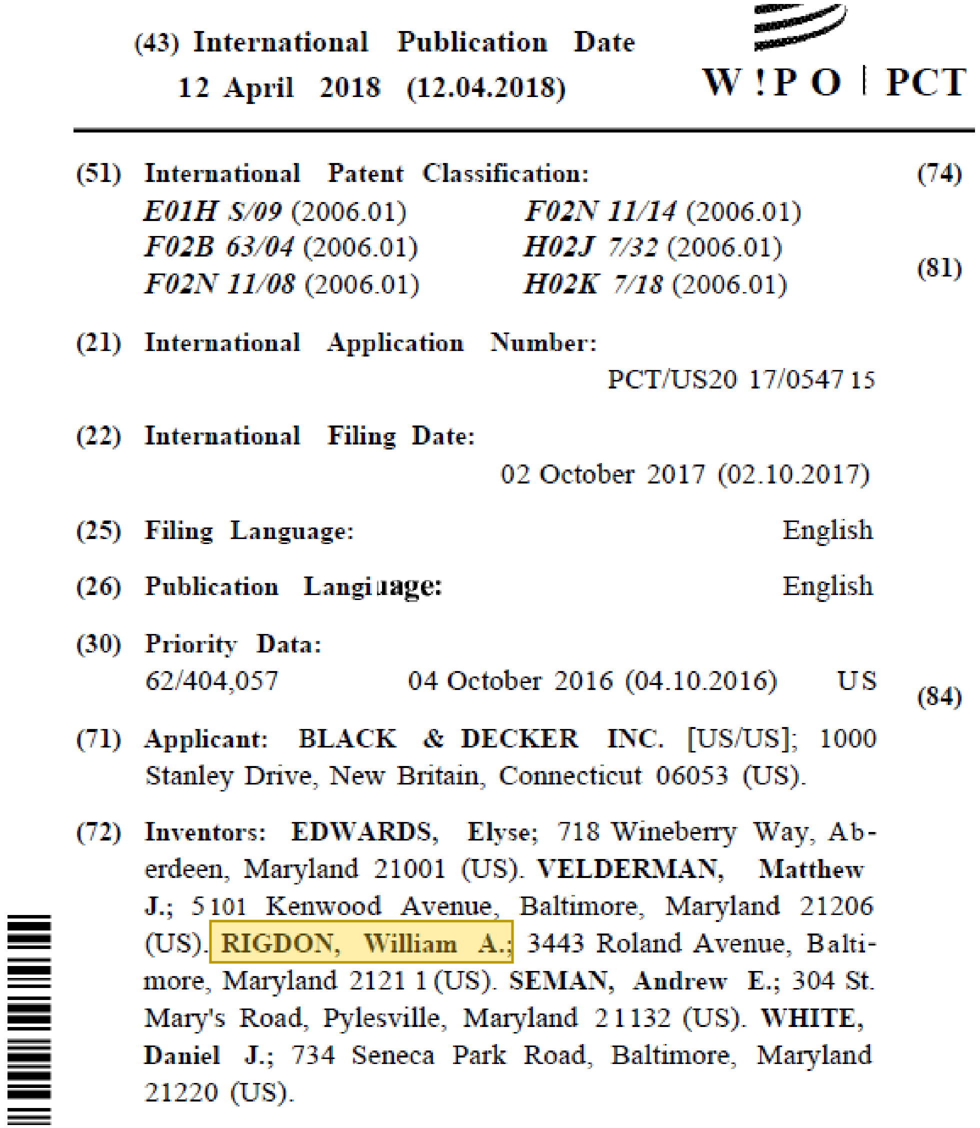
(22) Filed: **Oct. 26, 2017**



On-board mower charging directly from the starter & alternator

DCB412 MSRP $89 - Charged the 7.5 AH pack in ~3 hours

Fast Charging with High Power Alternator



(43) International Publication Date
12 April 2018 (12.04.2018)

WIPO | PCT

(51) International Patent Classification:
E01H S/09 (2006.01) *F02N 11/14* (2006.01)
F02B 63/04 (2006.01) *H02J 7/32* (2006.01)
F02N 11/08 (2006.01) *H02K 7/18* (2006.01)

(74)

(81)

(21) International Application Number:
PCT/US2017/054715

(22) International Filing Date:
02 October 2017 (02.10.2017)

(25) Filing Language: English

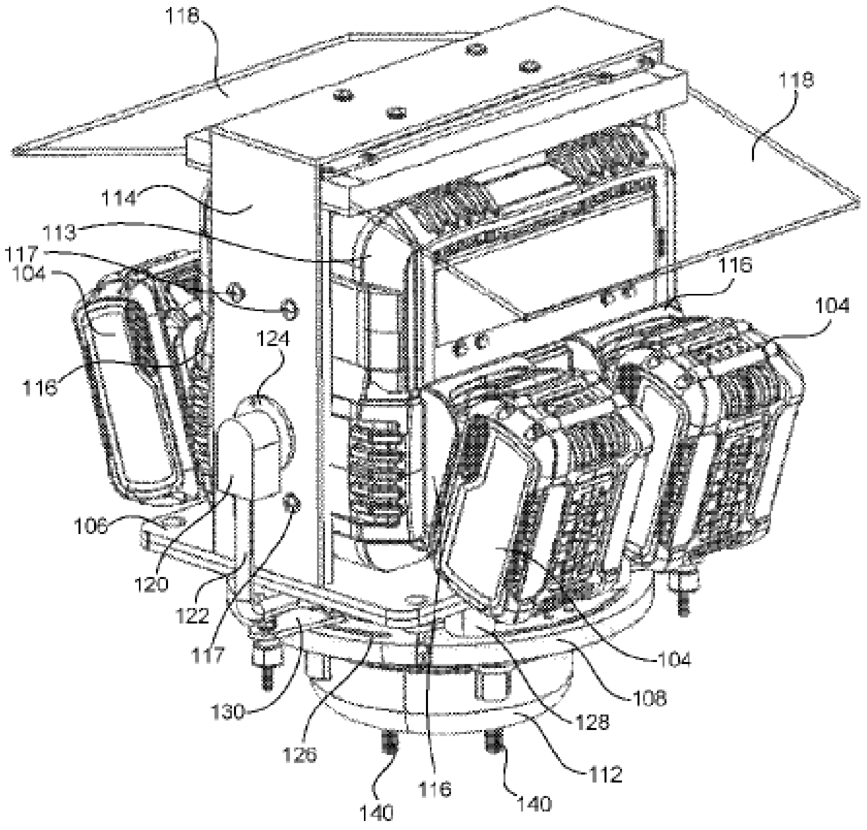
(26) Publication Language: English

(30) Priority Data:
62/404,057 04 October 2016 (04.10.2016) US

(84)

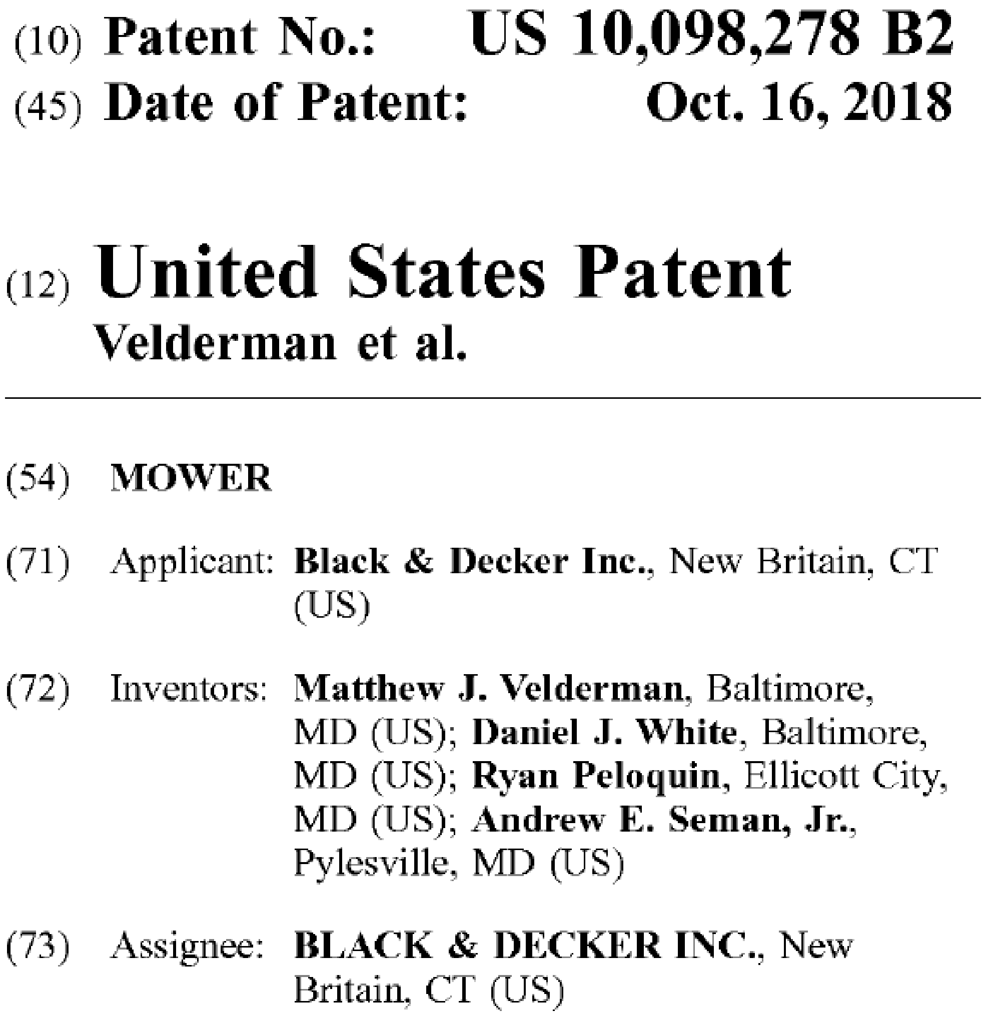
(71) Applicant: **BLACK & DECKER INC.** [US/US]; 1000 Stanley Drive, New Britain, Connecticut 06053 (US).

(72) Inventors: **EDWARDS, Elyse**; 718 Wineberry Way, Aberdeen, Maryland 21001 (US). **VELDERMAN, Matthew J.**; 5101 Kenwood Avenue, Baltimore, Maryland 21206 (US). **RIGDON, William A.**; 3443 Roland Avenue, Baltimore, Maryland 21211 (US). **SEMAN, Andrew E.**; 304 St. Mary's Road, Pylesville, Maryland 21132 (US). **WHITE, Daniel J.**; 734 Seneca Park Road, Baltimore, Maryland 21220 (US).



The battery pack charger system (mounted to rotating part of the mower engine) further comprising: an alternator that is electrically coupled to the charger and is mechanically coupled to the rotating component of the engine to generate and provide electrical power to the charger.

In-Hub Trailer Generator for Charging In-Tow



(10) **Patent No.:** **US 10,098,278 B2**
(45) **Date of Patent:** **Oct. 16, 2018**

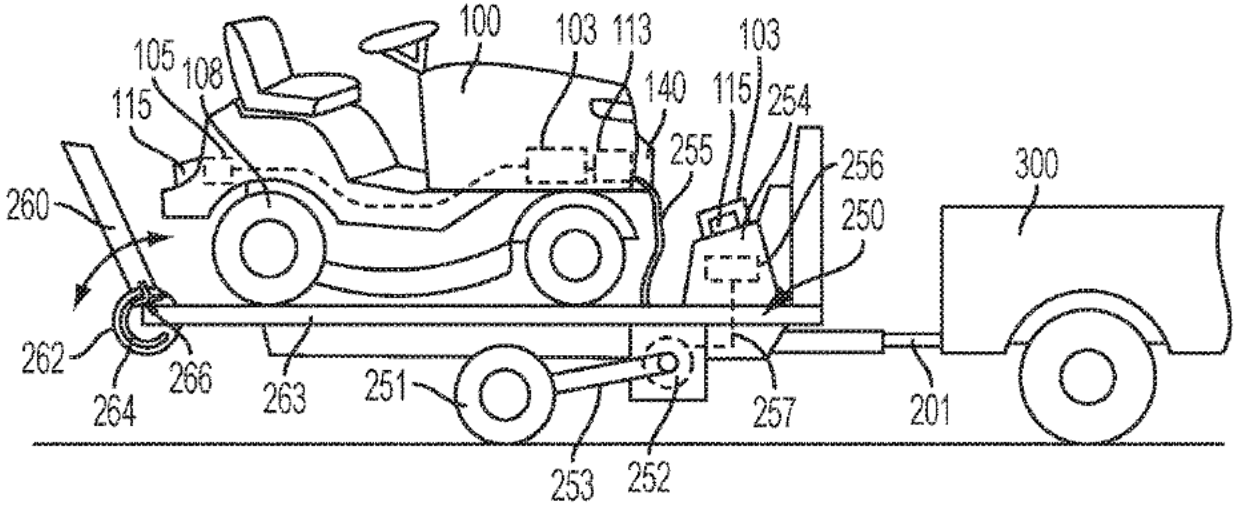
(12) **United States Patent**
Velderman et al.

(54) **MOWER**

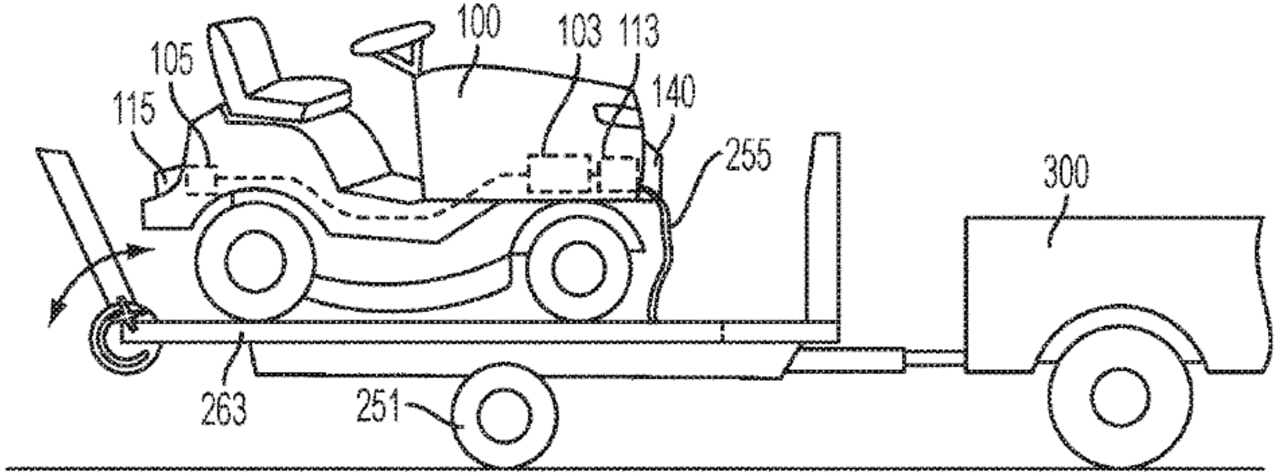
(71) Applicant: **Black & Decker Inc.**, New Britain, CT (US)

(72) Inventors: **Matthew J. Velderman**, Baltimore, MD (US); **Daniel J. White**, Baltimore, MD (US); **Ryan Peloquin**, Ellicott City, MD (US); **Andrew E. Seman, Jr.**, Pylesville, MD (US)

(73) Assignee: **BLACK & DECKER INC.**, New Britain, CT (US)

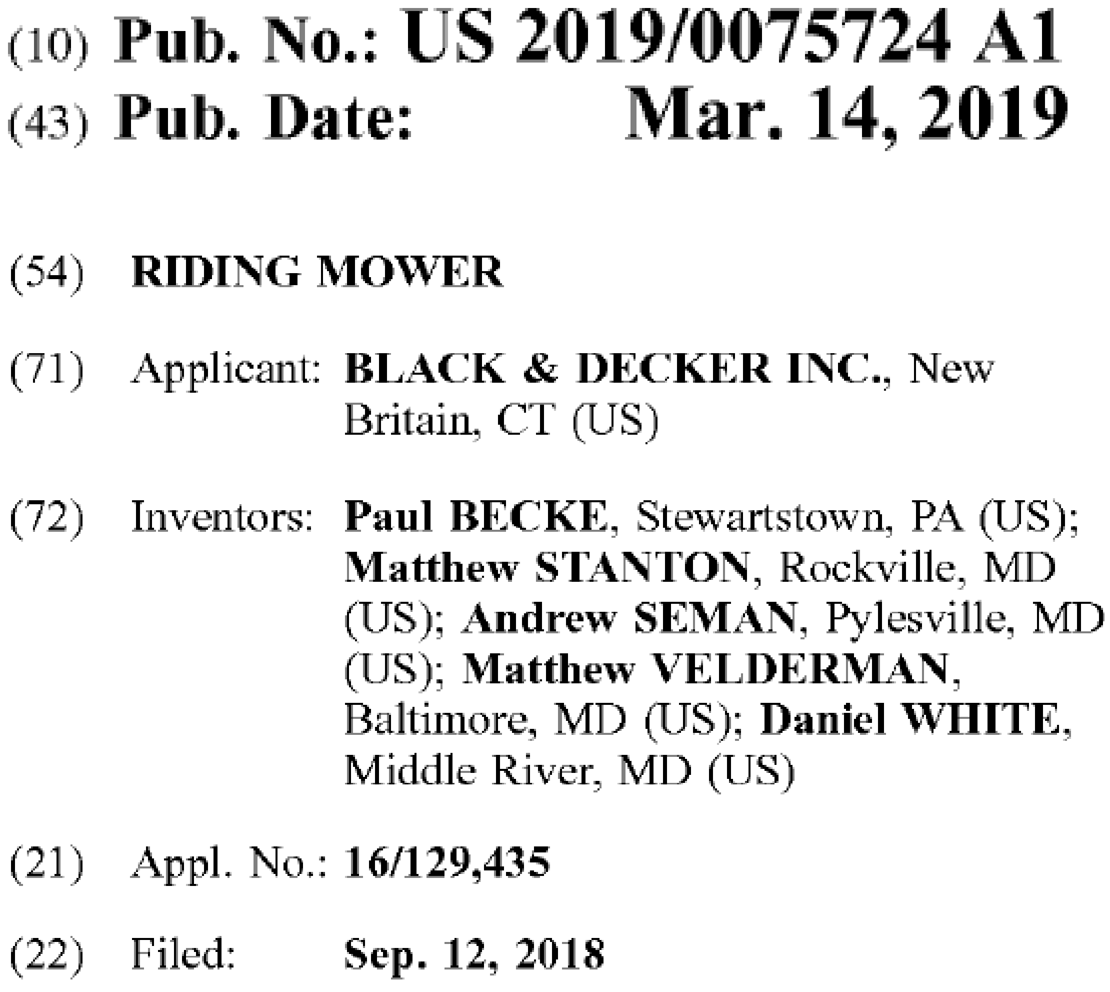


In-Hub Trailer Generator for Charging



Charging from Truck/Trailer Electrical System

Riding Mower with Removable Battery Pack



(10) **Pub. No.: US 2019/0075724 A1**
(43) **Pub. Date: Mar. 14, 2019**

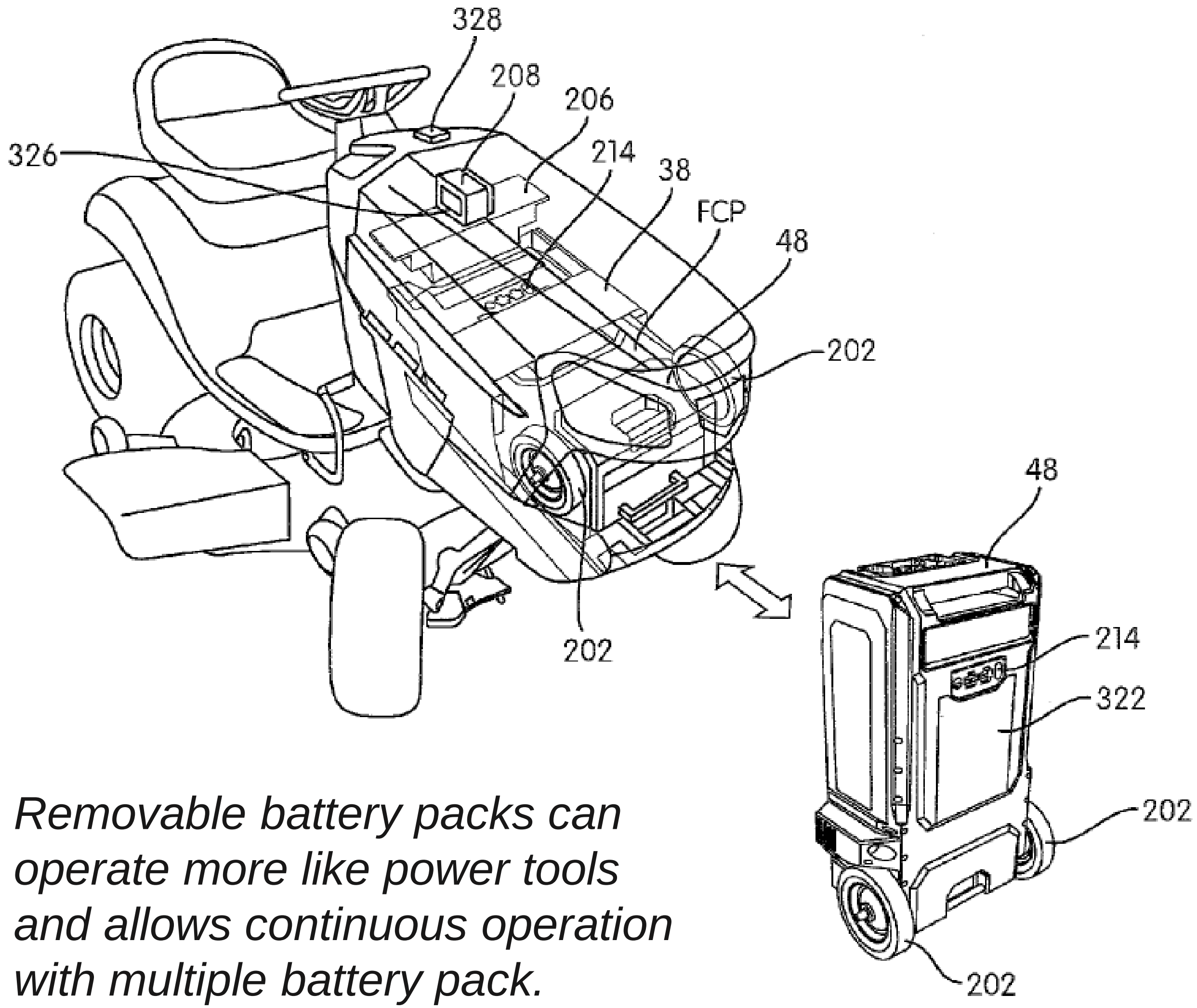
(54) **RIDING MOWER**

(71) Applicant: **BLACK & DECKER INC.**, New Britain, CT (US)

(72) Inventors: **Paul BECKE**, Stewartstown, PA (US); **Matthew STANTON**, Rockville, MD (US); **Andrew SEMAN**, Pylesville, MD (US); **Matthew VELDERMAN**, Baltimore, MD (US); **Daniel WHITE**, Middle River, MD (US)

(21) Appl. No.: **16/129,435**

(22) Filed: **Sep. 12, 2018**



Removable battery packs can operate more like power tools and allows continuous operation with multiple battery pack.

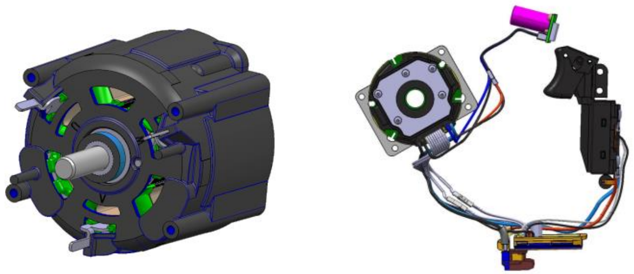
Case Study Conclusion - Need Faster Charging

DISCONTINUED JUNE 2019

Small Battery Packs w/ Best Performance Won

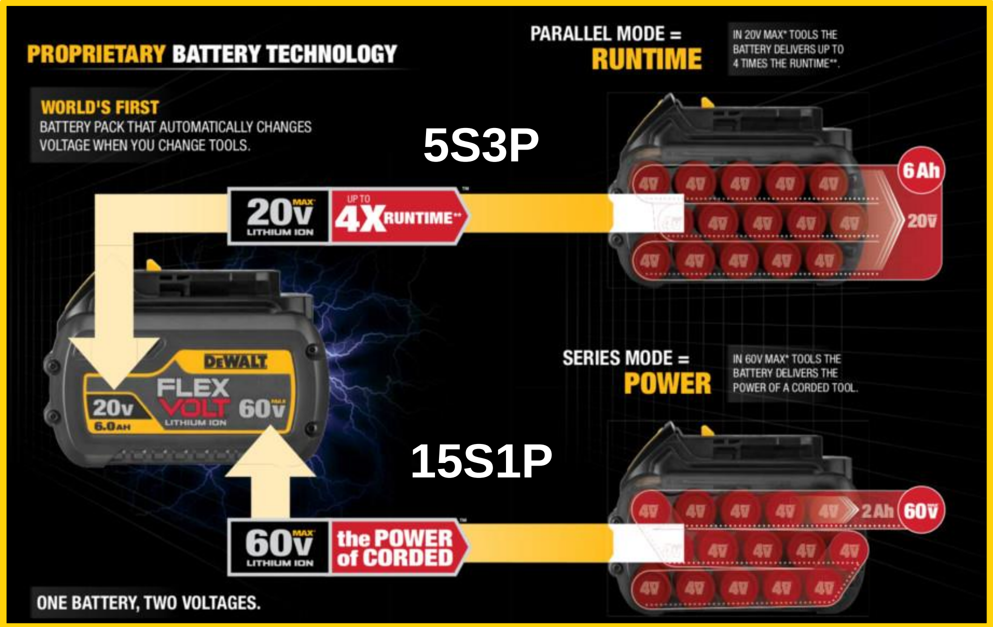
DeWalt FlexVolt 60V MAX Outdoor Platform

The DEWALT 60V MAX Outdoor Power Equipment provides gas performance for the construction pro for higher power applications and also works with the 20V MAX system of power tools.



Motors and electronic power density benefits from higher V

High Power Density Motors & Batteries



5S3P

15S1P

MTD is Largest OEM of Mowers in USA

MTD is the parent company for family of many lawn care brands

Contract manufacturing for John Deere Husqvarna CRAFTSMAN

- ☐ In Sept. 2018, SB&D announced a 20% stake in MTD for $234 million
- ☐ Annual revenue of $2.4 billion
- ☐ SB&D will have the option to acquire the remaining 80% of MTD starting July 1, 2021
- ☐ Lawn & Garden Market > $20B
- ☐ Largest mower OEM in N. A.

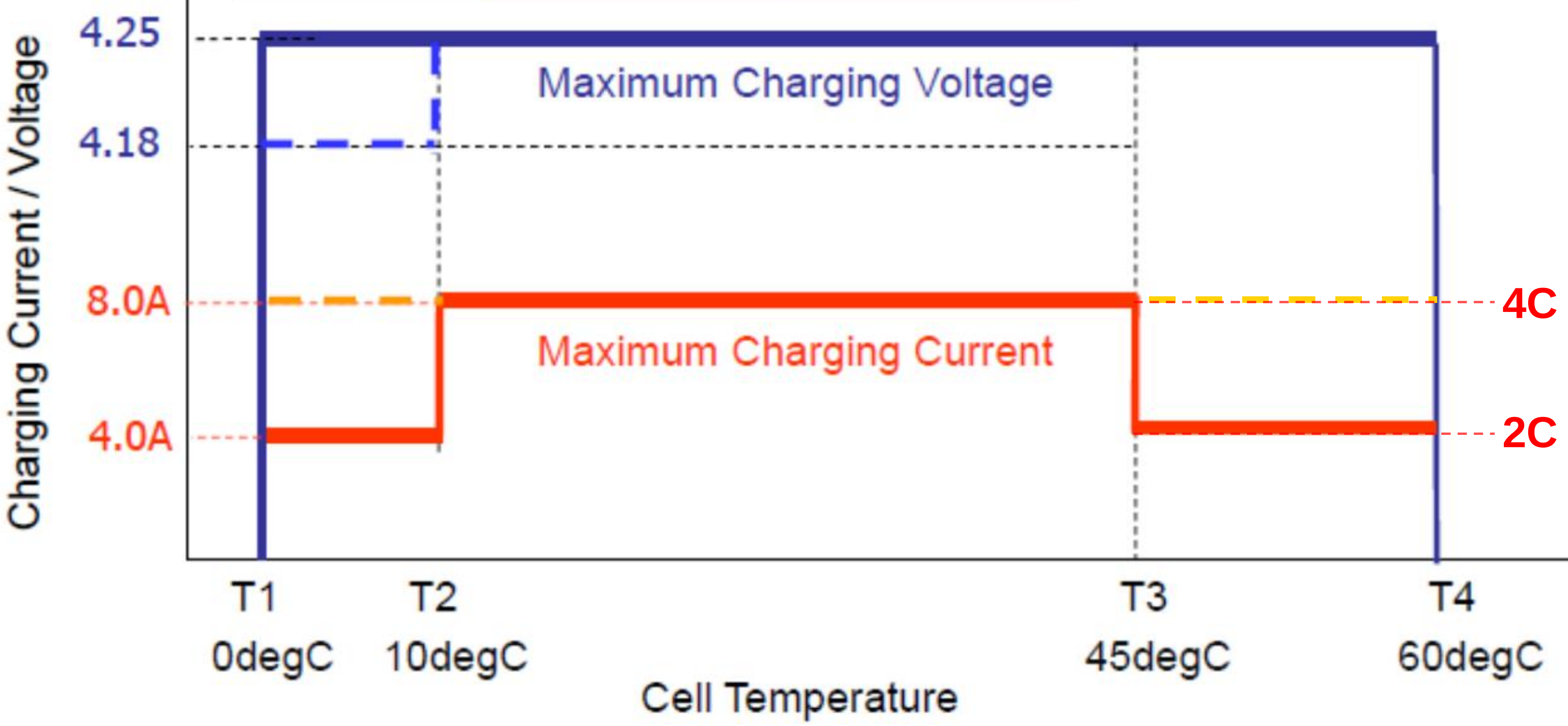
Making lawns look great since 1958.

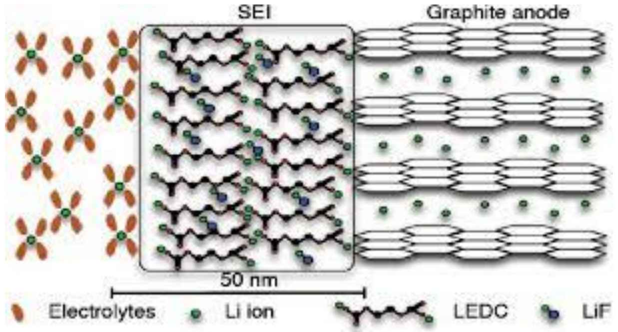
BAJ Charging Curve Limitations

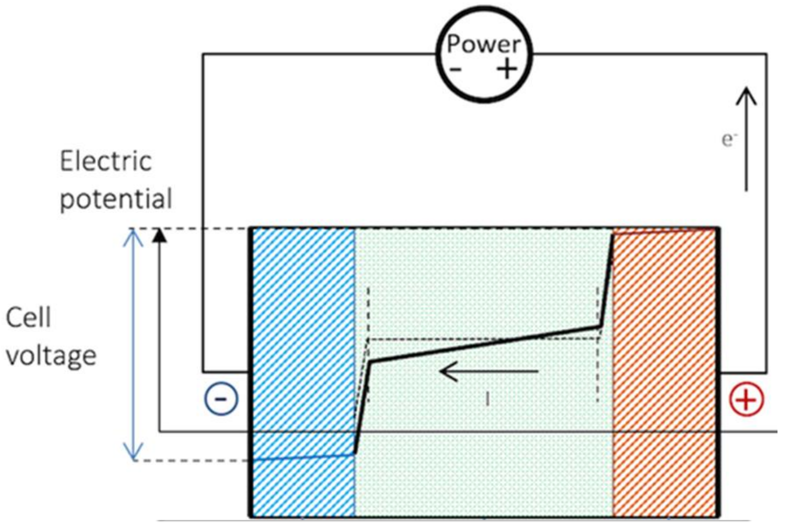
	Max. voltage*	Max. current*
T1~T2	4.18V / 4.25V	8.0A / 4.0A
T2~T3	4.25V	8.0A
T3~T4	4.25V	4.0A

* Including tolerance

State-of-the-Art
Li-ion power cell
charge limitations

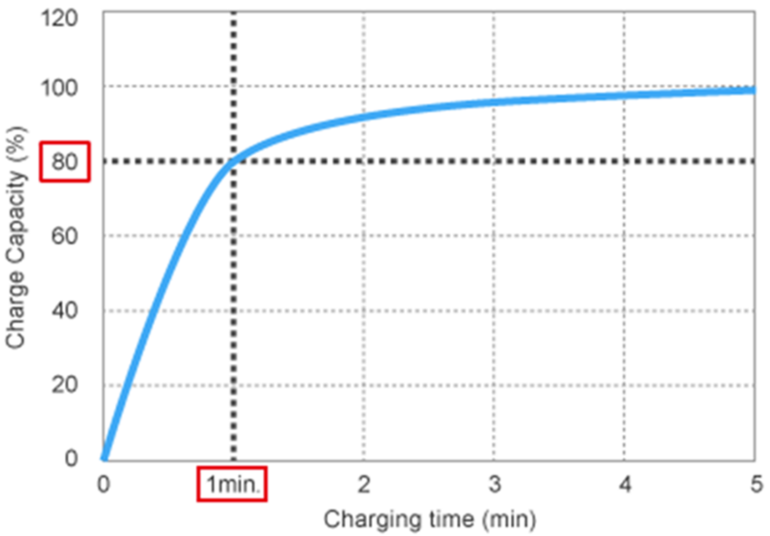




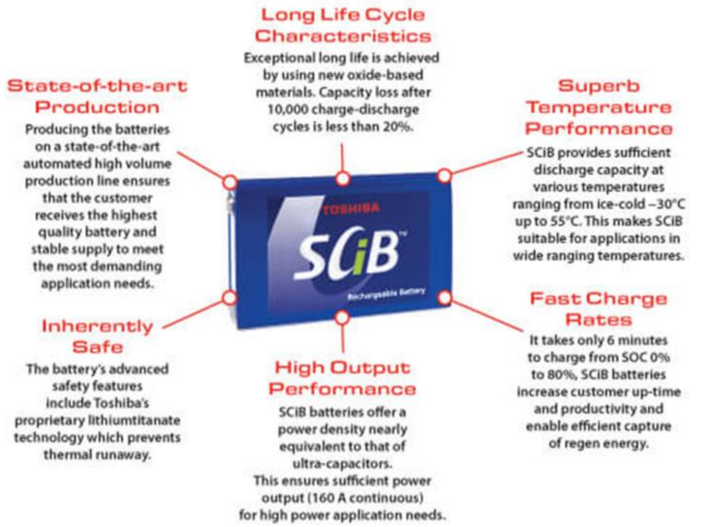


Graphite is a bottle neck to fast charging. New synthetic carbons help, but still limited C-rates

Opportunity for Extreme Fast Charge?



*Performance depends on usage conditions.



State-of-the-art Production
Producing the batteries on a state-of-the-art automated high volume production line ensures that the customer receives the highest quality battery and stable supply to meet the most demanding application needs.

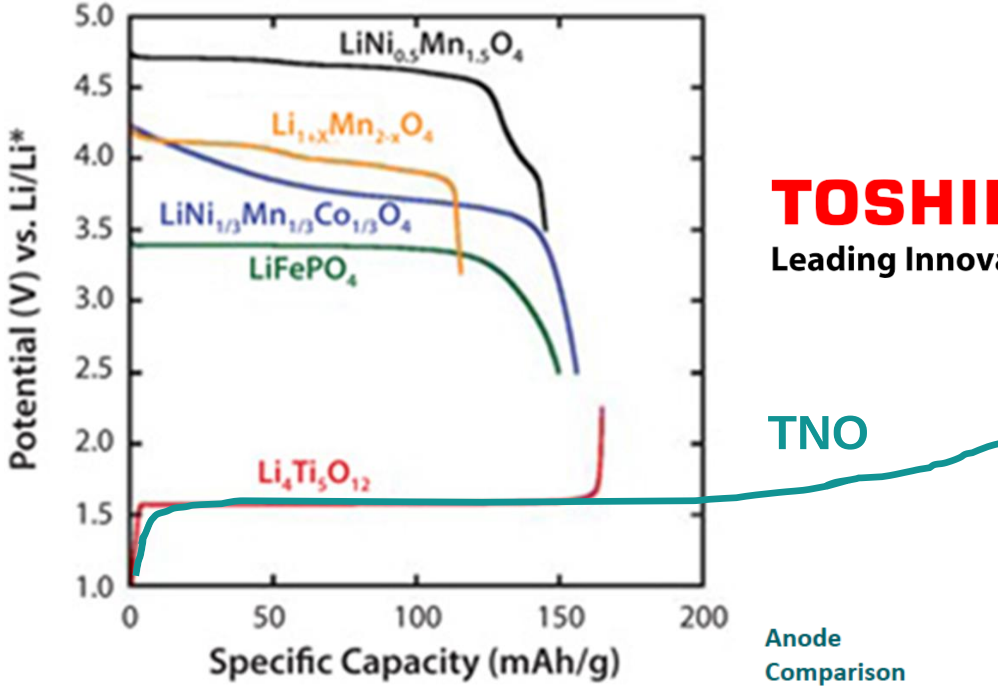
Long Life Cycle Characteristics
Exceptional long life is achieved by using new oxide-based materials. Capacity loss after 10,000 charge-discharge cycles is less than 20%.

Superb Temperature Performance
SCiB provides sufficient discharge capacity at various temperatures ranging from ice-cold –30°C up to 55°C. This makes SCiB suitable for applications in wide ranging temperatures.

Inherently Safe
The battery's advanced safety features include Toshiba's proprietary lithiumtitanate technology which prevents thermal runaway.

High Output Performance
SCiB batteries offer a power density nearly equivalent to that of ultra-capacitors.
This ensures sufficient power output (160 A continuous) for high power application needs.

Fast Charge Rates
It takes only 6 minutes to charge from SOC 0% to 80%, SCiB batteries increase customer up-time and productivity and enable efficient capture of regen energy.



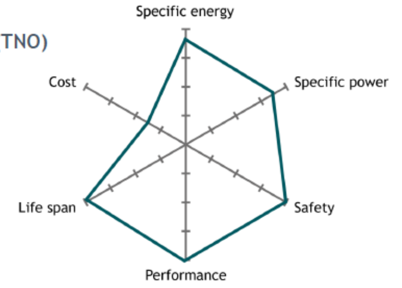
https://www.sigmaaldrich.com/technical-documents/articles/material-matters/electrode-materials-for-lithium-ion-batteries.html

TNO Anode benefits:

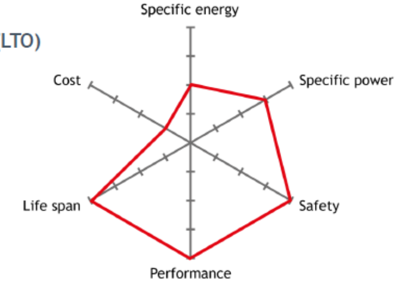
- *Ultra-rapid charge - 6 min;*
- *Double energy density capacity*
- *Extended driving range - 320 km*
- *Volumetric energy density higher than graphite*

TOSHIBA
Leading Innovation >>>

Titanium Niobate (TNO)



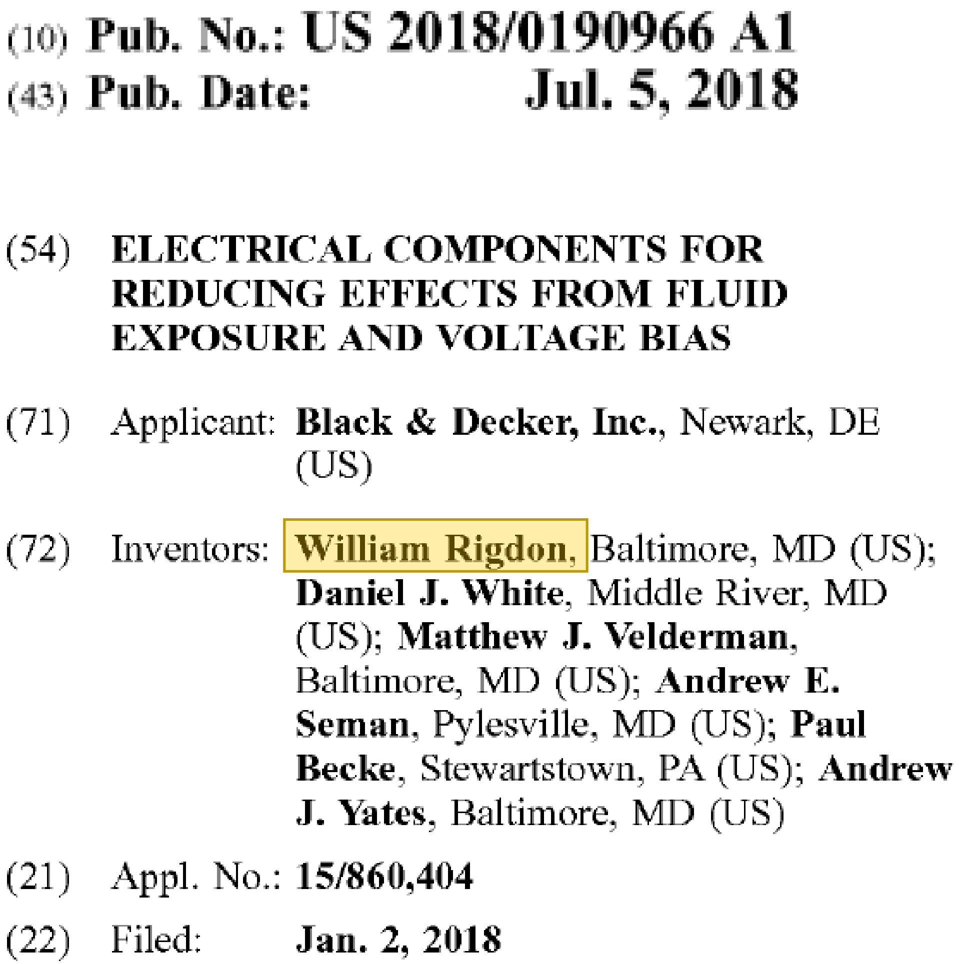
Lithium-Titanate (LTO)



Source: CBMM

Anode Comparison	Graphite	LTO~LLTO	TNO
Capacity mAh/g	372	175	388
Voltage	0.1	1.5	1.6
Density	2.3	3.5	4.3
Safety	--	++	++
Charging rate	--	++	++

High Voltage Battery Material Selections



(10) **Pub. No.: US 2018/0190966 A1**
(43) **Pub. Date: Jul. 5, 2018**

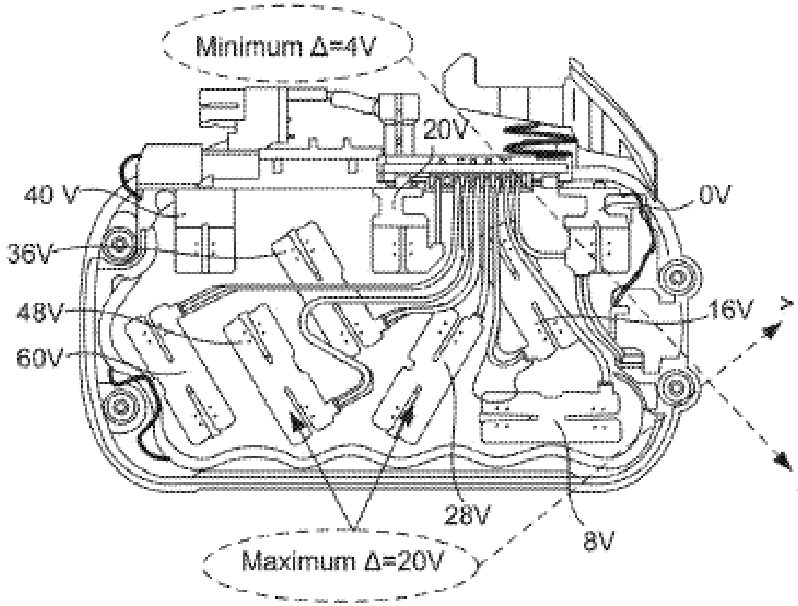
(54) **ELECTRICAL COMPONENTS FOR REDUCING EFFECTS FROM FLUID EXPOSURE AND VOLTAGE BIAS**

(71) Applicant: **Black & Decker, Inc.**, Newark, DE (US)

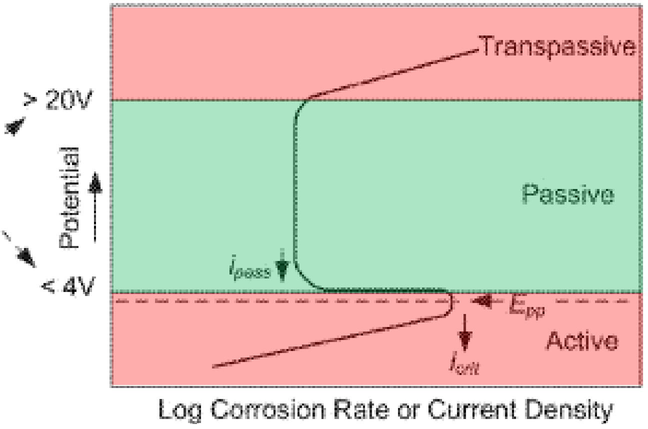
(72) Inventors: **William Rigdon**, Baltimore, MD (US); **Daniel J. White**, Middle River, MD (US); **Matthew J. Velderman**, Baltimore, MD (US); **Andrew E. Seman**, Pylesville, MD (US); **Paul Becke**, Stewartstown, PA (US); **Andrew J. Yates**, Baltimore, MD (US)

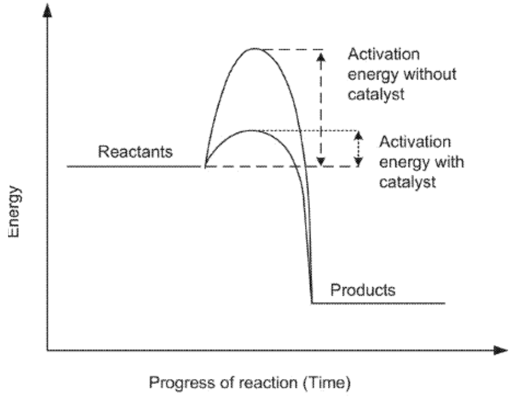
(21) Appl. No.: **15/860,404**

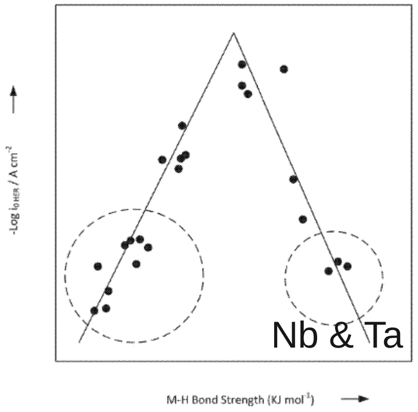
(22) Filed: **Jan. 2, 2018**

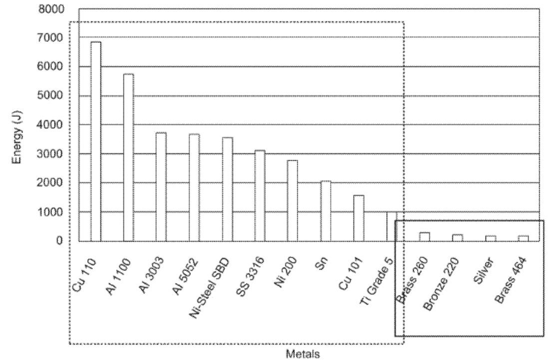


FlexVolt in 60V Mode:
Requires a wide passive regime









Thermo → low E_A

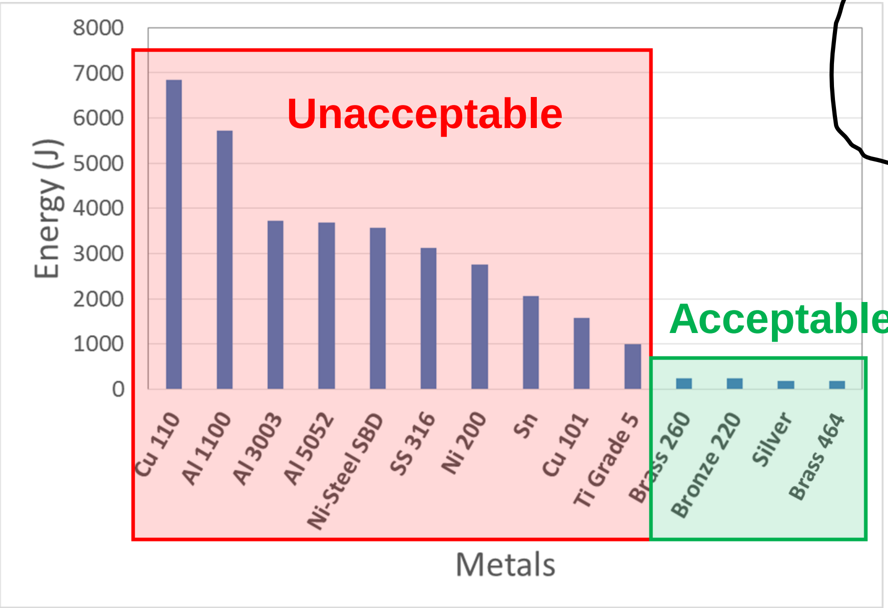
Kinetics → low i_0

Minimize energy lost

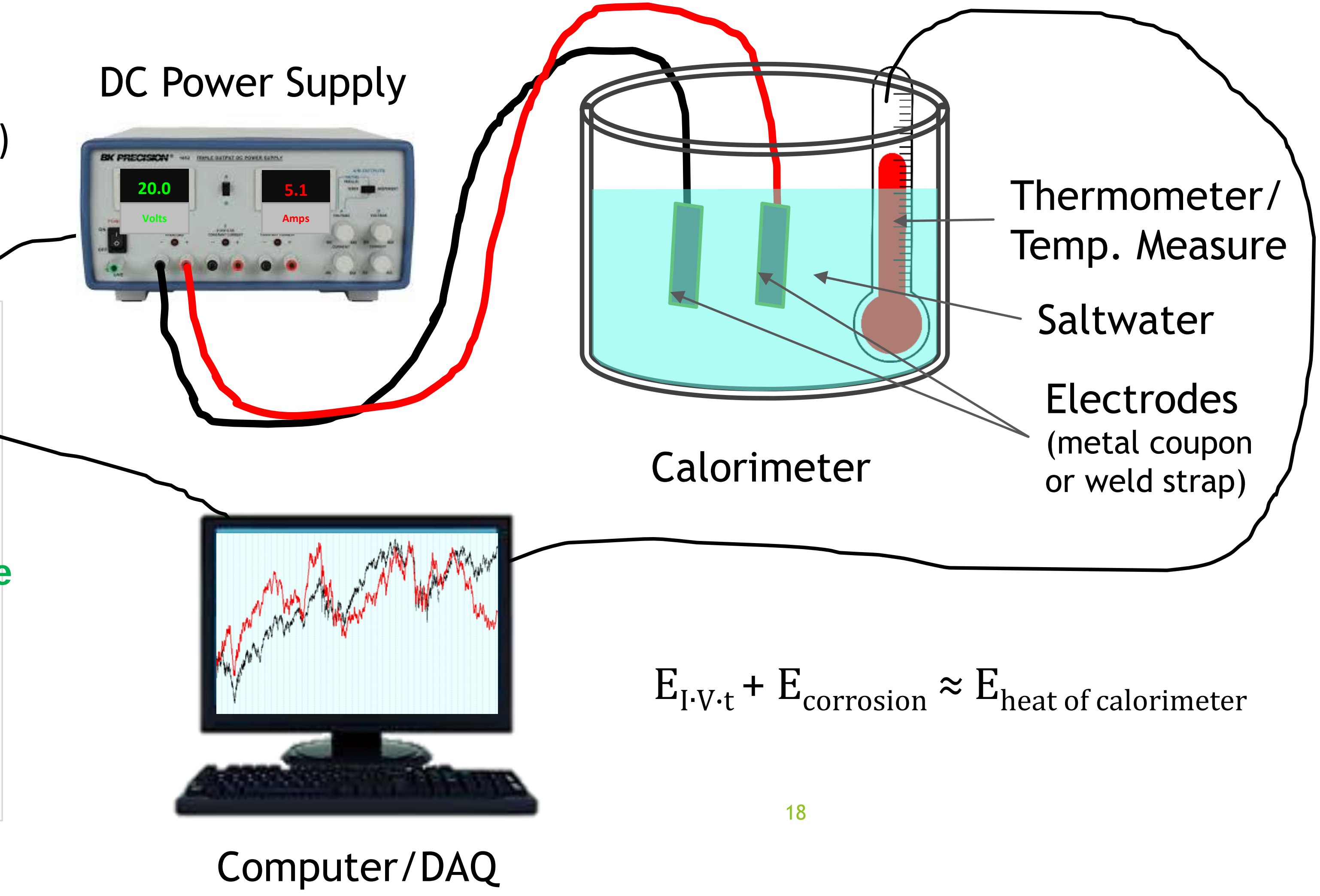
Corrosion & Electrolysis Procedure

Experimental Test Setup:

- Connect electrodes to power supply
- Seawater equivalent solution
- Potentiostatic (chronoamperometry)
- Measure Current vs Time
- Measure Temp. of Calorimeter



Electrochemical resistant metals are selected



DC Power Supply

Thermometer/ Temp. Measure

Saltwater

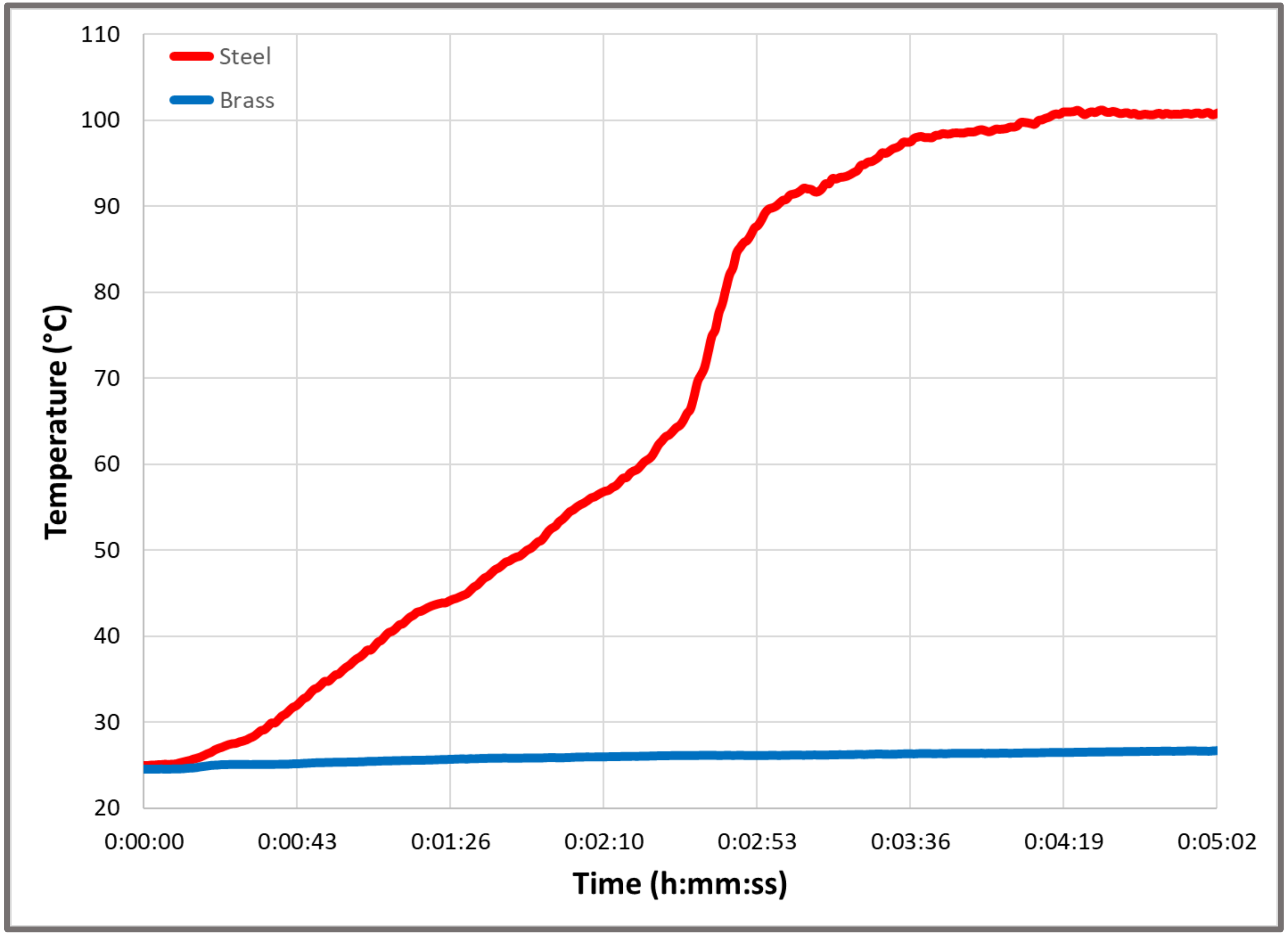
Electrodes (metal coupon or weld strap)

Calorimeter

Computer/DAQ

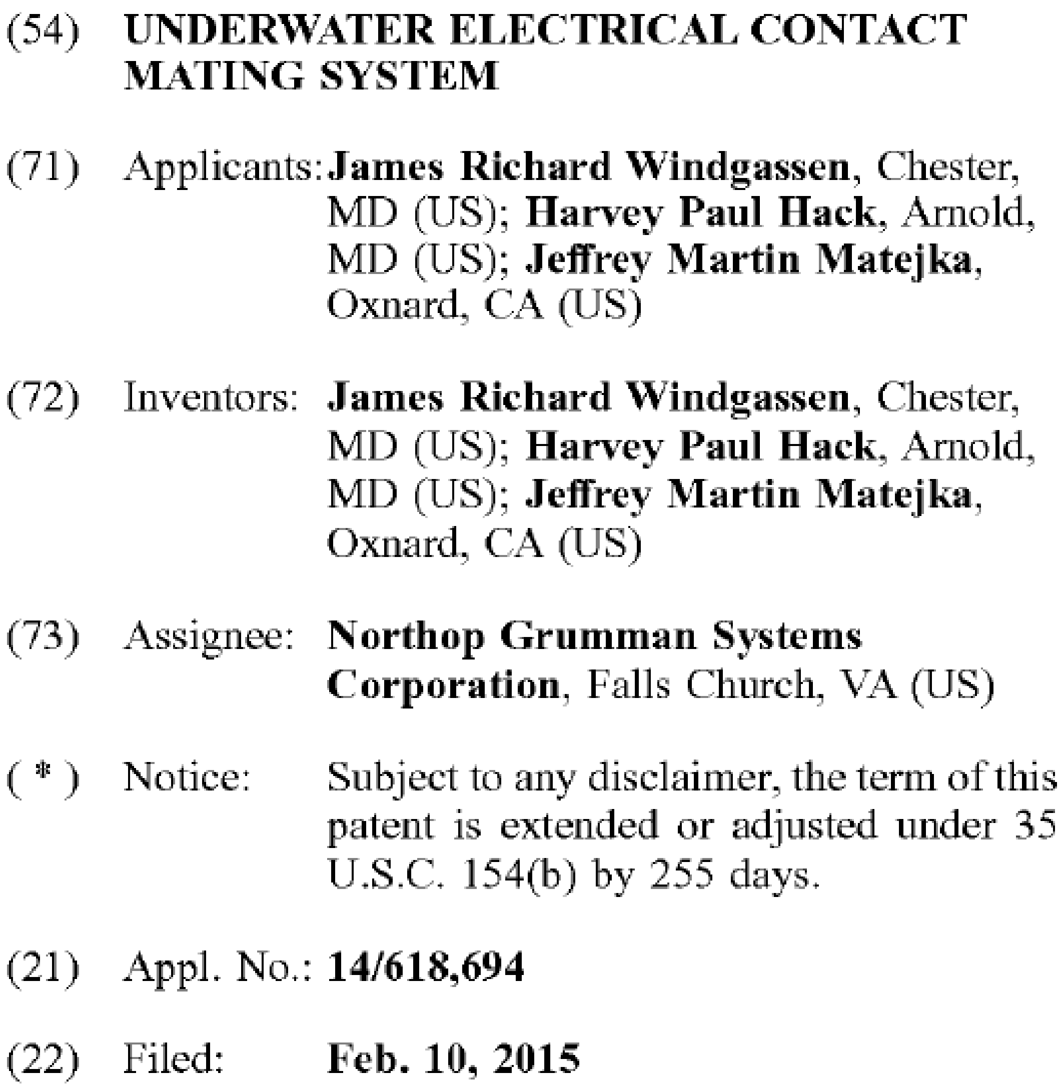
$$E_{I\cdot V\cdot t} + E_{corrosion} \approx E_{heat\ of\ calorimeter}$$

Comparison of Steel vs. Brass Terminals



- In 5 minutes, Tin plated steel has completely corroded away @ 20V
- > 35x amount of heat generated from corrosion and electrochemical reactions
- Enough heat to boil salt water!!!
- Steel battery cans become weak link

IP for Electrical Terminals Underwater



(54) **UNDERWATER ELECTRICAL CONTACT MATING SYSTEM**

(71) Applicants: **James Richard Windgassen**, Chester, MD (US); **Harvey Paul Hack**, Arnold, MD (US); **Jeffrey Martin Matejka**, Oxnard, CA (US)

(72) Inventors: **James Richard Windgassen**, Chester, MD (US); **Harvey Paul Hack**, Arnold, MD (US); **Jeffrey Martin Matejka**, Oxnard, CA (US)

(73) Assignee: **Northop Grumman Systems Corporation**, Falls Church, VA (US)

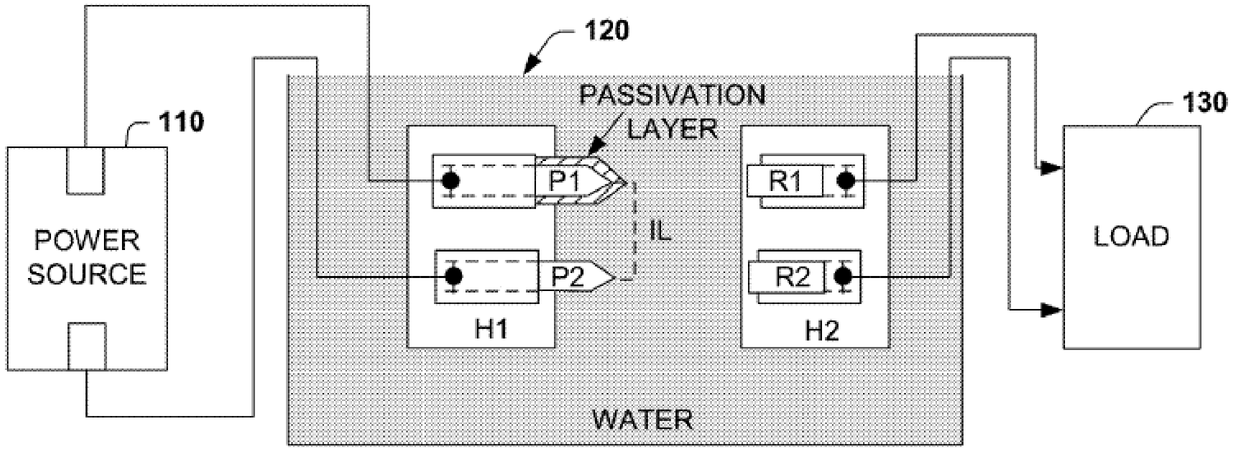
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 255 days.

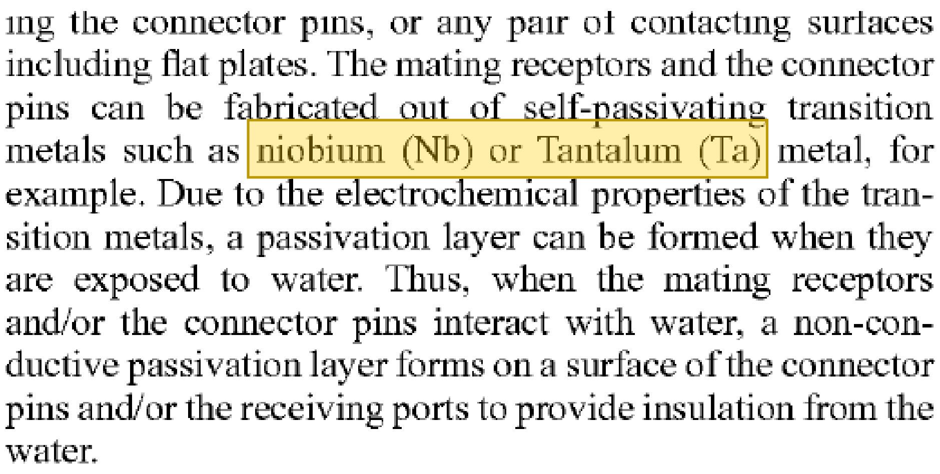
(21) Appl. No.: **14/618,694**

(22) Filed: **Feb. 10, 2015**

(10) **Patent No.: US 9,893,460 B2**

(45) **Date of Patent: Feb. 13, 2018**





ing the connector pins, or any pair of contacting surfaces including flat plates. The mating receptors and the connector pins can be fabricated out of self-passivating transition metals such as niobium (Nb) or Tantalum (Ta) metal, for example. Due to the electrochemical properties of the transition metals, a passivation layer can be formed when they are exposed to water. Thus, when the mating receptors and/or the connector pins interact with water, a non-conductive passivation layer forms on a surface of the connector pins and/or the receiving ports to provide insulation from the water.

Niobium Connectors (NiobiCon^{TM})

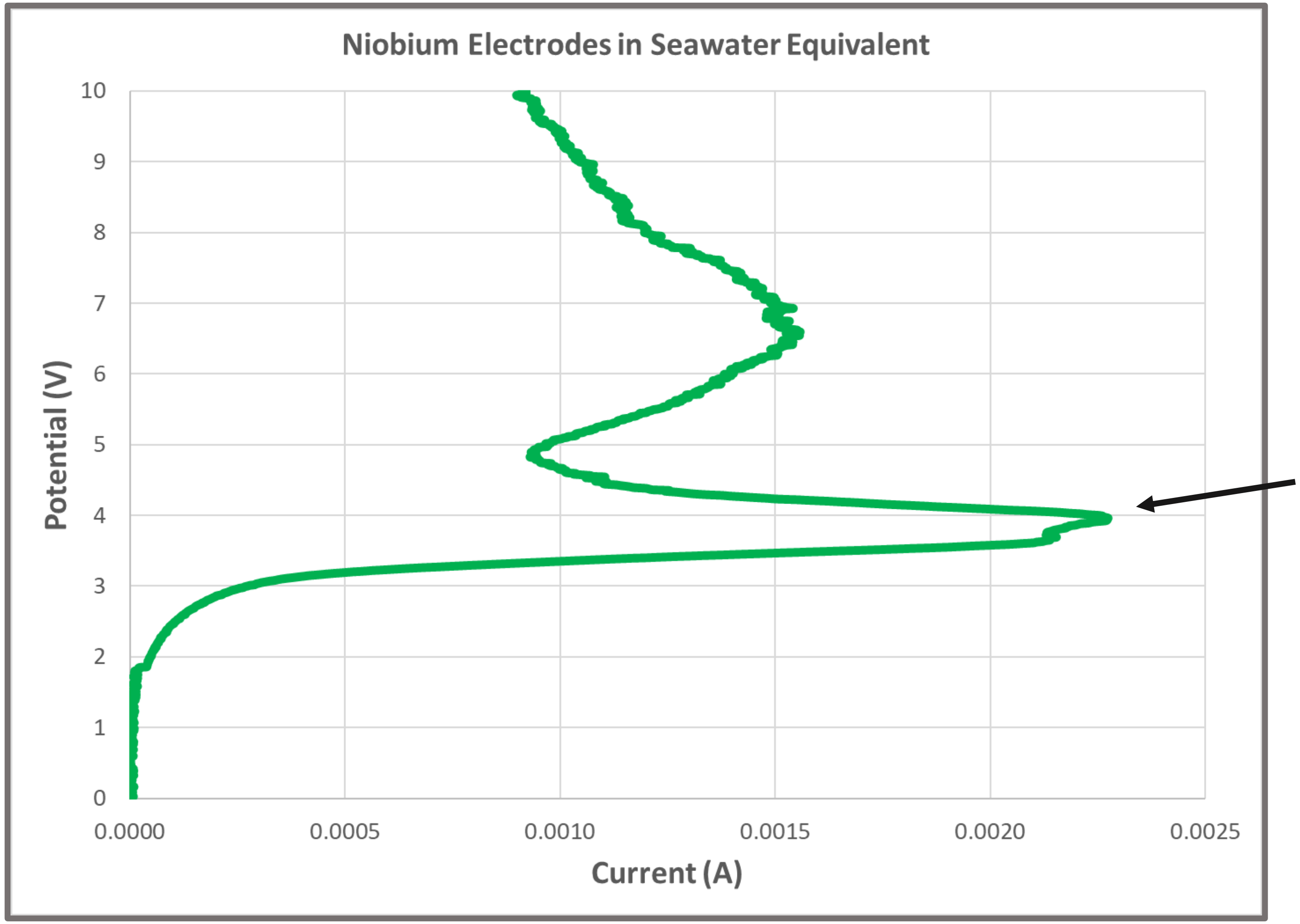
https://youtu.be/-54cBaLuUQY

NiobiCon™ Wet-Mate Electrical Connector

Benefits of the NiobiCon™ technology include:

- No seals, O-rings or oil
- Wet-mate above water or fully submerged
- Ideal for operations to at least 60V DC
- Nearly infinite number of mates/de-mates
- No inherent water depth limit
- In-water/underwater safety
- Mate and de-mate while power is on
- Can be designed for loose alignment tolerances
- Low mating force (mechanical contacts)
- Not susceptible to corrosion
- Does not require complex mechanical components
- Simple design enables miniaturization
- Can use with high frequency (GHz) signals

Niobium Corrosion Behavior



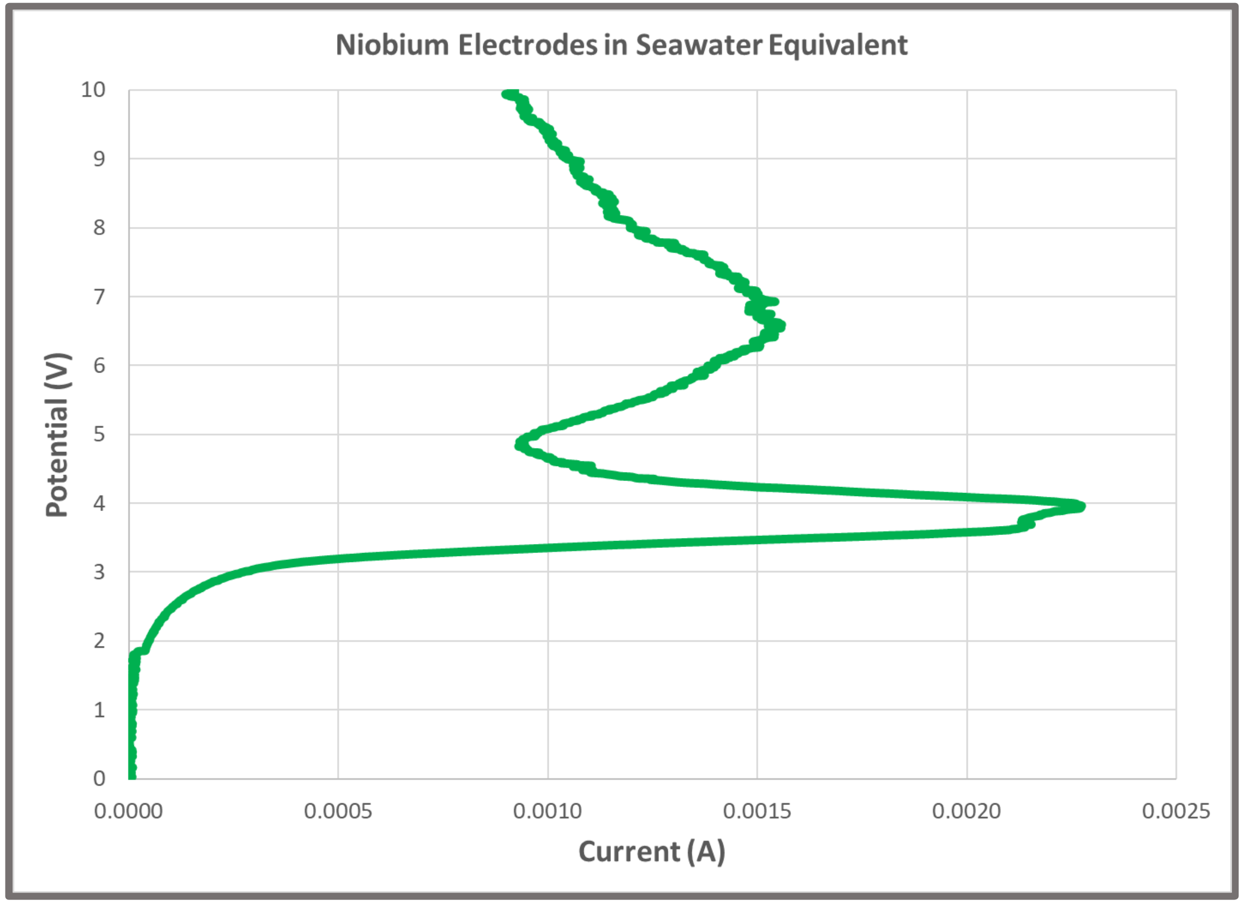
Experimental Test Setup:

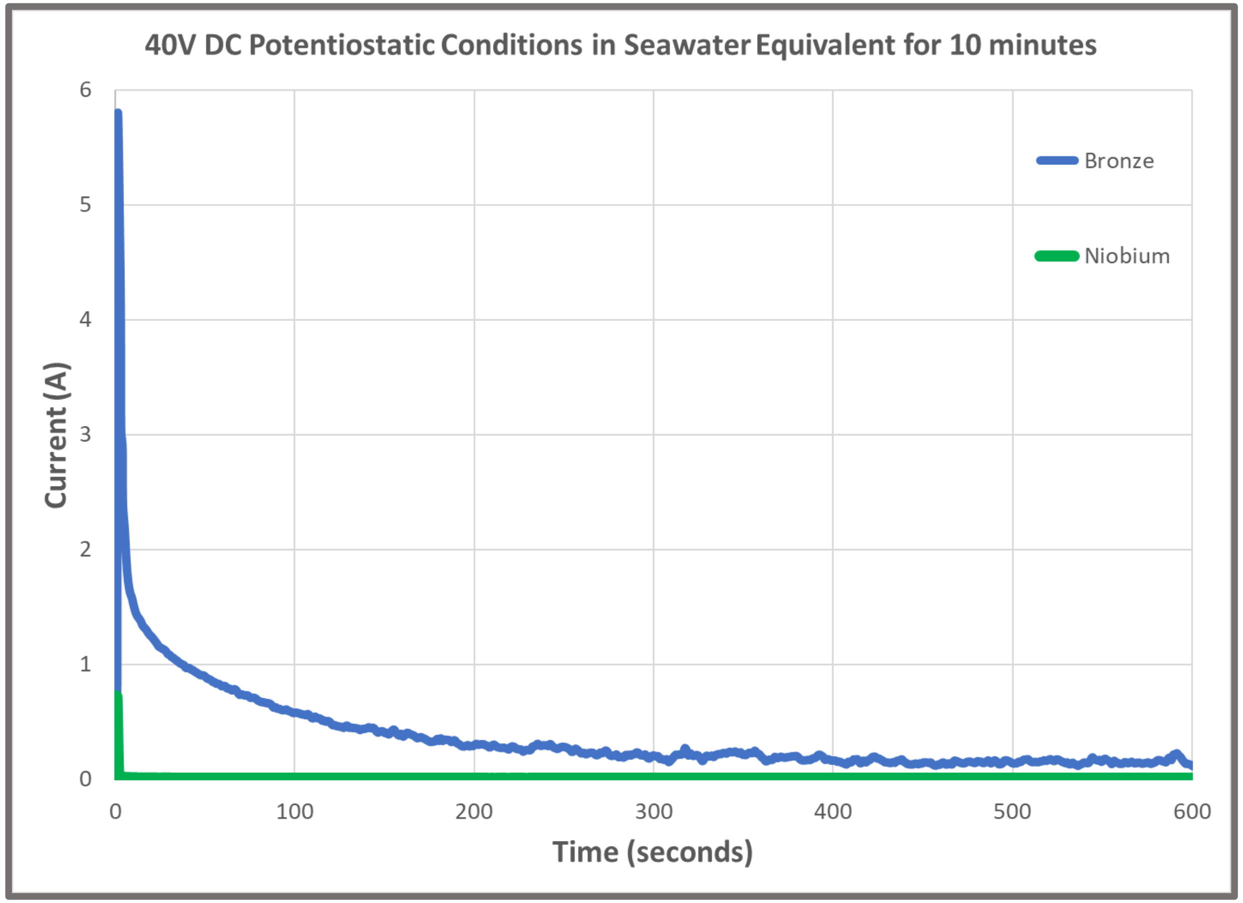
- Linear sweep voltammetry (LSV) in NaCl solution (seawater equiv.) at 50 mV/sec
- High purity Nb electrodes (Area = 2 cm^2)
- Extremely low corrosion currents
- Passivation potential ~ 4V
- Where does passivation film breakdown?
- It is at least > 60V DC in this electrolyte

Niobium before test

Niobium after 60V

Putting Niobium Corrosion into Perspective

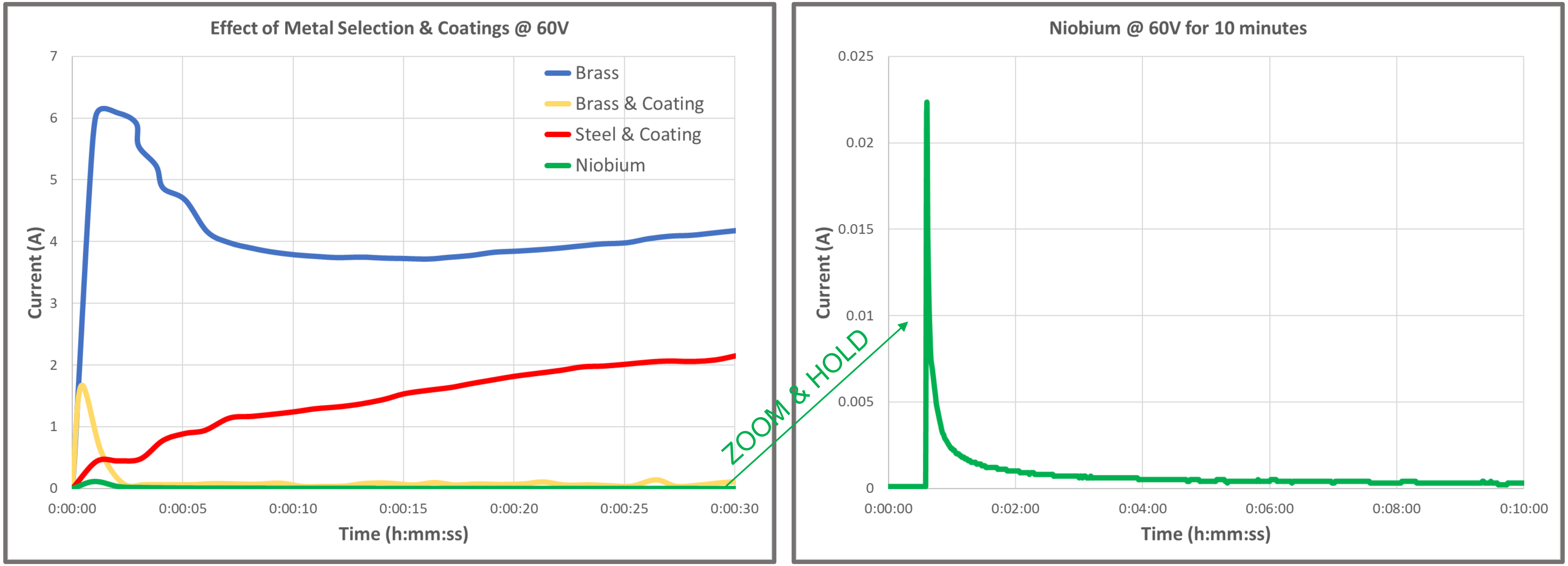




LSV to 10V shows the impact of metal selection

Chronoamperometry (I vs. t) @ 40V Nb vs. bronze

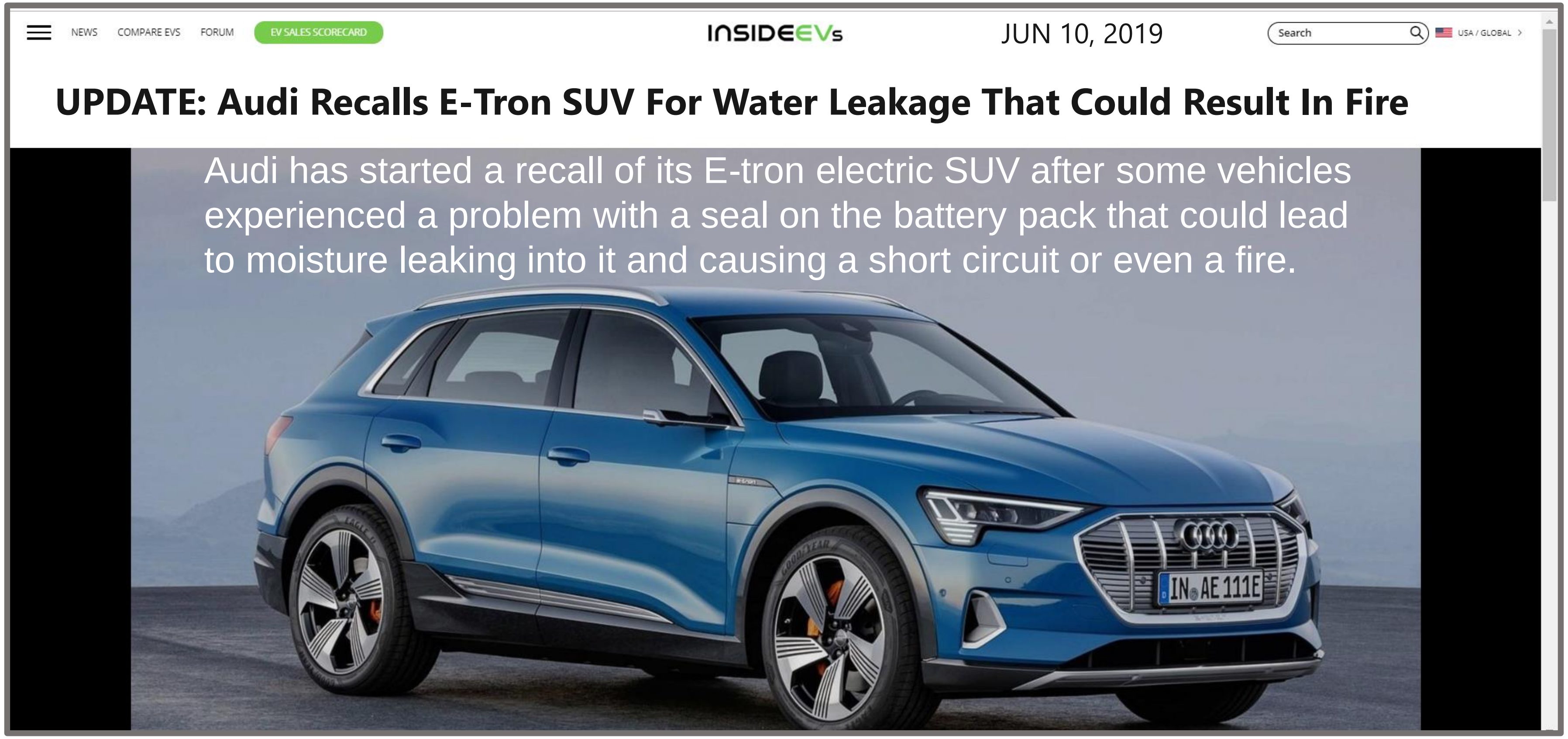
Bronze with Coating vs Niobium at High V DC



Best coatings on steel or brass don’t rival Nb

Passivation on Nb can be held for long times at high V

Water Can and Will Lead to Battery Fires!

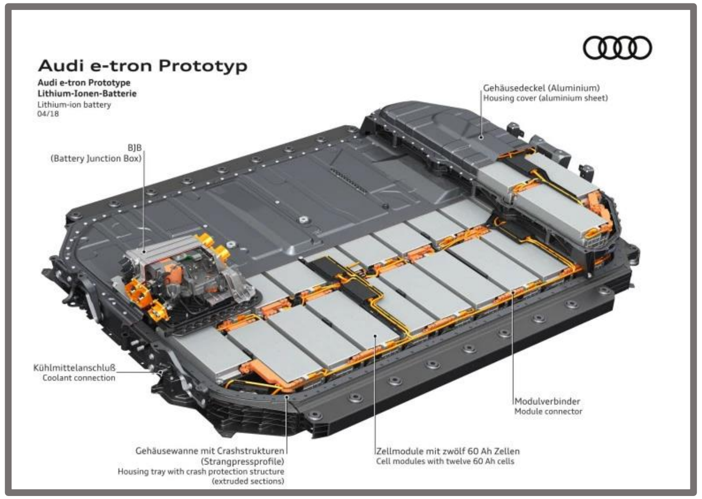


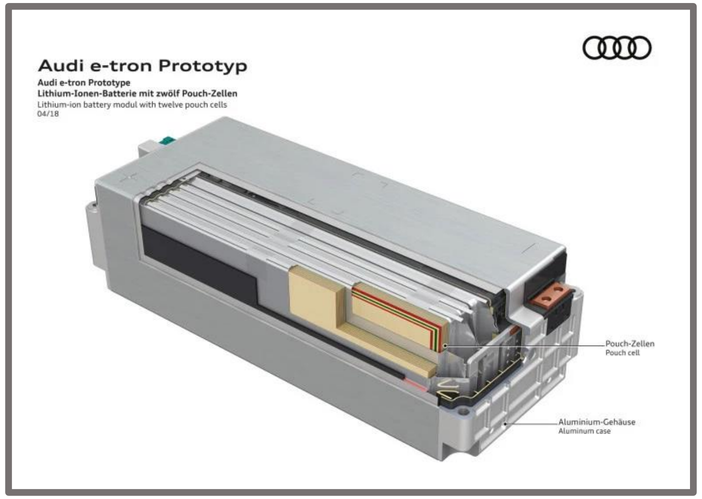
JUN 10, 2019

UPDATE: Audi Recalls E-Tron SUV For Water Leakage That Could Result In Fire

Audi has started a recall of its E-tron electric SUV after some vehicles experienced a problem with a seal on the battery pack that could lead to moisture leaking into it and causing a short circuit or even a fire.

It turns out that water can get into the high-voltage charging port of affected vehicles, making its way to the high voltage electronics and potentially leading to a battery fire.



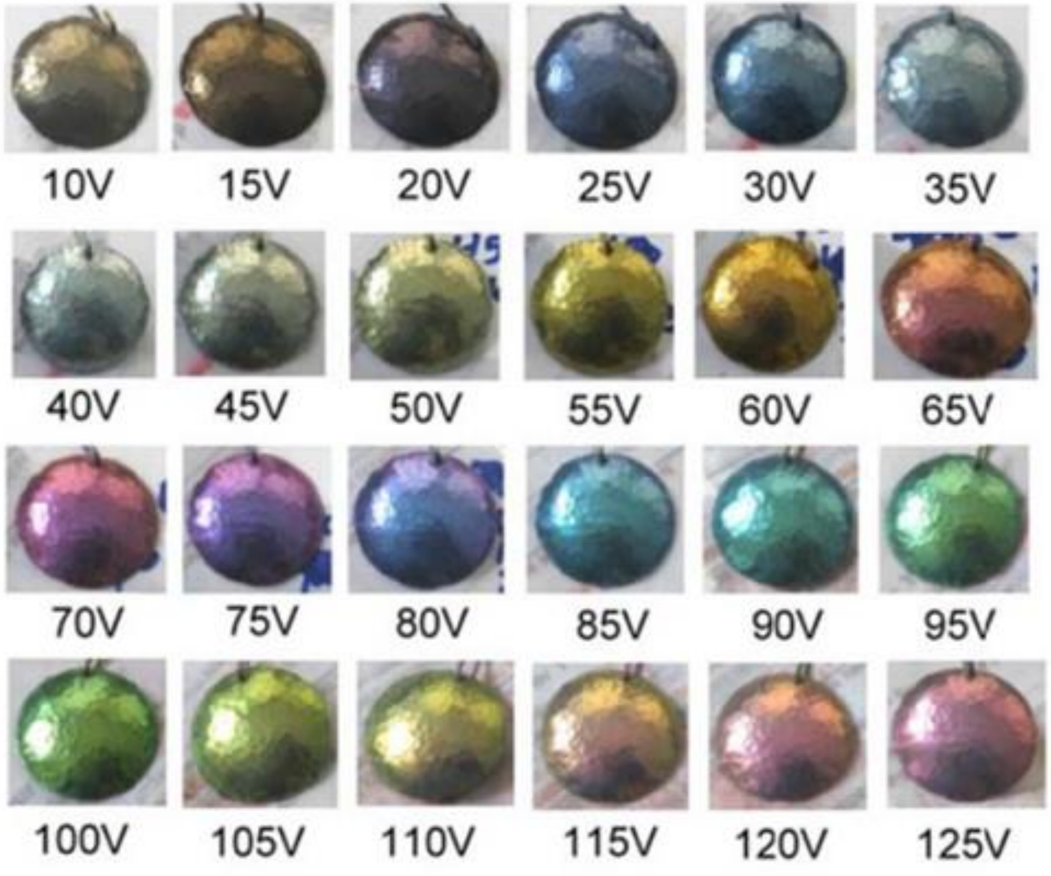


https://insideevs.com/news/353790/audi-recall-e-tron-charging-water-fire/

450V max & 95 kWh battery

Fast Charging and Corrosion Conclusion

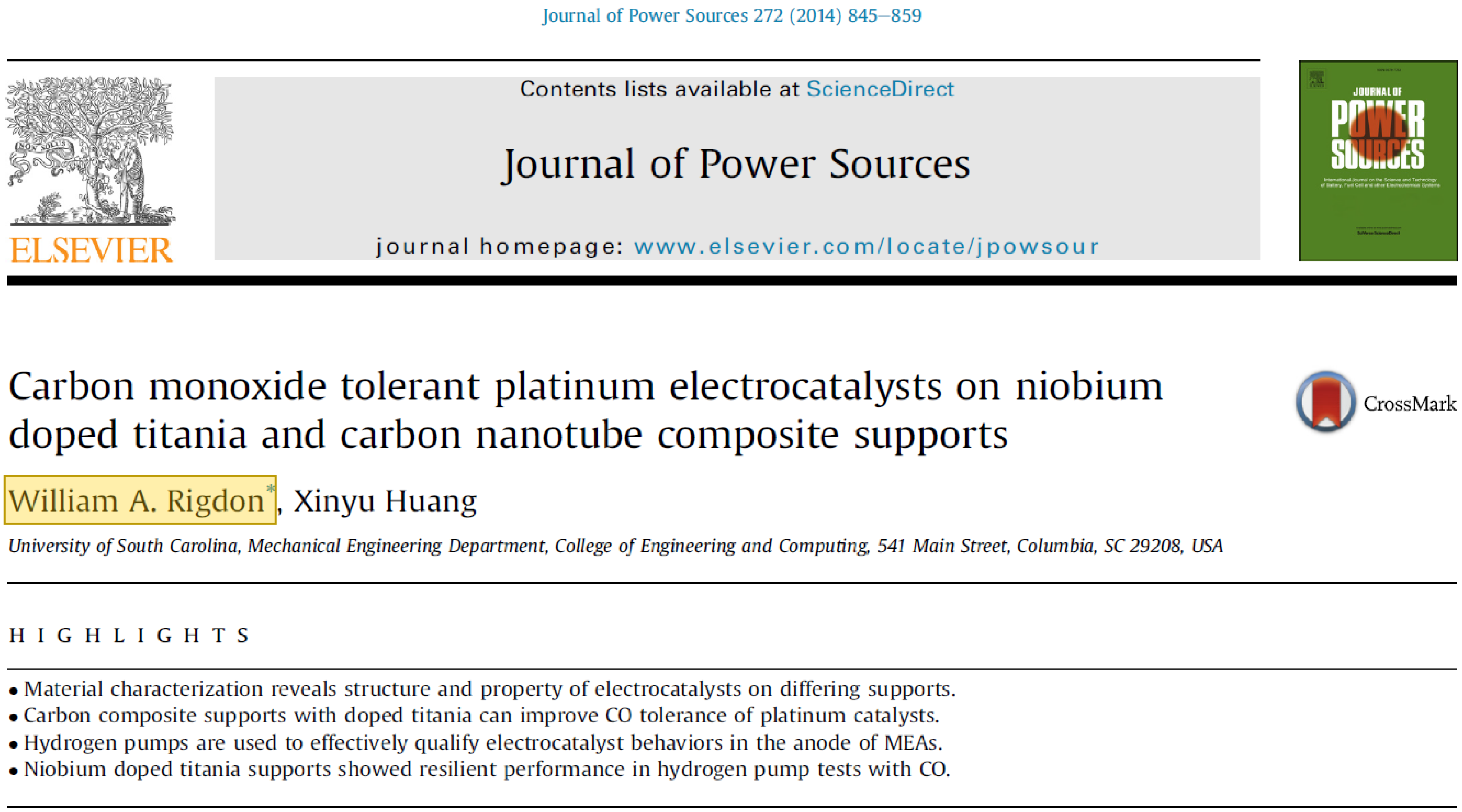
- Fast charging is needed to "cut the cord" for professional users (e.g. Outdoor equipment)
- High power tools and fast charging can benefit from new Li-ion chemistry (e.g. niobium titanates - TNO)
- High power equipment is aided by higher voltages (e.g. **FlexVolt** system & small electronics/motors)
- High voltage presents new concerns from a corrosion and safety perspective when exposed to water & fluids
- Niobium could serve a role in mechanical terminals, interconnects, as well as battery casings
- Can niobium be alloyed or plated to reduce costs?
- We can use niobium inside & outside our batteries…. It's a **HUGE** opportunity across entire battery industry!



Niobium voltage color chart VDC

Image Credit to Northrup Grumman Systems Corporation

Niobium Titanate and Defect Electrochemistry



Journal of Power Sources 272 (2014) 845–859

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/jpowsour

Carbon monoxide tolerant platinum electrocatalysts on niobium doped titania and carbon nanotube composite supports

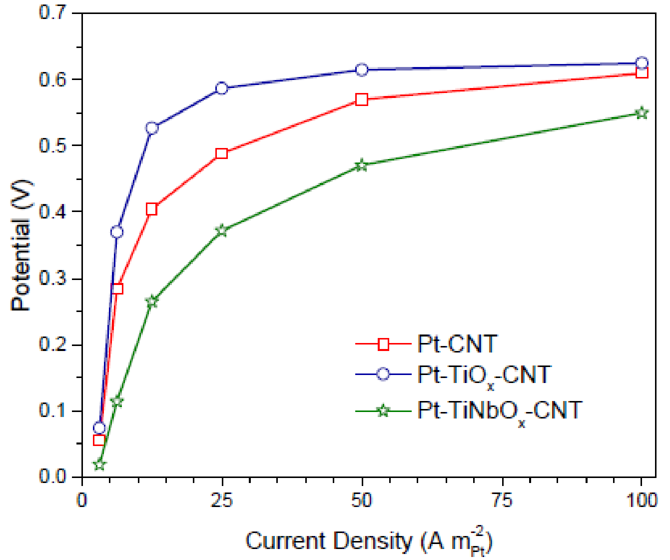
William A. Rigdon*, Xinyu Huang

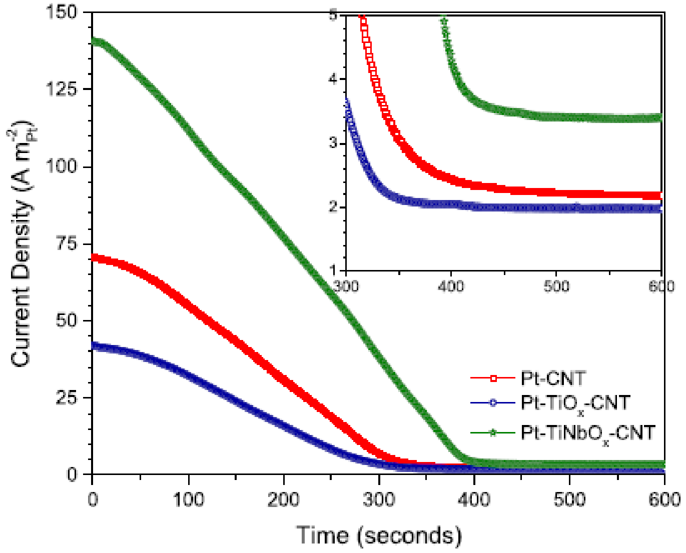
University of South Carolina, Mechanical Engineering Department, College of Engineering and Computing, 541 Main Street, Columbia, SC 29208, USA

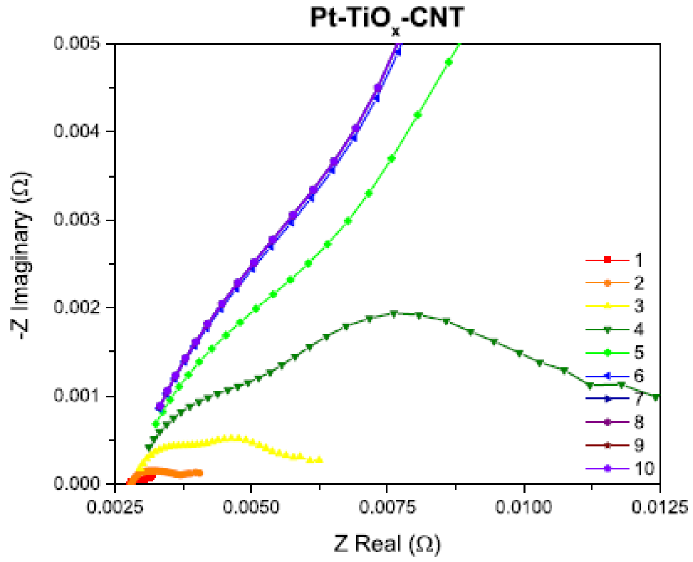
HIGHLIGHTS

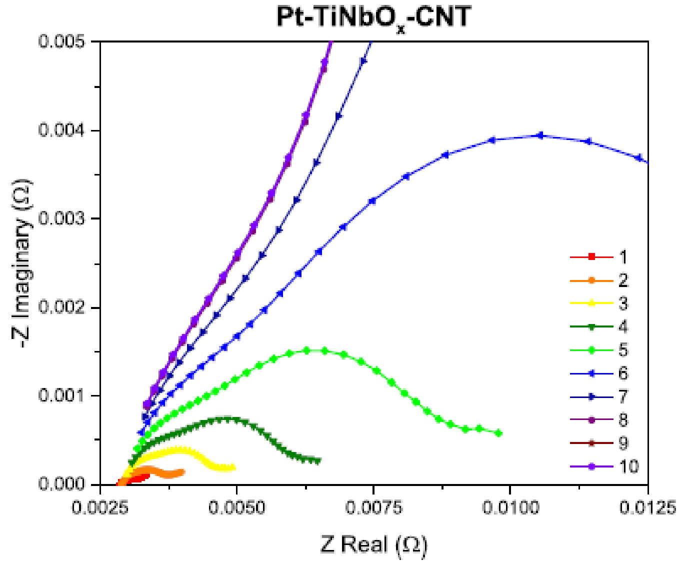
- Material characterization reveals structure and property of electrocatalysts on differing supports.
- Carbon composite supports with doped titania can improve CO tolerance of platinum catalysts.
- Hydrogen pumps are used to effectively qualify electrocatalyst behaviors in the anode of MEAs.
- Niobium doped titania supports showed resilient performance in hydrogen pump tests with CO.

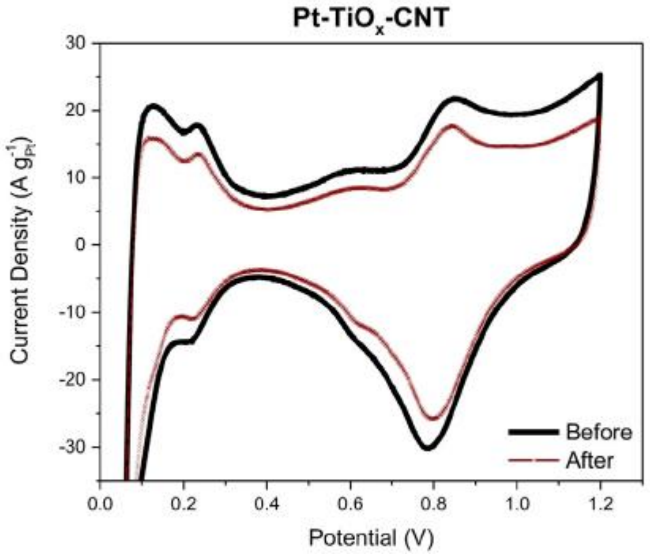
Nb-TiOx Catalyst Supports Improve CO Tolerance

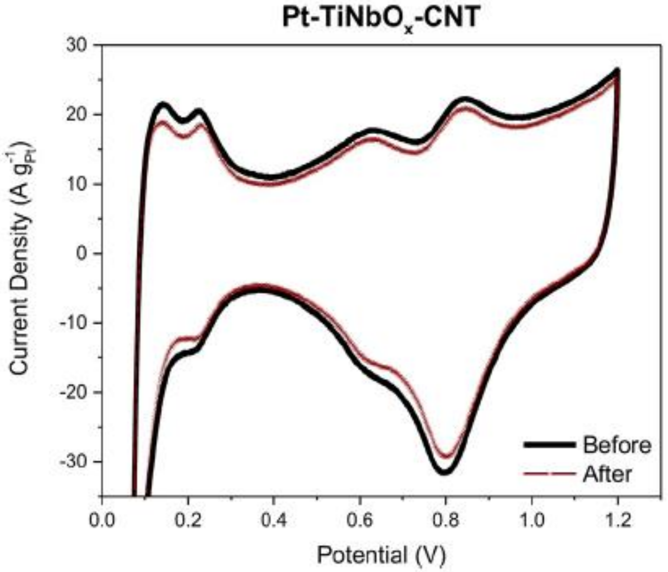




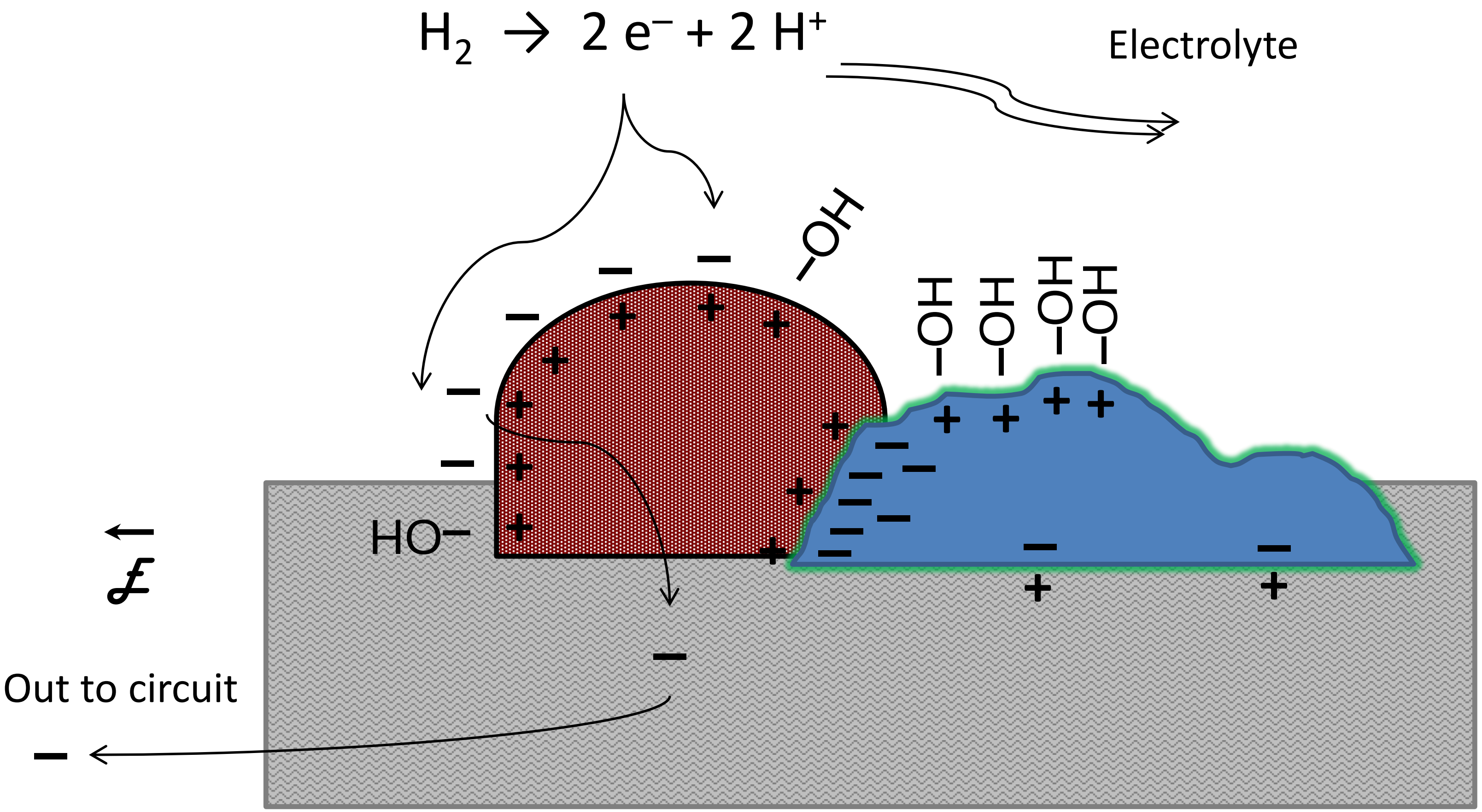




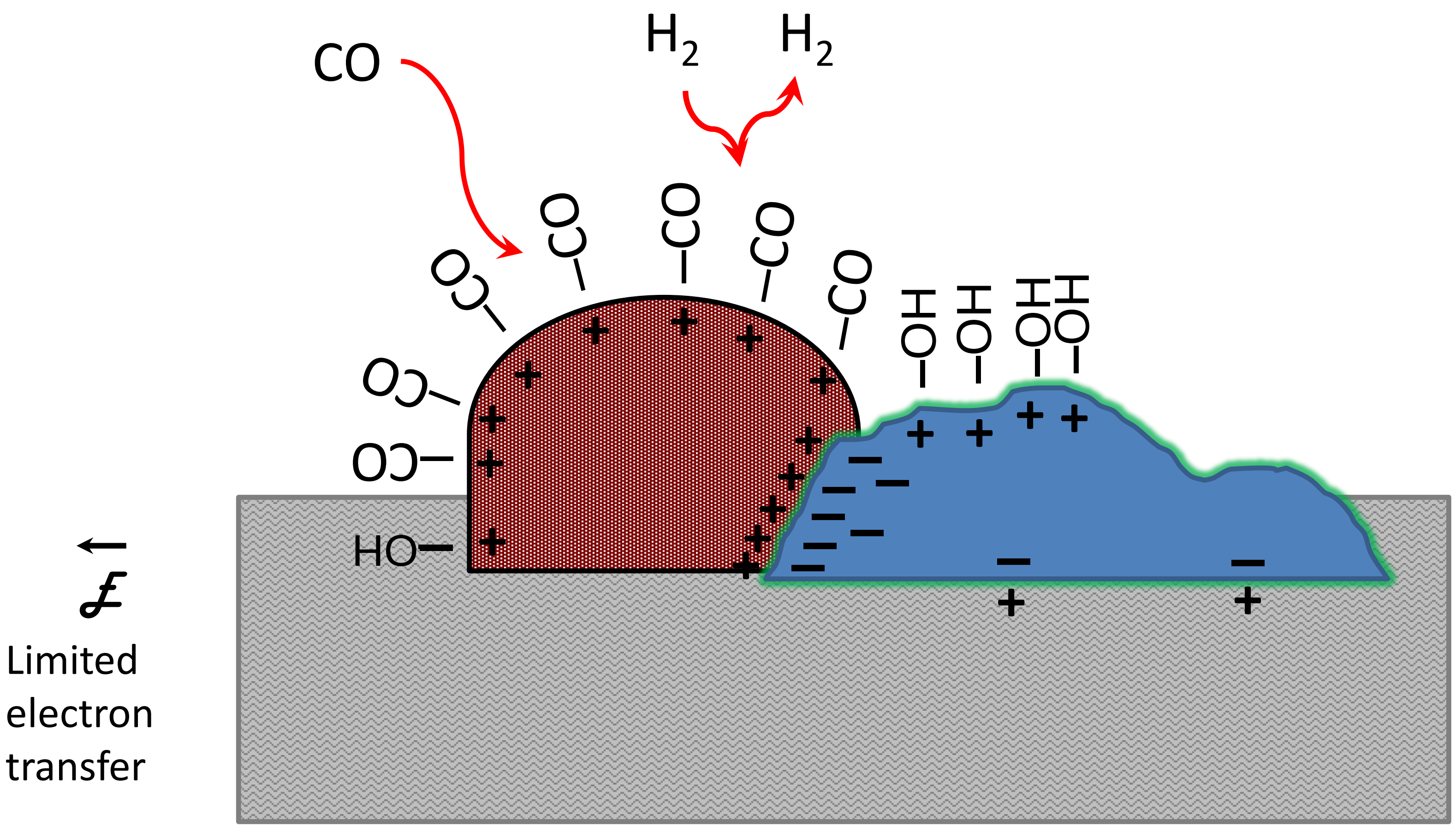




Hydrogen Oxidation Reaction

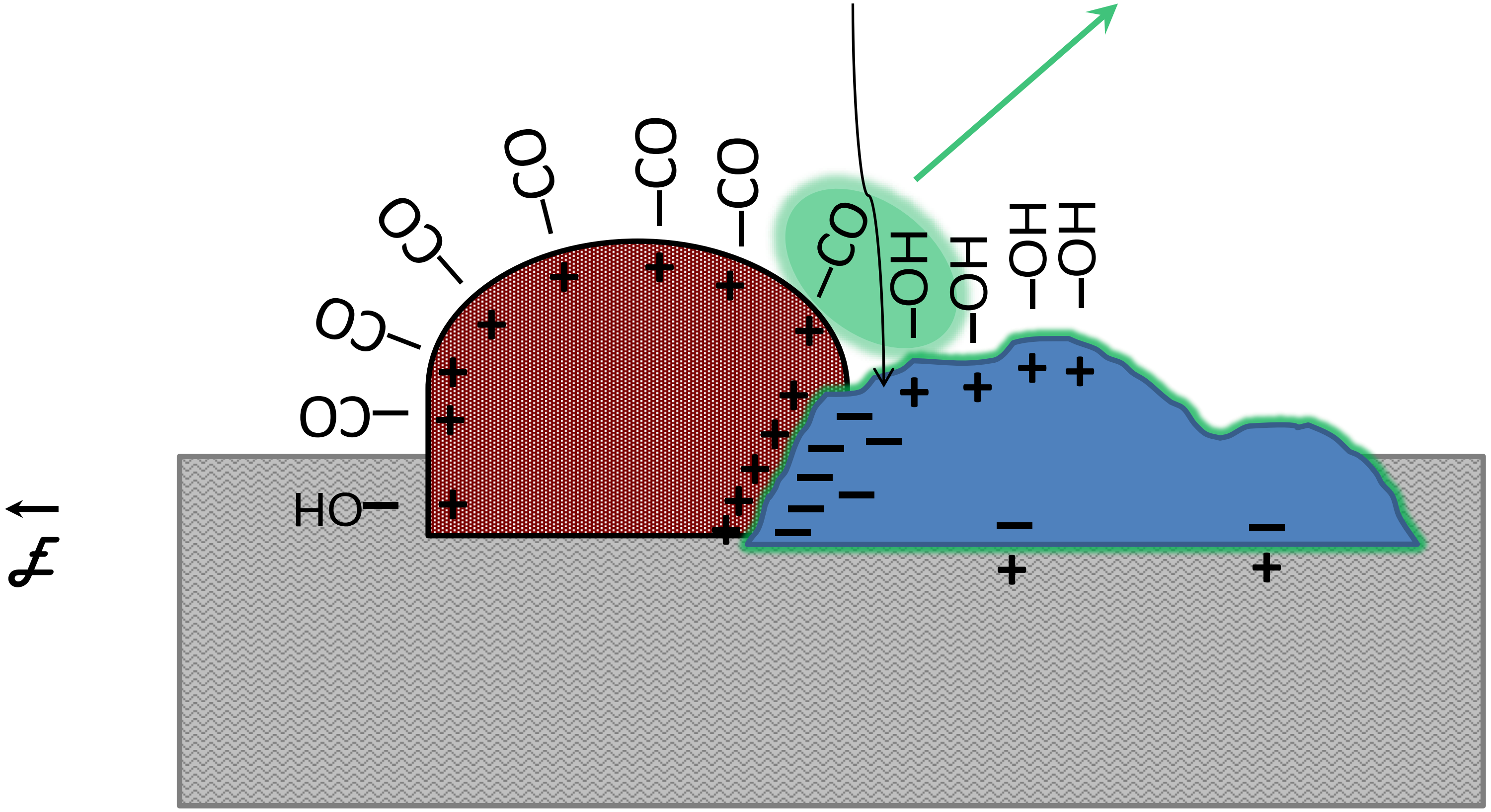


CO Poisoning!

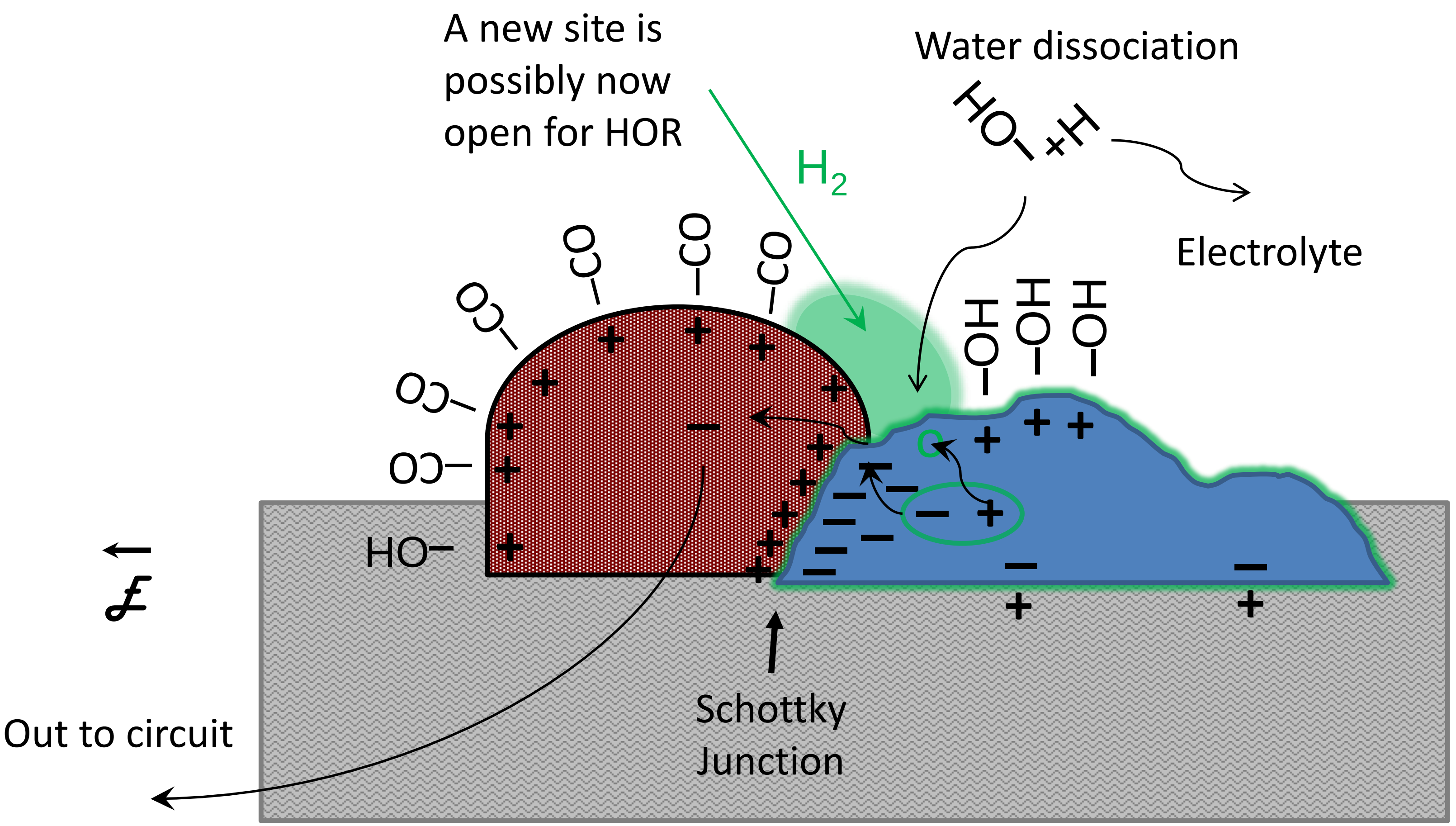


Bifunctional Reaction

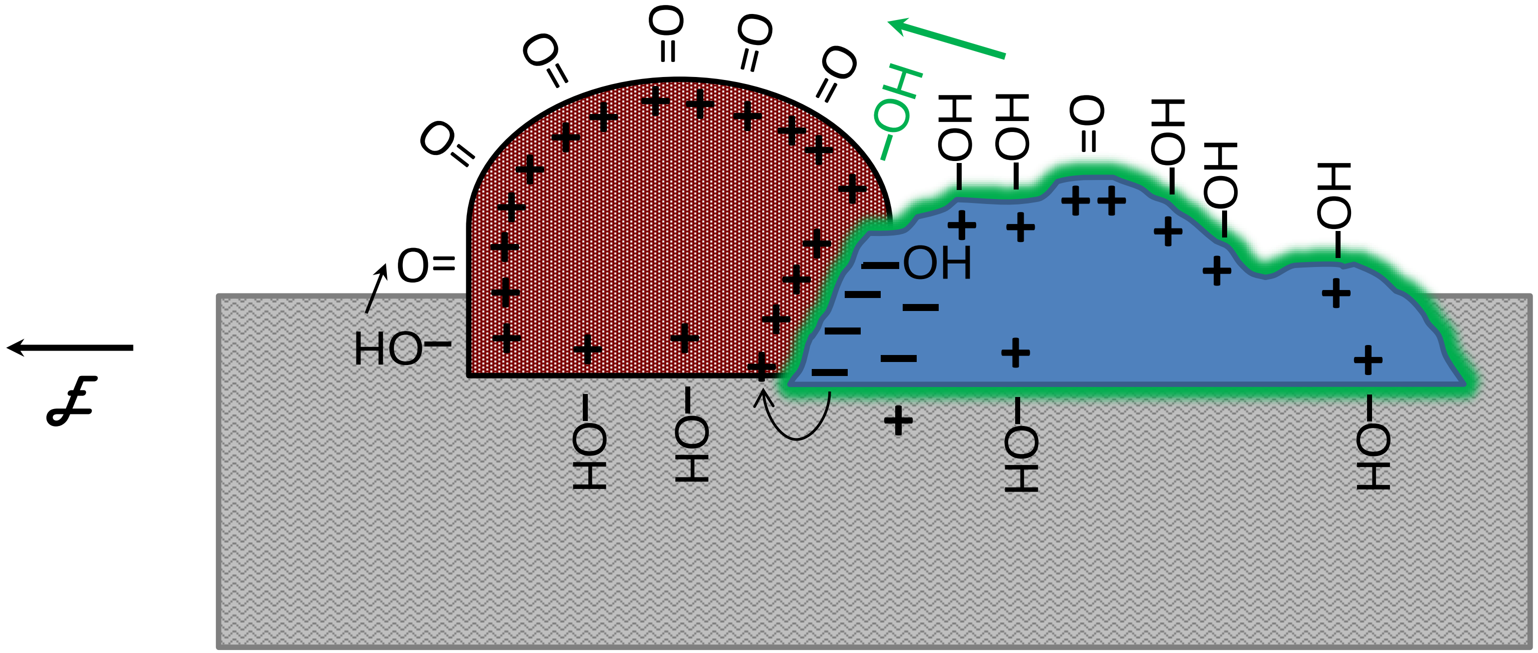
$Pt\text{-}CO + M\text{-}OH \rightarrow e^- + H^+ + CO_2$



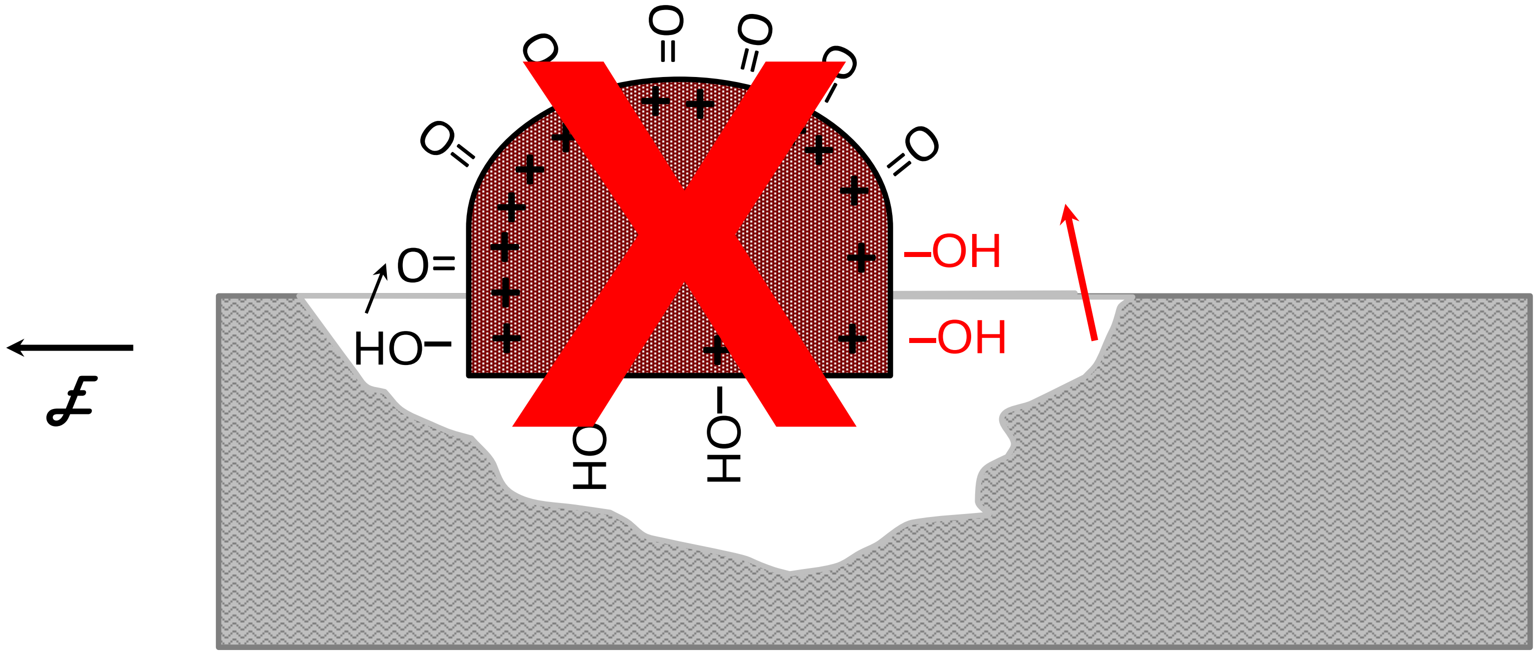
CO Tolerance



Passivation and Protection



Carbon Corrosion

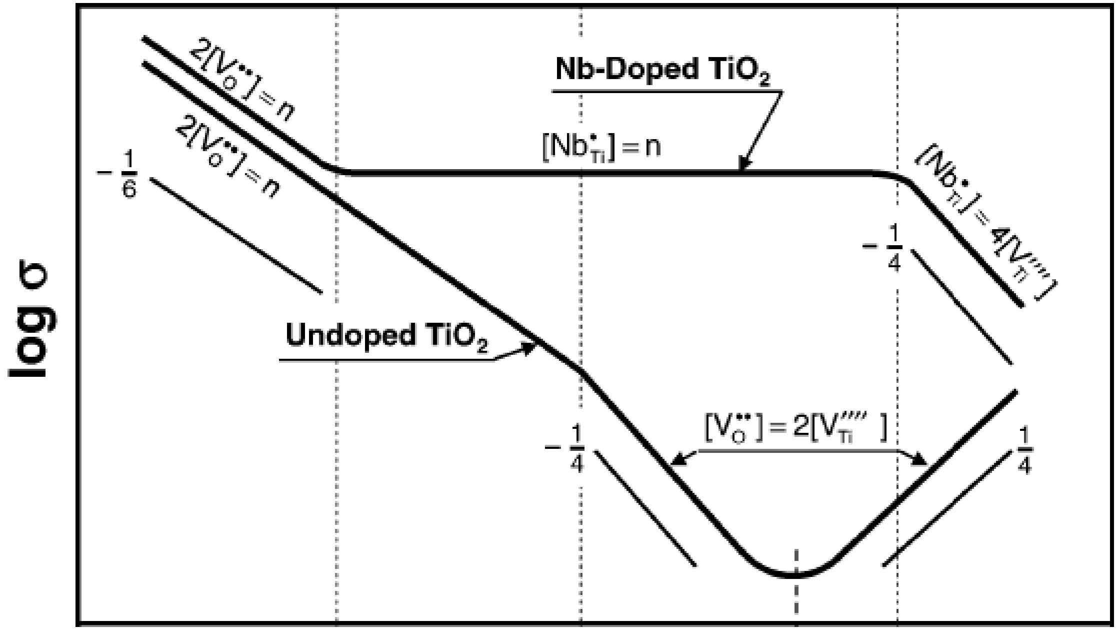


Electrical Properties of Niobium-Doped Titanate

ELECTRONICS & ELECTRICAL SYSTEMS
Innovation in Development

Electrical Properties of Niobium-Doped Titanium Dioxide.

L. R. Sheppard, T. Bak, and J. Nowotny*



Reduced ↔ Oxidized

J. Phys. Chem. C **2008**, *112*, 611−617

$$Nb_2O_5 \rightleftarrows 2Nb^{\bullet}_{Ti} + 2e' + 4O_O + \frac{1}{2}O_2 \qquad (19)$$

This regime is governed by the electronic charge compensation of niobium:

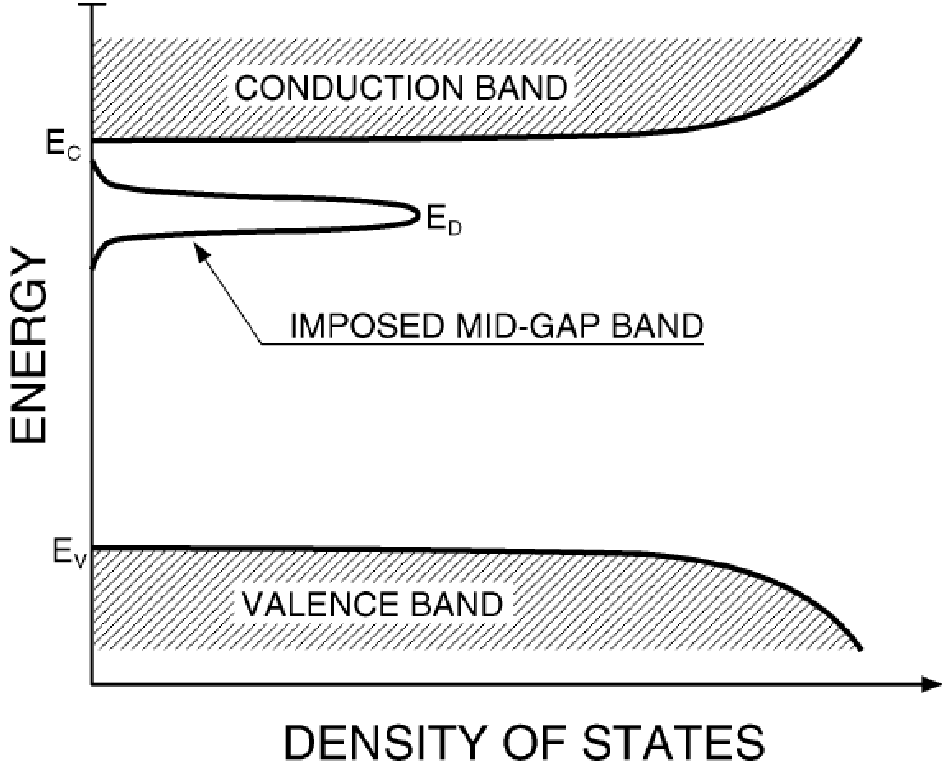


Figure 10. Schematic representation of the electronic structure for Nb-doped TiO$_2$.

Titania Doping & Metal Oxide Defect Chemistry

Guidelines for Selection of Donor Dopants

- Prefers passivation regime in electrochemical system
- Equilibrium oxidation state ± from host metal valence
- Same coordination number in crystal structure
- Ionic radius of metal cation similar for substitution

Metal	Oxidation	CN	AMU	Radius (Å)
Ti	**+4**	**6**	**47.867**	**0.61**
Nb	+5	6	92.906	0.64
W	+6	6	183.84	0.60
Ta	+5	6	180.95	0.64

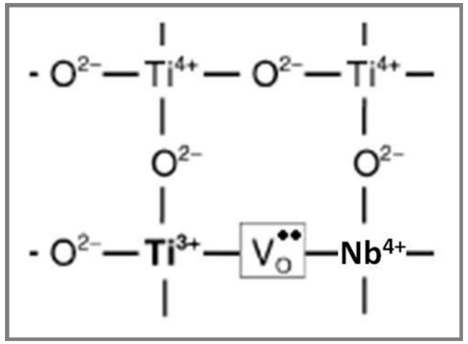
By metal oxide doping of Ti site with Nb in TiO_2:

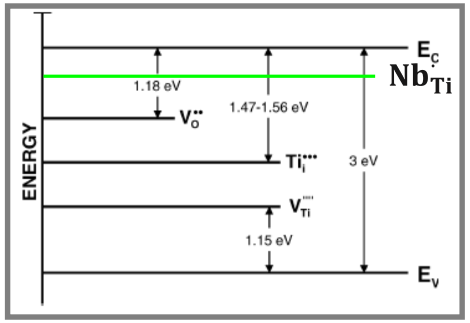
$$Nb_2O_5 \xrightarrow{2\,TiO_2} 2\,Nb^{\cdot}_{Ti} + 4\,O_O^X + \frac{1}{2}\,O_2 + 2\,e^-$$

The equilibrium reaction at low oxygen pressures, by **Kröger-Vink** notation is:

$$O_O^X \rightleftharpoons V_O^{\cdot\cdot} + 2\,e^- + \frac{1}{2}O_2$$

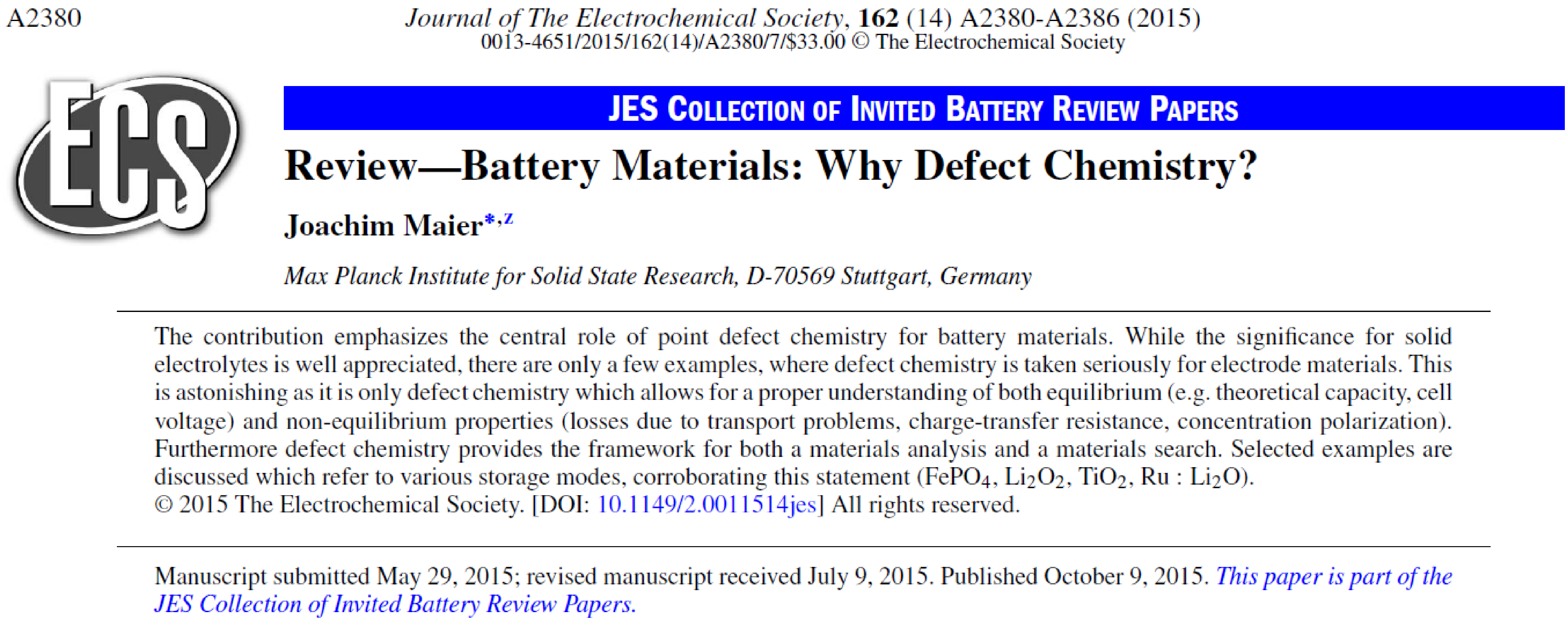
Oxygen vacancies $V_O^{\cdot\cdot}$ are of primary concern at low temperatures which are compensated by e^- carriers like Ti^{3+} or Nb^{4+} to contribute n-type conductivity to the oxide by “defect” formation in donor doping strategy preferred at low p O_2





M. K. Nowotny, L. R. Sheppard, T. Bak, J. Nowotny. Defect Chemistry of Titanium Dioxide. *J. Physical Chemistry C.* 112, 2008

Why Defect Chemistry is Relevant to Batteries



A2380 *Journal of The Electrochemical Society*, **162** (14) A2380-A2386 (2015)
0013-4651/2015/162(14)/A2380/7/$33.00 © The Electrochemical Society

JES COLLECTION OF INVITED BATTERY REVIEW PAPERS

Review—Battery Materials: Why Defect Chemistry?

Joachim Maier[*,z]

Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany

The contribution emphasizes the central role of point defect chemistry for battery materials. While the significance for solid electrolytes is well appreciated, there are only a few examples, where defect chemistry is taken seriously for electrode materials. This is astonishing as it is only defect chemistry which allows for a proper understanding of both equilibrium (e.g. theoretical capacity, cell voltage) and non-equilibrium properties (losses due to transport problems, charge-transfer resistance, concentration polarization). Furthermore defect chemistry provides the framework for both a materials analysis and a materials search. Selected examples are discussed which refer to various storage modes, corroborating this statement ($FePO_4$, Li_2O_2, TiO_2, $Ru : Li_2O$).

© 2015 The Electrochemical Society. [DOI: 10.1149/2.0011514jes] All rights reserved.

Manuscript submitted May 29, 2015; revised manuscript received July 9, 2015. Published October 9, 2015. *This paper is part of the JES Collection of Invited Battery Review Papers.*

Defect Chemical Engineering Examples

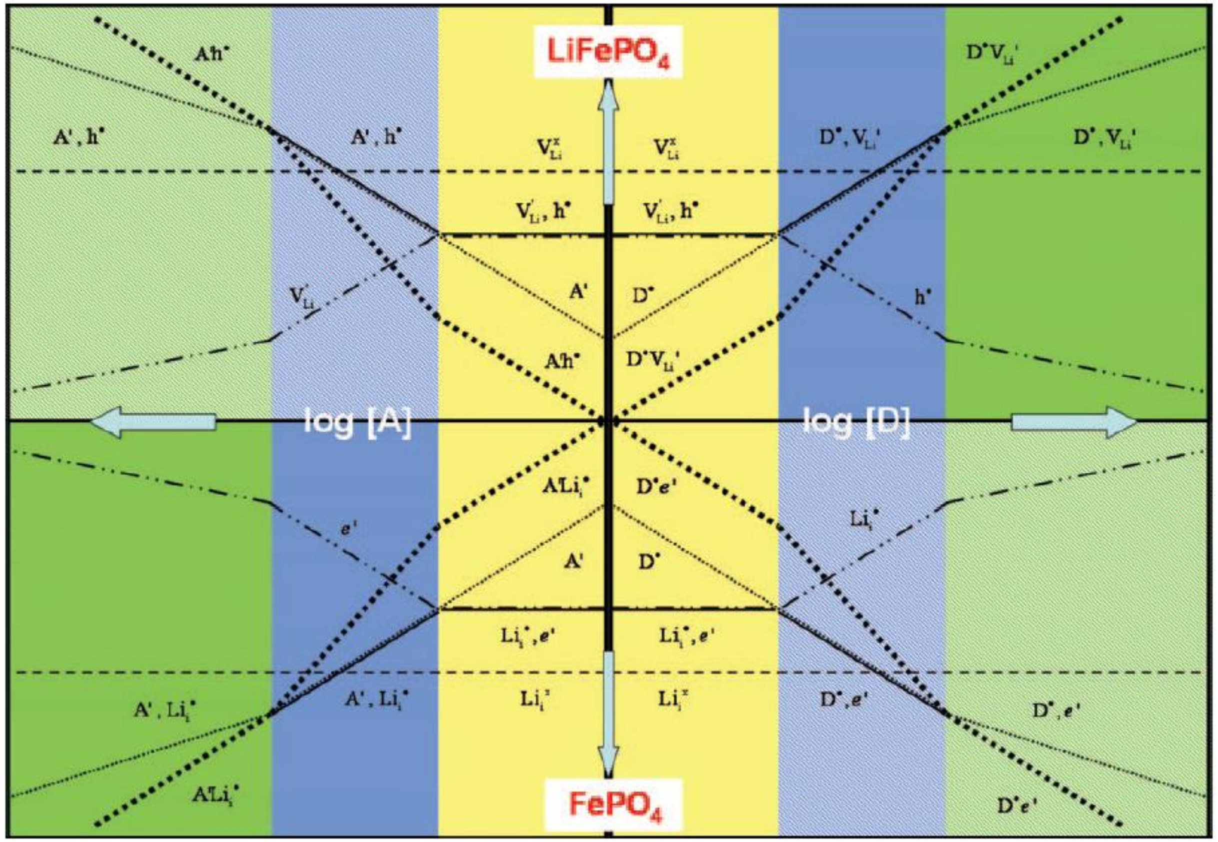


Figure 6. The variation of the logarithm of the defect concentrations in $LiFePO_4$ and $FePO_4$ on varying the acceptor [A] or donor [D] content showing a wide range of modified properties for the materials. This is to illustrate the sheer complexity of defect equilibria in battery materials. From Ref. 32 with permission from de Gruyter.

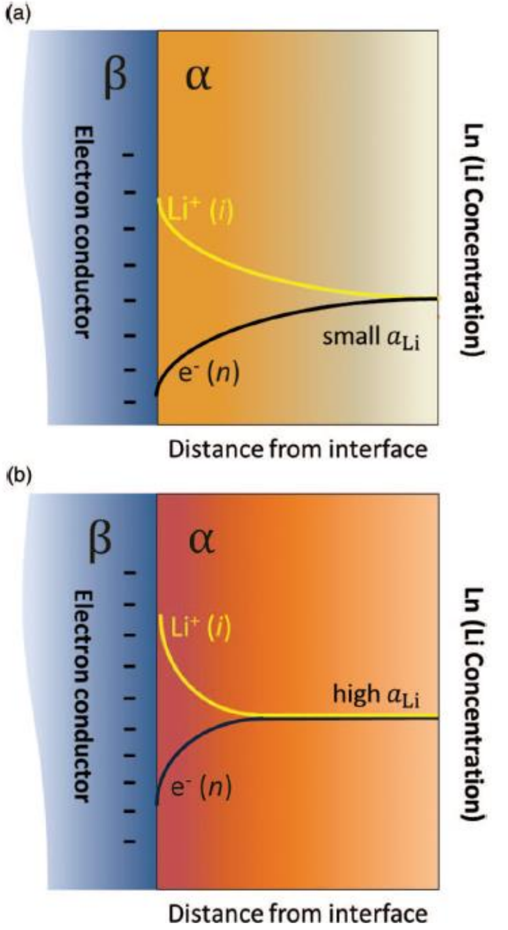
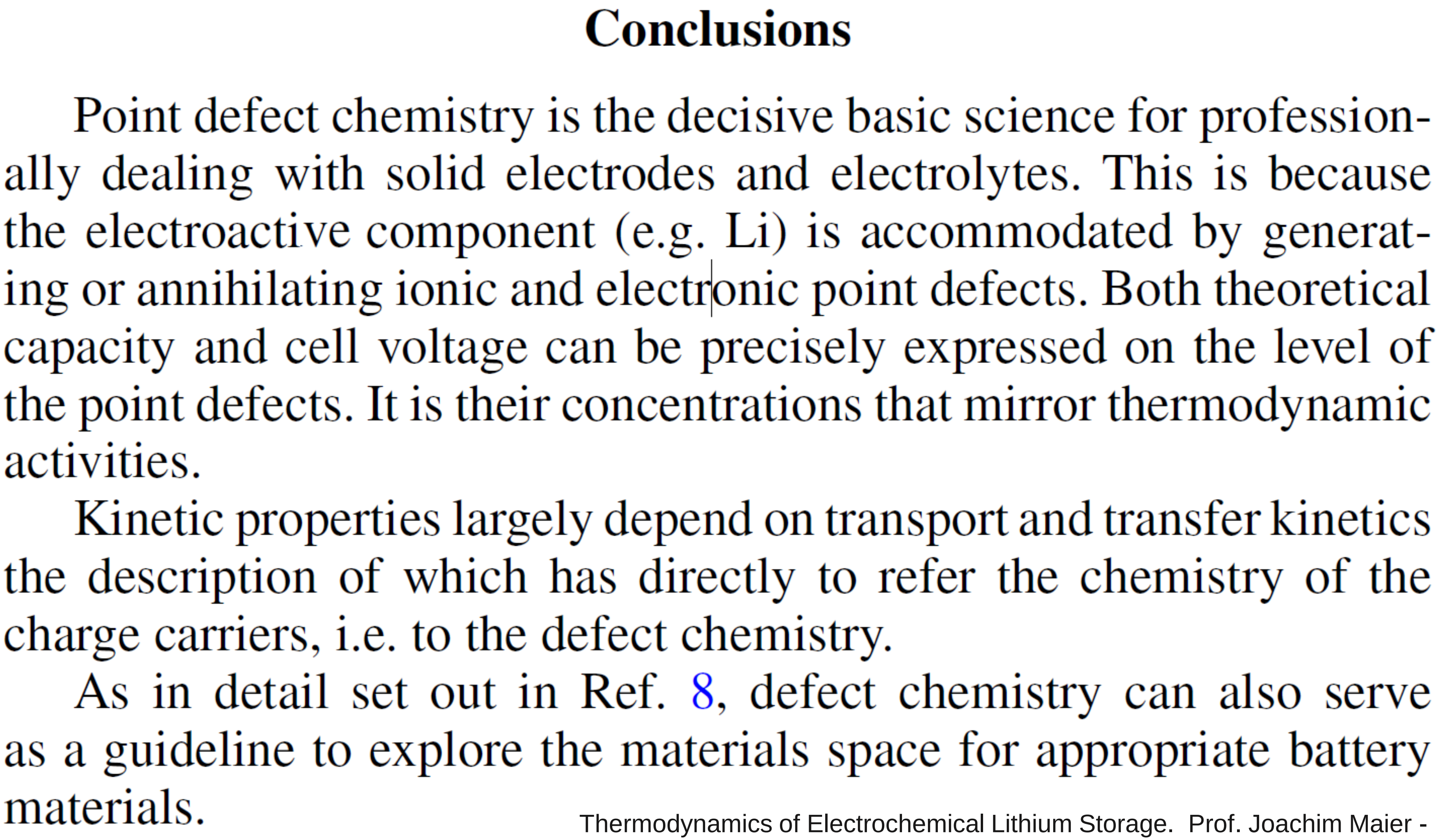


Figure 10. Defect chemical variation at the contact of electroactive mass/electronic conductor. The two pictures compare two different states of storage. (a) small and (b) high a_{Li}. Note different defect levels, different magnitude of variation and different sharpness of the profiles. From Ref. 14 with permission from The American Physical Society.

Point Defect Chemistry is the Decisive Science



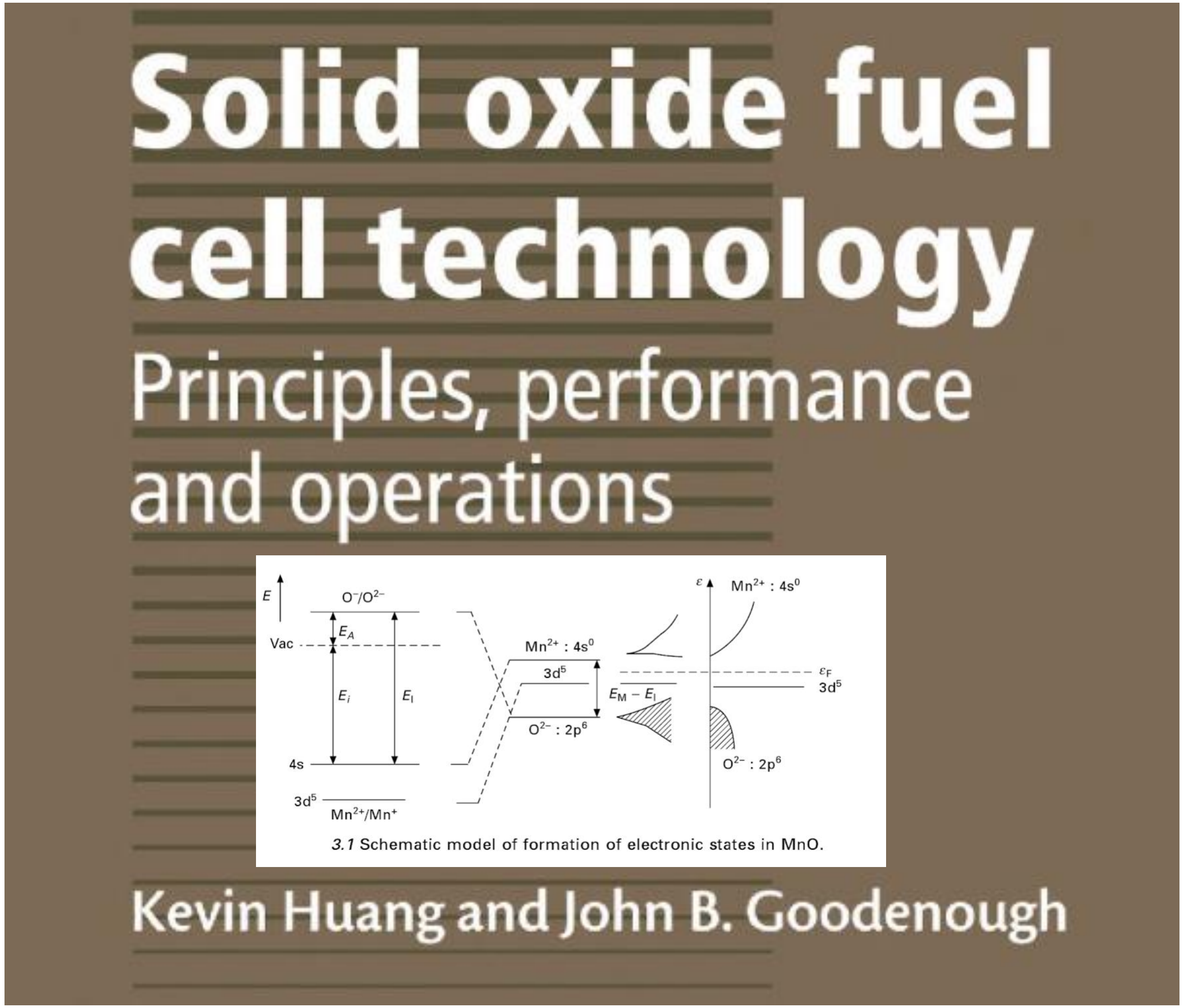
Conclusions

Point defect chemistry is the decisive basic science for professionally dealing with solid electrodes and electrolytes. This is because the electroactive component (e.g. Li) is accommodated by generating or annihilating ionic and electronic point defects. Both theoretical capacity and cell voltage can be precisely expressed on the level of the point defects. It is their concentrations that mirror thermodynamic activities.

Kinetic properties largely depend on transport and transfer kinetics the description of which has directly to refer the chemistry of the charge carriers, i.e. to the defect chemistry.

As in detail set out in Ref. 8, defect chemistry can also serve as a guideline to explore the materials space for appropriate battery materials.

Thermodynamics of Electrochemical Lithium Storage. Prof. Joachim Maier - *Angewandte Chemie - 2013* https://doi.org/10.1002/anie.201205569

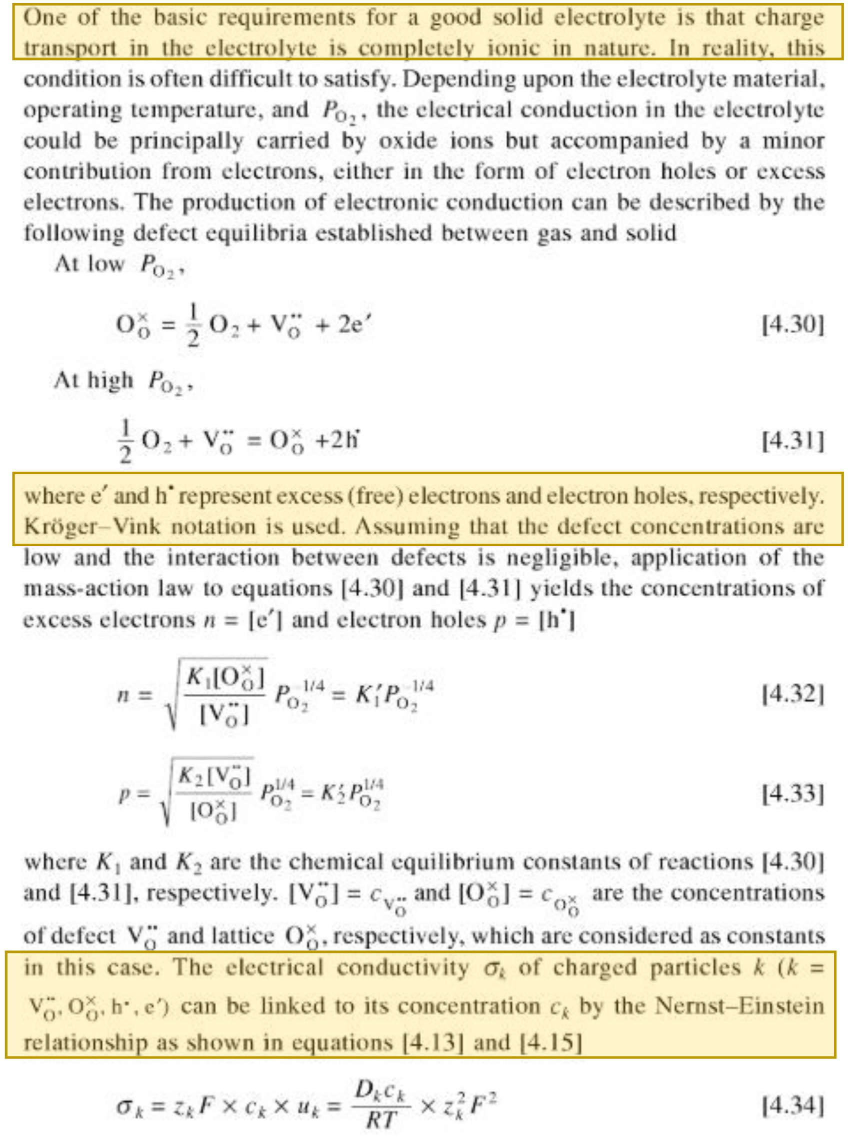


Solid oxide fuel cell technology

Principles, performance and operations

3.1 Schematic model of formation of electronic states in MnO.

Kevin Huang and John B. Goodenough



One of the basic requirements for a good solid electrolyte is that charge transport in the electrolyte is completely ionic in nature. In reality, this condition is often difficult to satisfy. Depending upon the electrolyte material, operating temperature, and P_{O_2}, the electrical conduction in the electrolyte could be principally carried by oxide ions but accompanied by a minor contribution from electrons, either in the form of electron holes or excess electrons. The production of electronic conduction can be described by the following defect equilibria established between gas and solid

At low P_{O_2},

$$O_O^\times = \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \qquad [4.30]$$

At high P_{O_2},

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} = O_O^\times + 2h^\bullet \qquad [4.31]$$

where e′ and h˙ represent excess (free) electrons and electron holes, respectively. Kröger–Vink notation is used. Assuming that the defect concentrations are low and the interaction between defects is negligible, application of the mass-action law to equations [4.30] and [4.31] yields the concentrations of excess electrons $n = [e']$ and electron holes $p = [h^\bullet]$

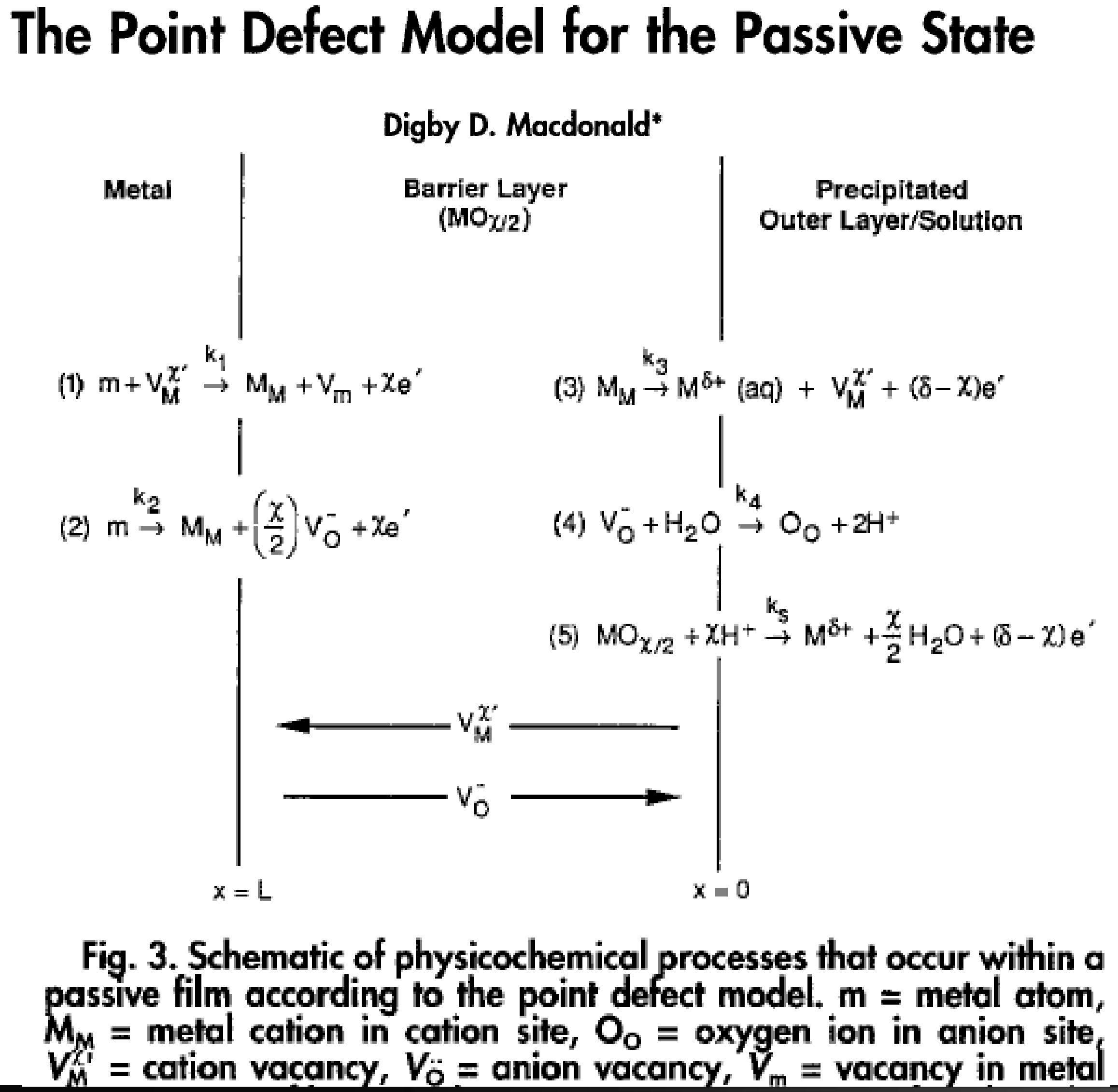
$$n = \sqrt{\frac{K_1[O_O^\times]}{[V_O^{\bullet\bullet}]}}\,P_{O_2}^{-1/4} = K_1' P_{O_2}^{-1/4} \qquad [4.32]$$

$$p = \sqrt{\frac{K_2[V_O^{\bullet\bullet}]}{[O_O^\times]}}\,P_{O_2}^{1/4} = K_2' P_{O_2}^{1/4} \qquad [4.33]$$

where K_1 and K_2 are the chemical equilibrium constants of reactions [4.30] and [4.31], respectively. $[V_O^{\bullet\bullet}] = c_{V_O^{\bullet\bullet}}$ and $[O_O^\times] = c_{O_O^\times}$ are the concentrations of defect $V_O^{\bullet\bullet}$ and lattice $O_O^\times$, respectively, which are considered as constants in this case. The electrical conductivity σ_k of charged particles k ($k = V_O^{\bullet\bullet}, O_O^\times, h^\bullet, e'$) can be linked to its concentration c_k by the Nernst–Einstein relationship as shown in equations [4.13] and [4.15]

$$\sigma_k = z_k F \times c_k \times u_k = \frac{D_k c_k}{RT} \times z_k^2 F^2 \qquad [4.34]$$

Point Defect Model for the Passivation State



The Point Defect Model for the Passive State

Digby D. Macdonald*

$$(1)\quad m + V_M^{\chi'} \xrightarrow{k_1} M_M + V_m + \chi e'$$

$$(2)\quad m \xrightarrow{k_2} M_M + \left(\frac{\chi}{2}\right) V_O^{\cdot\cdot} + \chi e'$$

$$(3)\quad M_M \xrightarrow{k_3} M^{\delta+}(aq) + V_M^{\chi'} + (\delta-\chi)e'$$

$$(4)\quad V_O^{\cdot\cdot} + H_2O \xrightarrow{k_4} O_O + 2H^+$$

$$(5)\quad MO_{\chi/2} + \chi H^+ \xrightarrow{k_5} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta-\chi)e'$$

Fig. 3. Schematic of physicochemical processes that occur within a passive film according to the point defect model. m = metal atom, M_M = metal cation in cation site, O_O = oxygen ion in anion site, $V_M^{\chi'}$ = cation vacancy, $V_O^{\cdot\cdot}$ = anion vacancy, V_m = vacancy in metal

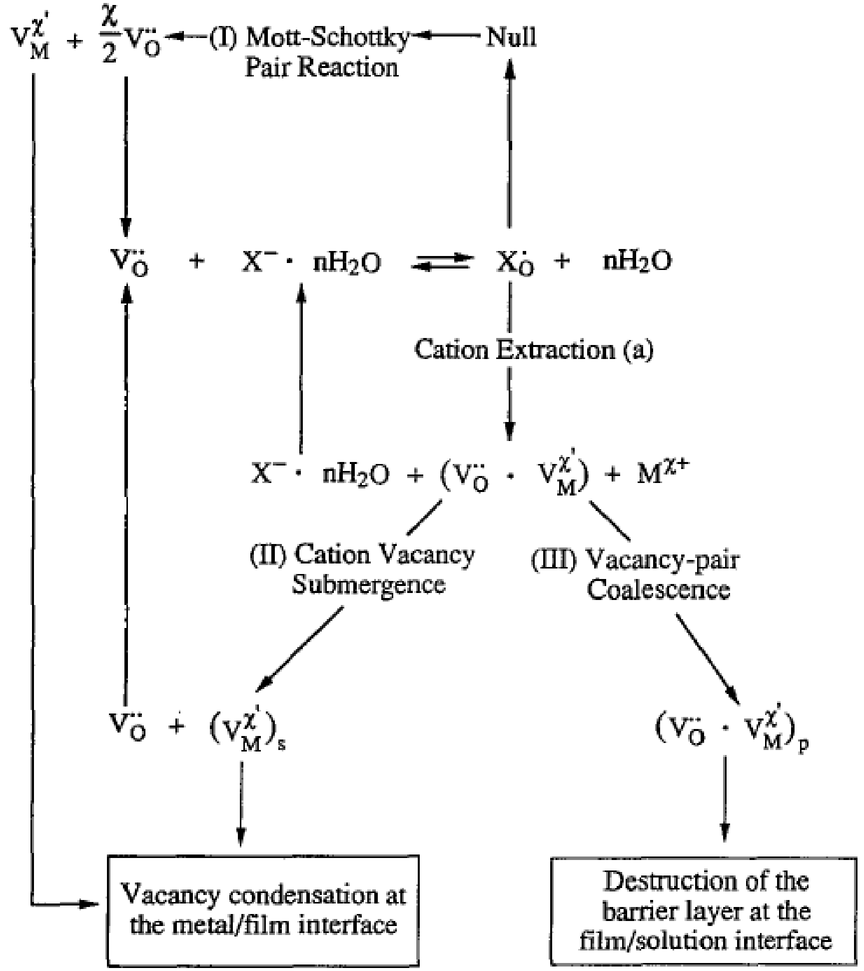


Fig. 7. Summary of proposed reactions leading to passivity breakdown.

J. Electrochem. Soc. 1992, Vol. 139, issue 12, 3434-3449

Passive Film Growth, Breakdown, and Pitting

The Point Defect Model for the Passive State

Digby D. Macdonald*

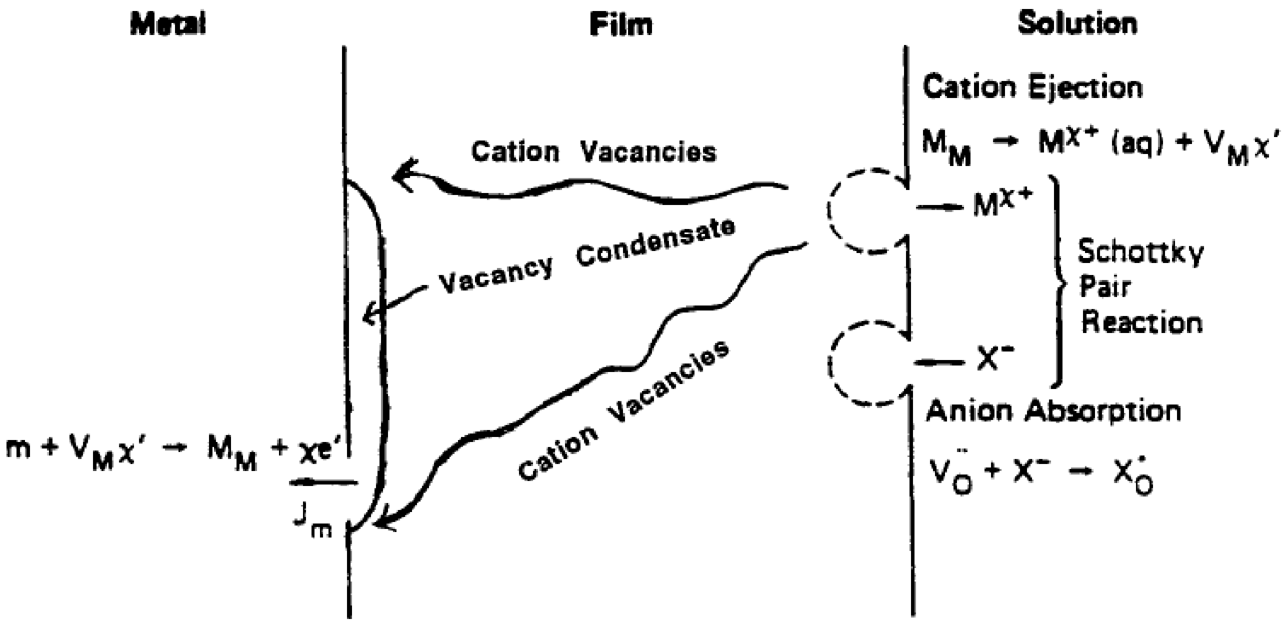


Fig. 8. One process leading to the breakdown of passive films according to the PDM.

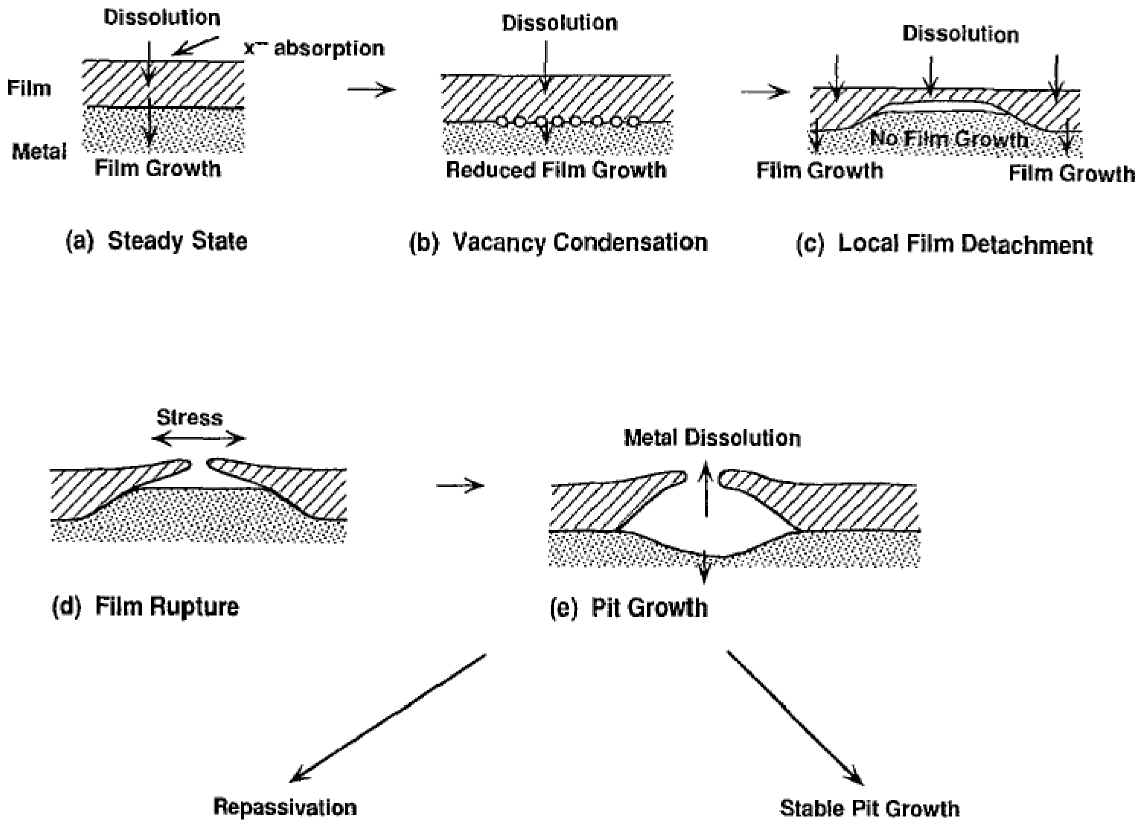


Fig. 9. Cartoon outlining various stages of pit nucleation according to the PDM.

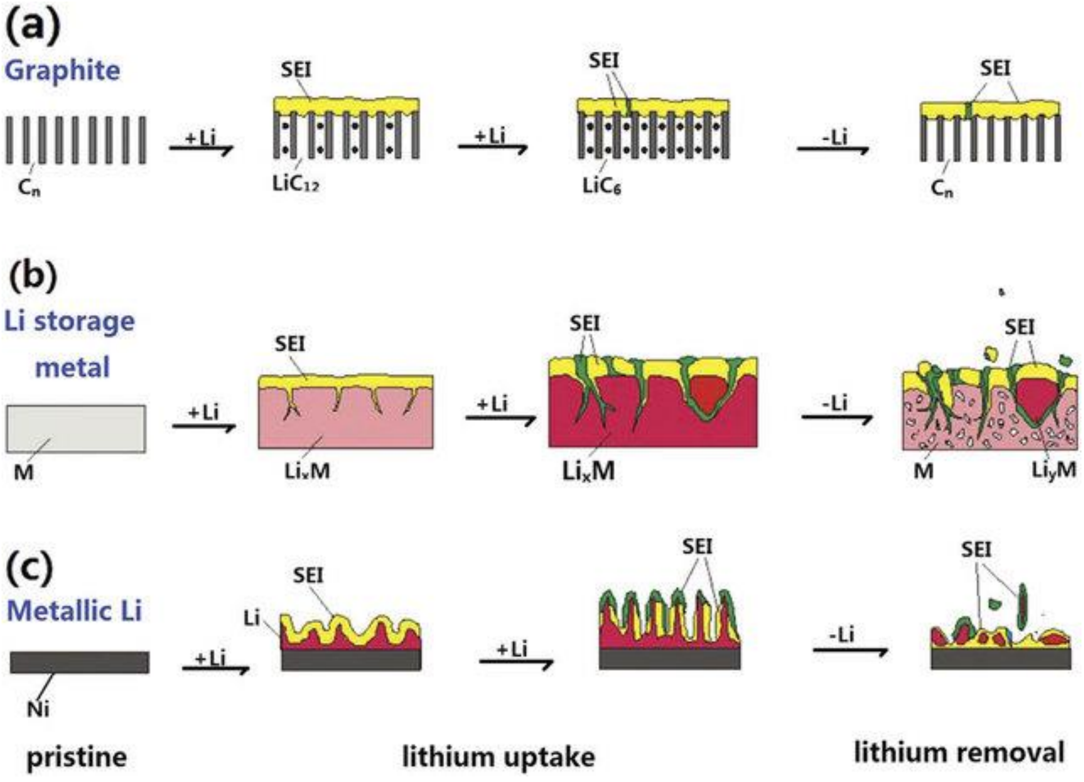
SEI Passivation and Battery Materials

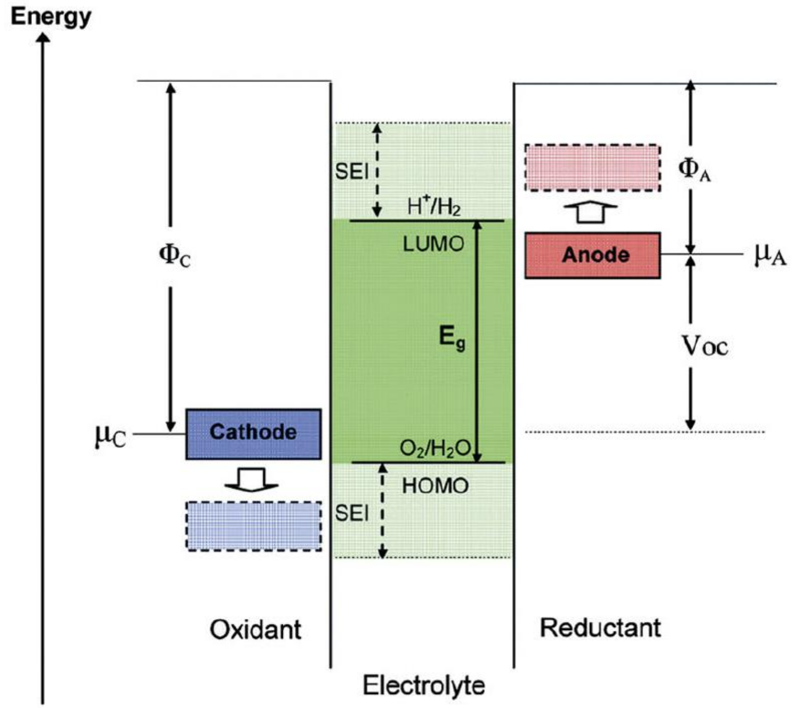
REVIEW ARTICLE OPEN

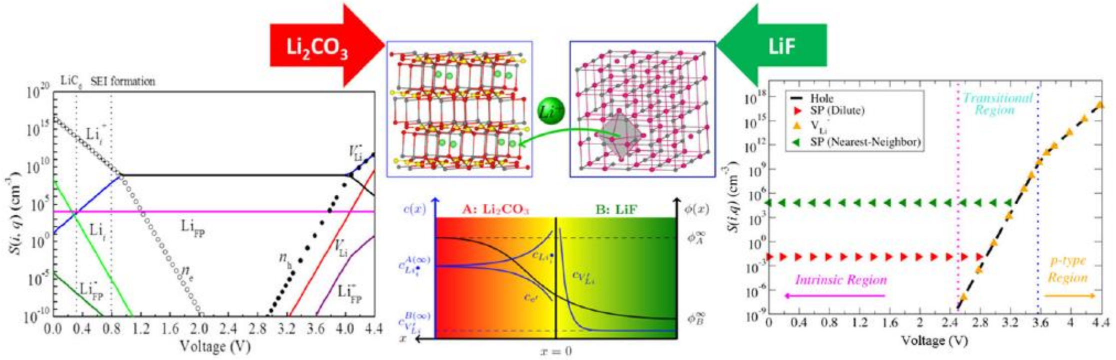
Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries

Aiping Wang[1,2], Sanket Kadam[3], Hong Li[4], Siqi Shi[1,2] and Yue Qi[3]

npj Computational Materials (2018)4:15 ; doi:10.1038/s41524-018-0064-0



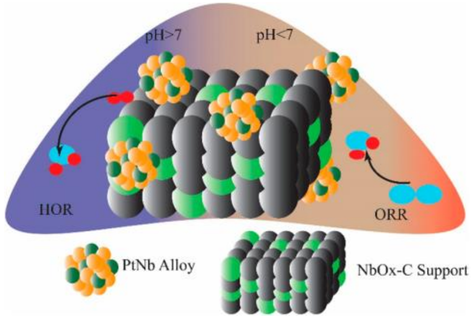




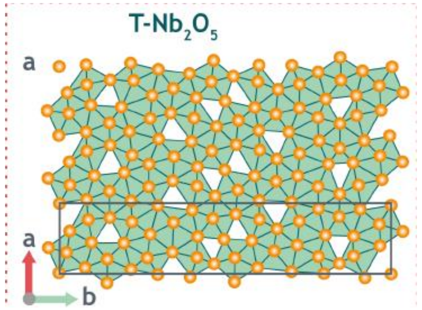
Summary of Niobium Defect Electrochemistry

- Defect chemistry is highly relevant to electrochemistry applications
  - Fuel cells, electrolyzers, electrocatalysts, batteries, corrosion, and more
- We need some guidelines for doping to improve material design that have proven to be so beneficial in semiconductor advances and even alloys
- The existence and understanding of passivation states is critical to electrochem.
  - SEI, anodization, active → passive transitions, and transpassive breakdown
- Niobium and niobates demonstrate a wide range of passivation behavior
- Defect chemistry goes beyond crystal microstructures to atomic/electronic level

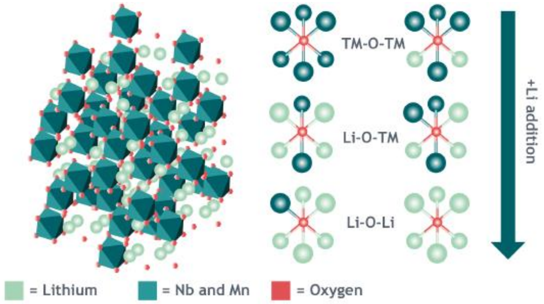
ACS Catal. 2017, 7, 4936–4946



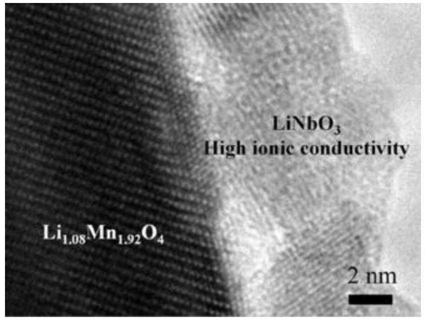
Journal of the American Chemical Society, 2016



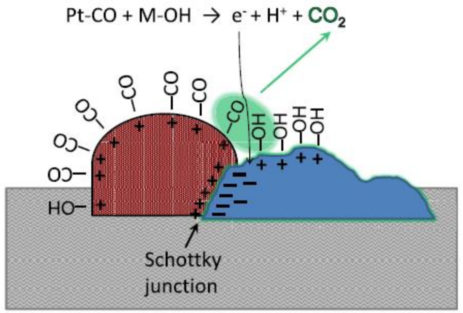
Proceedings of National Academy of Science, 2015



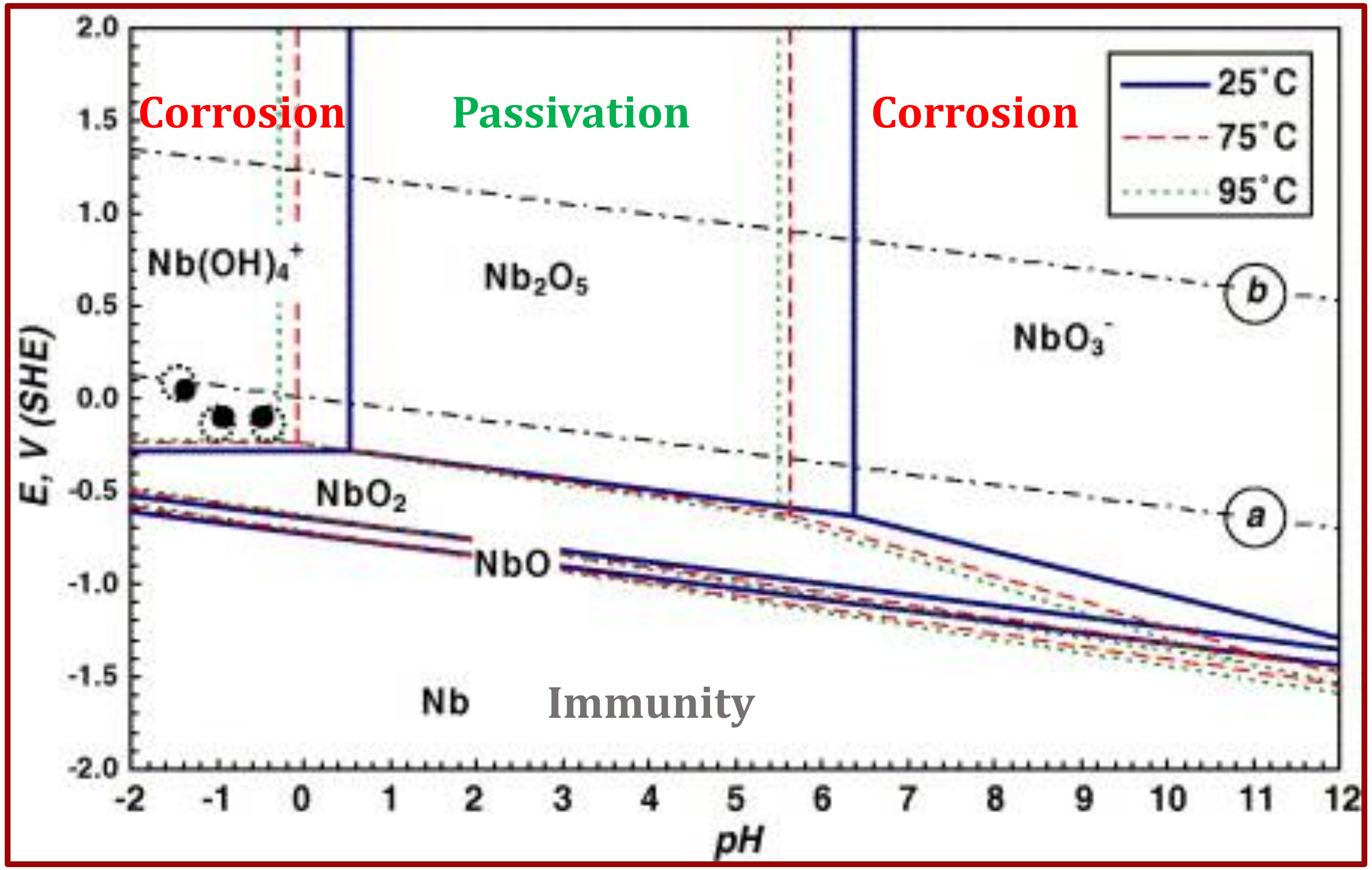
ACS Appl Material Interfaces, 2014



Journal of Power Sources 272 (2014)



Niobium Pourbaix Diagram



E. Asselin , T. M. Ahmed , A. Alfantazi. Corrosion of niobium in sulphuric and hydrochloric acid solutions at 75 and 95 °C. *Corrosion Science*. 49, 694-700, 2007.