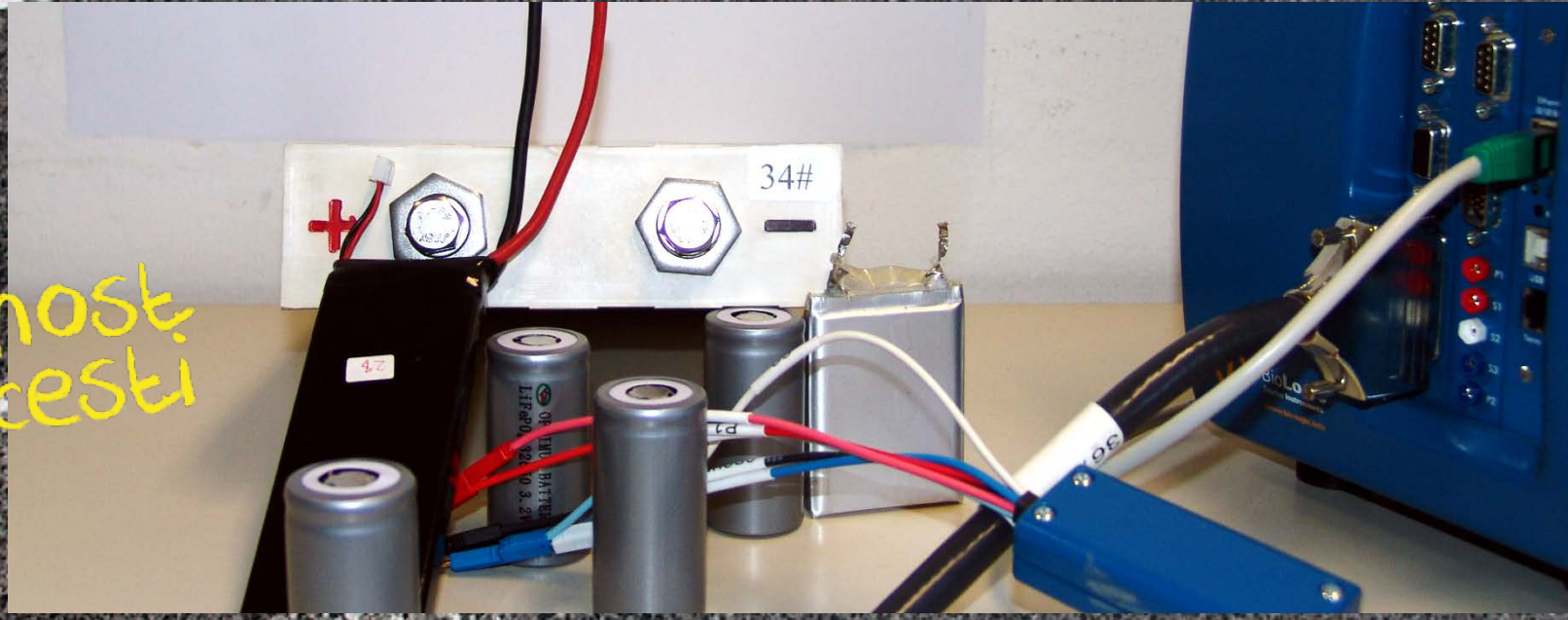
Znanost na cesti



5. maj 2016 ob 19h

Kje so meje zmogljivosti baterij

doc.dr. Robert Dominko, Kemijski inštitut

Maja Ratej, Val 202

SATENA

Institut "Jožef Stefan" Ljubljana, Slovenija

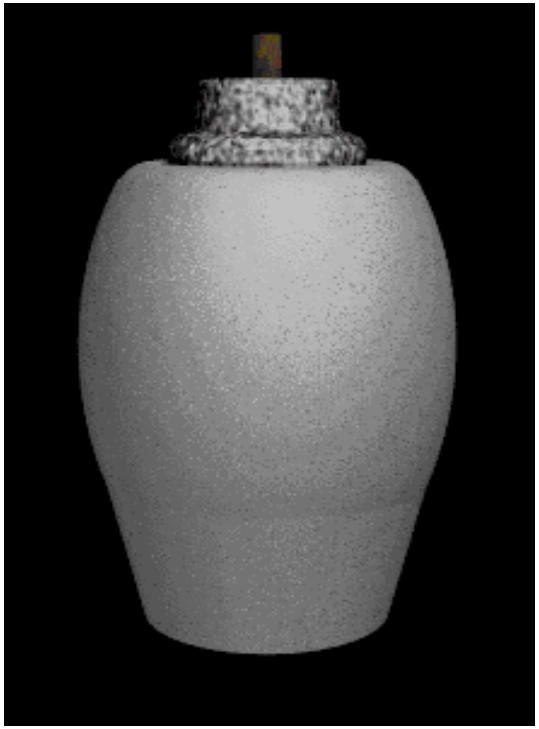
Univerza v Ljubljani
Fakulteta za matematiko in fiziko

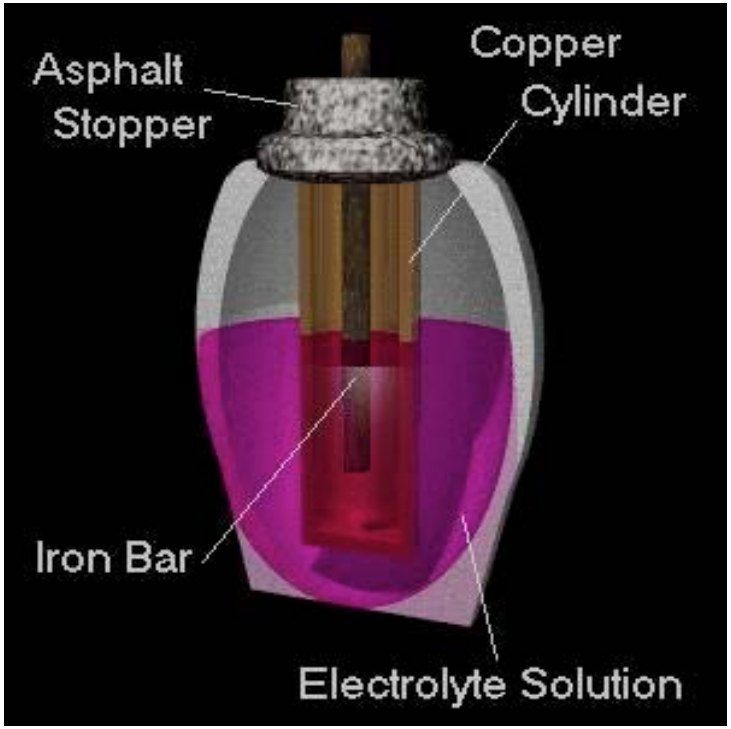
UstnaMedicina

KAVARNA UNION

Zgodovina baterij – BAGDADSKA BATERIJA

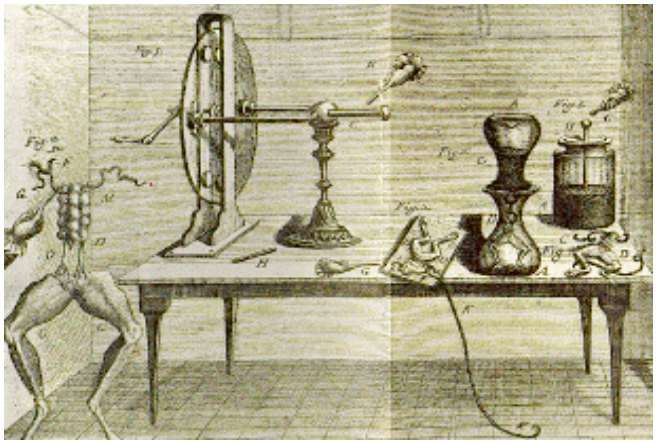
Okoli leta 1930 so v okolici Bagdada našli lončene posode, ki spominjajo na baterije: domnevajo da so stare več kot 2000 let. Rekonstrukcija je pokazala, da je napetost baterije približno 2V, če se uporabi grozdni sok kot elektrolit.
Nikomur ni znano zakaj so jh uporabljali...

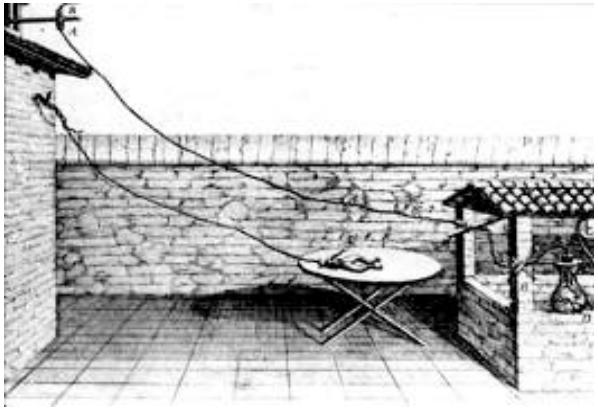


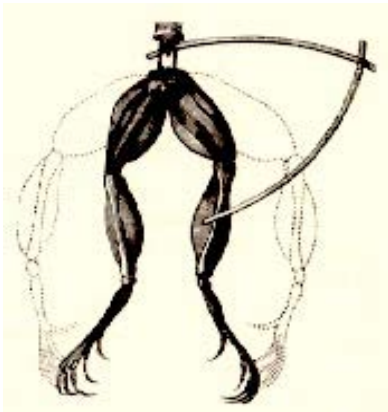


Zgodovina baterij – LUIGI GALVANI

Leta 1780 je Luigi Galvani (Bologna, Italy) je pri eksperimentiranju z žabjimi kraki opazil:
- krčenje krakov kot posledica udara strele in povzročeno z napravami, ki so proizvajale elektriko;
- krčenje krakov, ko jih je priključil na različne kovine brez dodatnega izvora elektrike – to je poimenoval elektrika živalskega izvora.





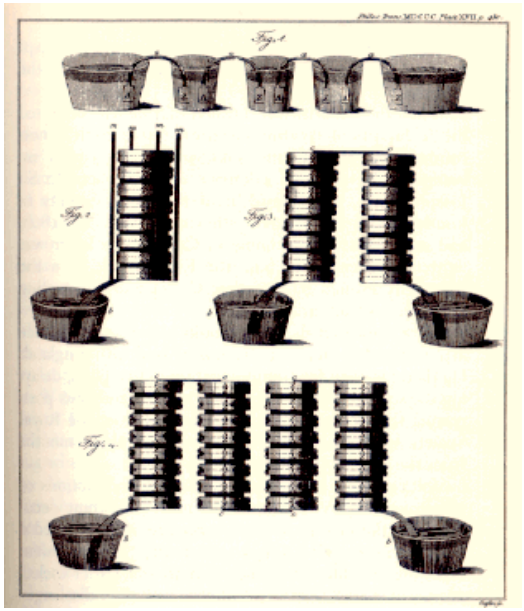


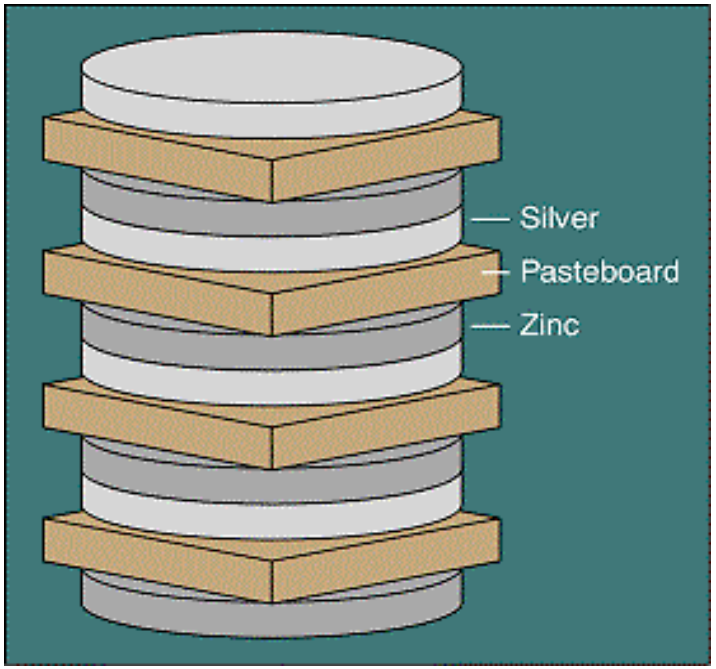
Zgodovina baterij – ALESSANDRO VOLTA

Alessandro Volta (Pavia, Italy) je sklepal, da so vzrok za elektriko telesne tekočine žabe (elektrolit) in različne kovine, in ne žabji kraki

-Okoli leta 1800 je naredil prvo baterijo iz izmenjajočih kovinskih diskov, ki jih je ločil z vlažno porozno tkanino namočeno v raztopino soli;

-Baterija je omogočala generirati strele podobne tistim, ki so jih dobili s pomočjo naprav, ki so proizvajale elektriko.



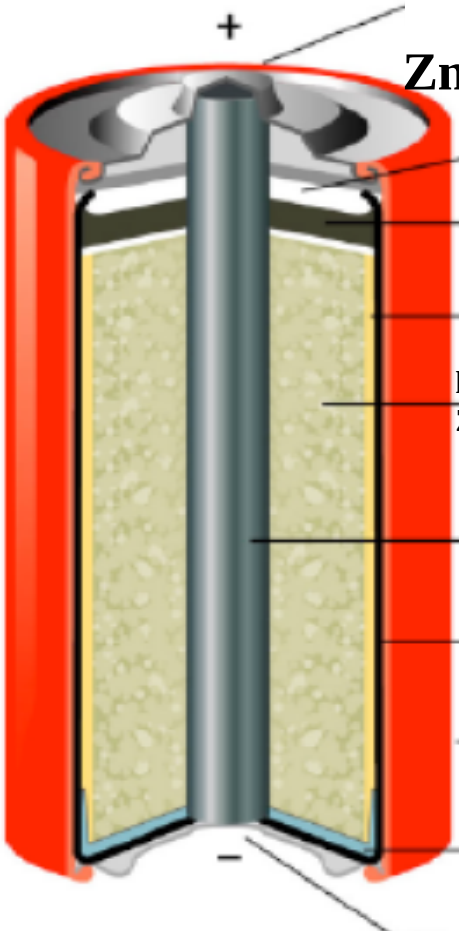


Zn – kisla primarna baterija

Leclanche tip baterije

$E_o \sim 1.5V$

$E_{real} \sim 1.0V$



ANODA

$Zn(s) \rightarrow Zn^{2+} + 2e^-$

plinska kletka

bitumen

separator

katodni kompozit (MnO_2, $ZnCl_2$, NH_4Cl, in ogljik)

grafitna palica

cikova pločevina

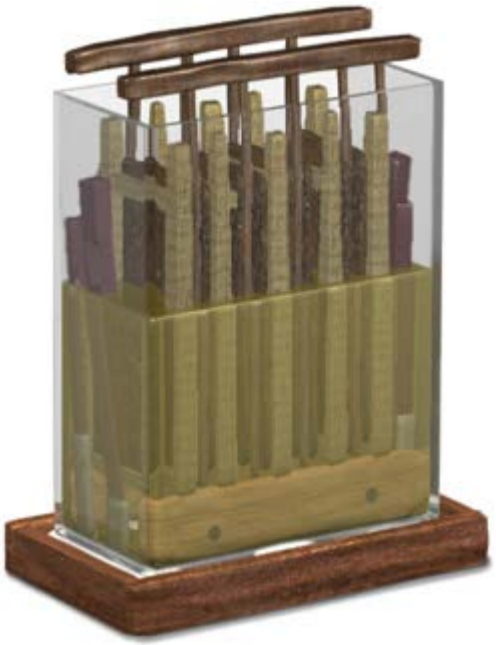
ohišje

izolator

KATODA

$NH_4^+ + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l) + 2\,NH_3(aq)$

Gaston Planté (1859) – Pb akumulator

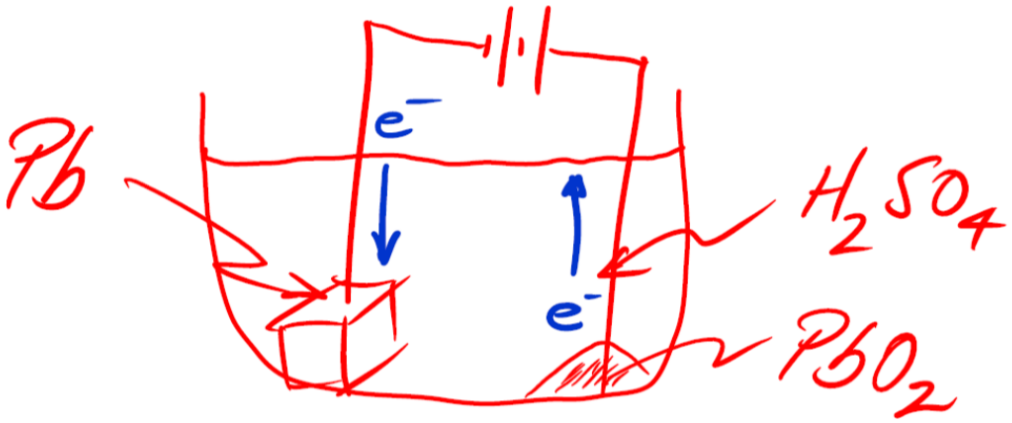


Svinčev akumulator - polnjenje

$$PbSO_4 + 2\,e^- \rightleftharpoons Pb + SO_4^{2-}{}_{(aq)}$$

$$2\,H_2O + PbSO_4 \rightleftharpoons$$

$$PbO_2 + 4\,H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\,e^-$$



$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$ $\quad E_o = -0.3588\,V$

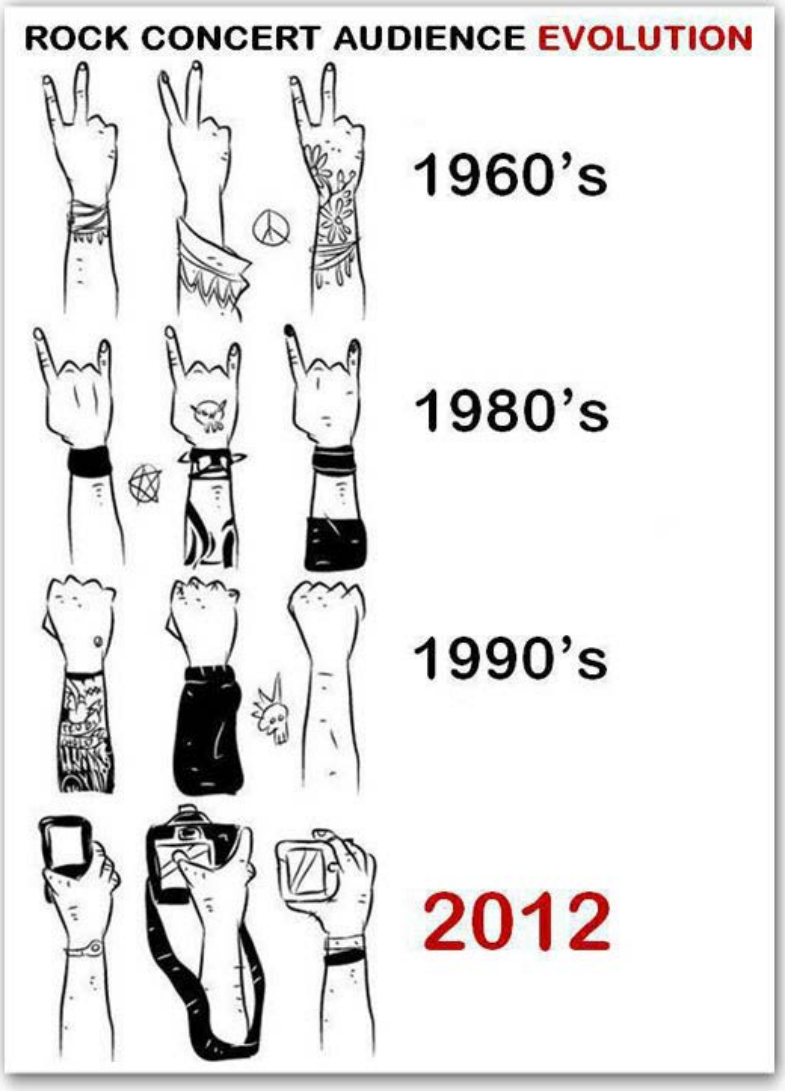
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$ $\quad E_o = +1.460$

25 let Li ionskega akumulatorja

http://www.sonyenergy-devices.co.jp/en/keyword/

„ In 1991 Sony was the first in the world to commercialize a lithium-ion rechargeable battery, forever changing the history of mobile devices.„

Spremembe v navadah in načinu življenja



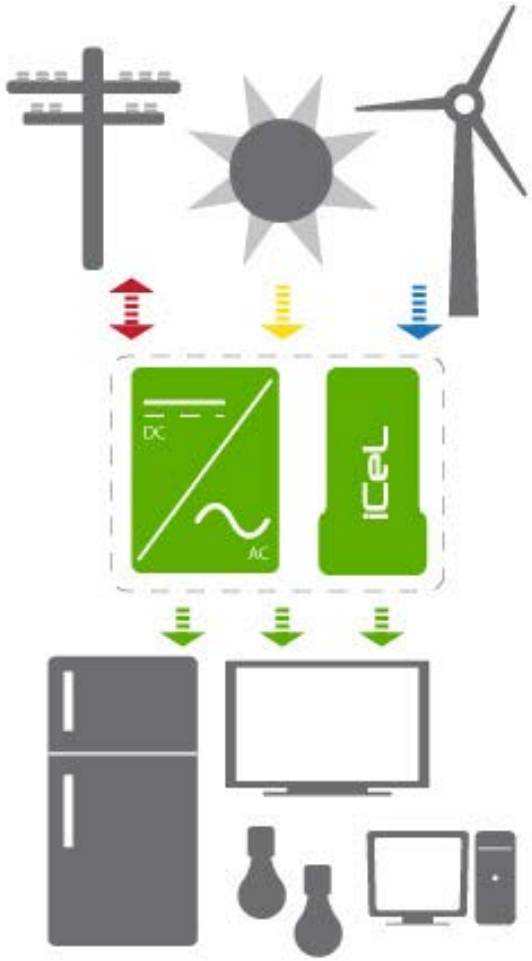
http://www.funelf.net/rock-concert-evolution/

http://www.dezeen.com/2008/07/29/charger-frame-by-naolab/

https://blog.mysms.com/wp-content/uploads/2012/05/mysms_blog_mobile_phones_now_and_then.jpg

Zakaj potrebujemo boljše akumulatorje

E = f (prostor, čas, vremenske razmere, ...)



http://wisepoweruseexpo.blogspot.com/2010/08/free-analysis-of-energy-storage-system.html

Potreba po superbateriji

http://www.engineering.com/ElectronicsDesign/ElectronicsDesignArticles/ArticleID/11811/ARPA-E-and-the-Quest-for-the-Holy-Grail-of-Batteries.aspx

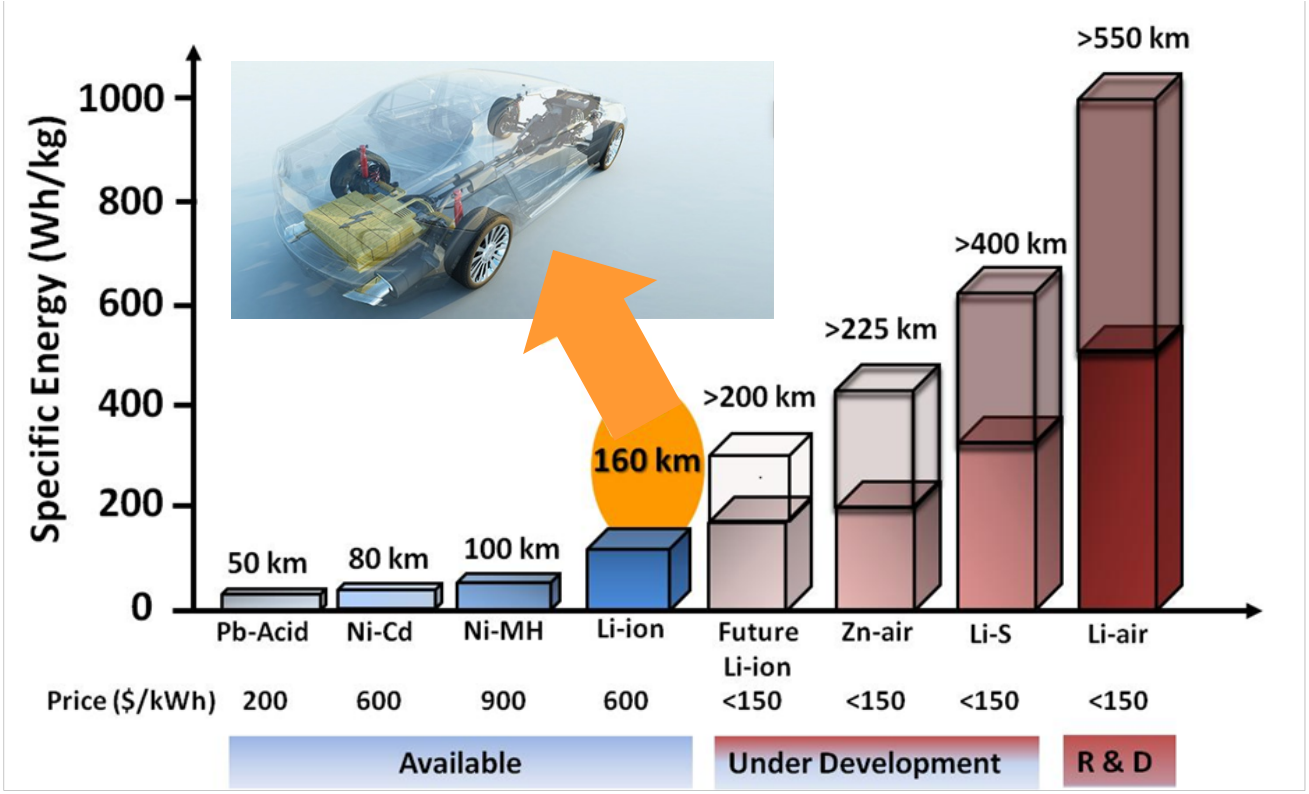
Potreba po superbateriji

Električno letalo za 100 potnikov in doseg 3000 km potrebuje baterijo z eenrgijo 1000 Wh/kg

4 krat več kot je imamo danes na voljo

Akumulatorske tehnologije

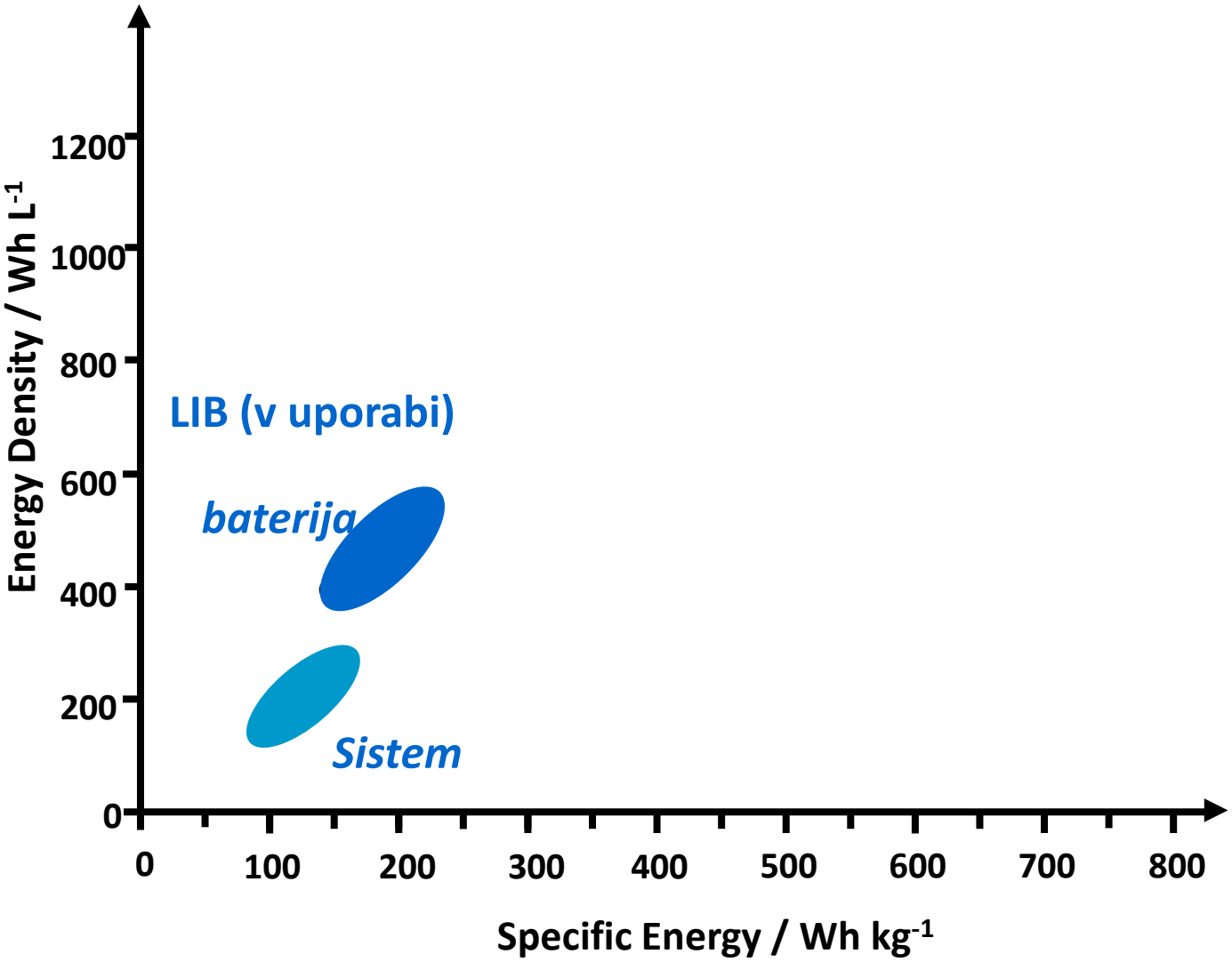
Potreba po ekonomsko in okoljsko vzdržnih baterijskih sistemih z višjo energijsko gostoto



Li–O_2 and Li–S batteries with high energy storage

Peter G. Bruce, Stefan A. Freunberger, Laurence J. Hardwick & Jean-Marie Tarascon, Nature Materials, 11 (2012) 19-29

Energijska gostota (LIB)



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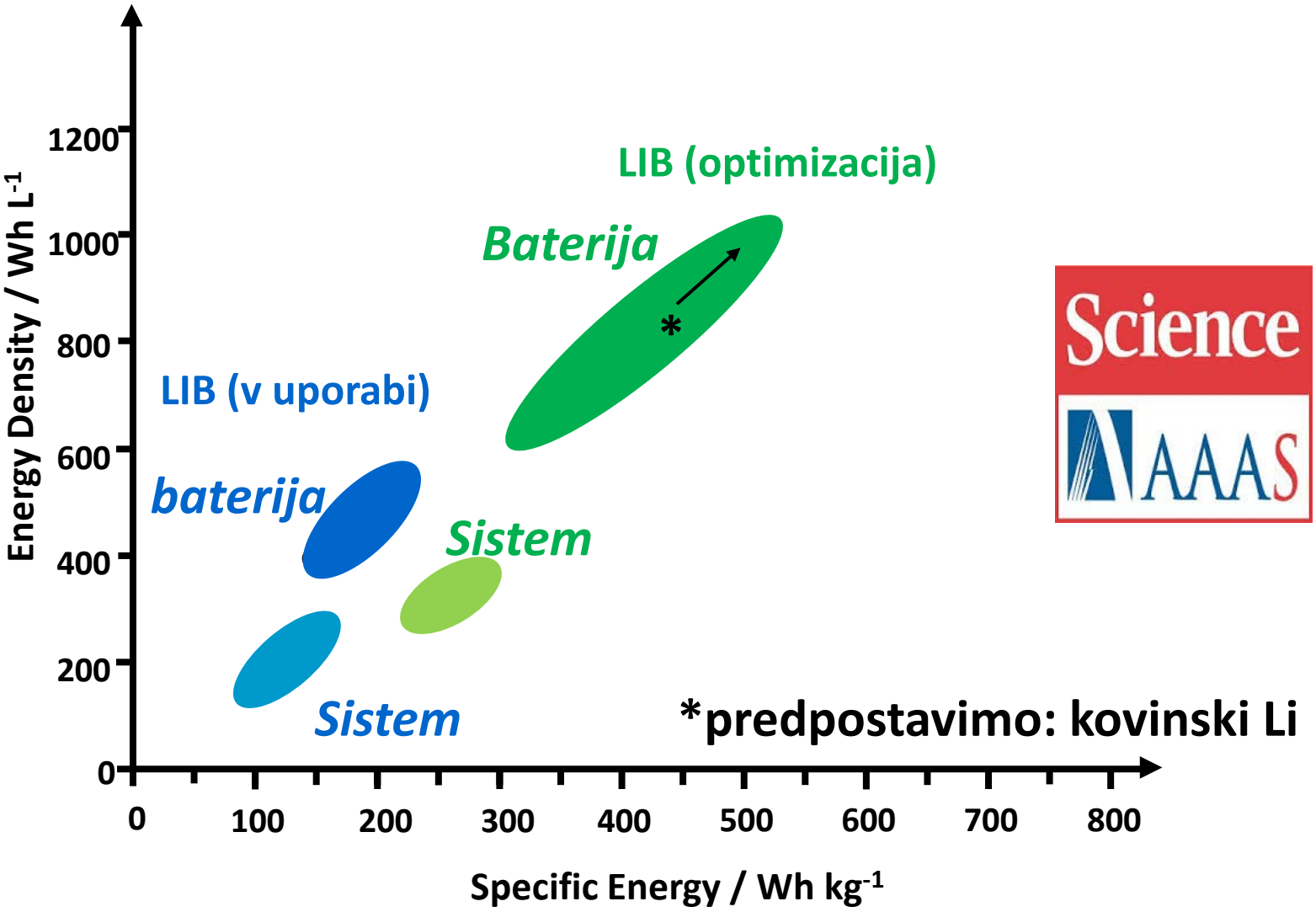


Science

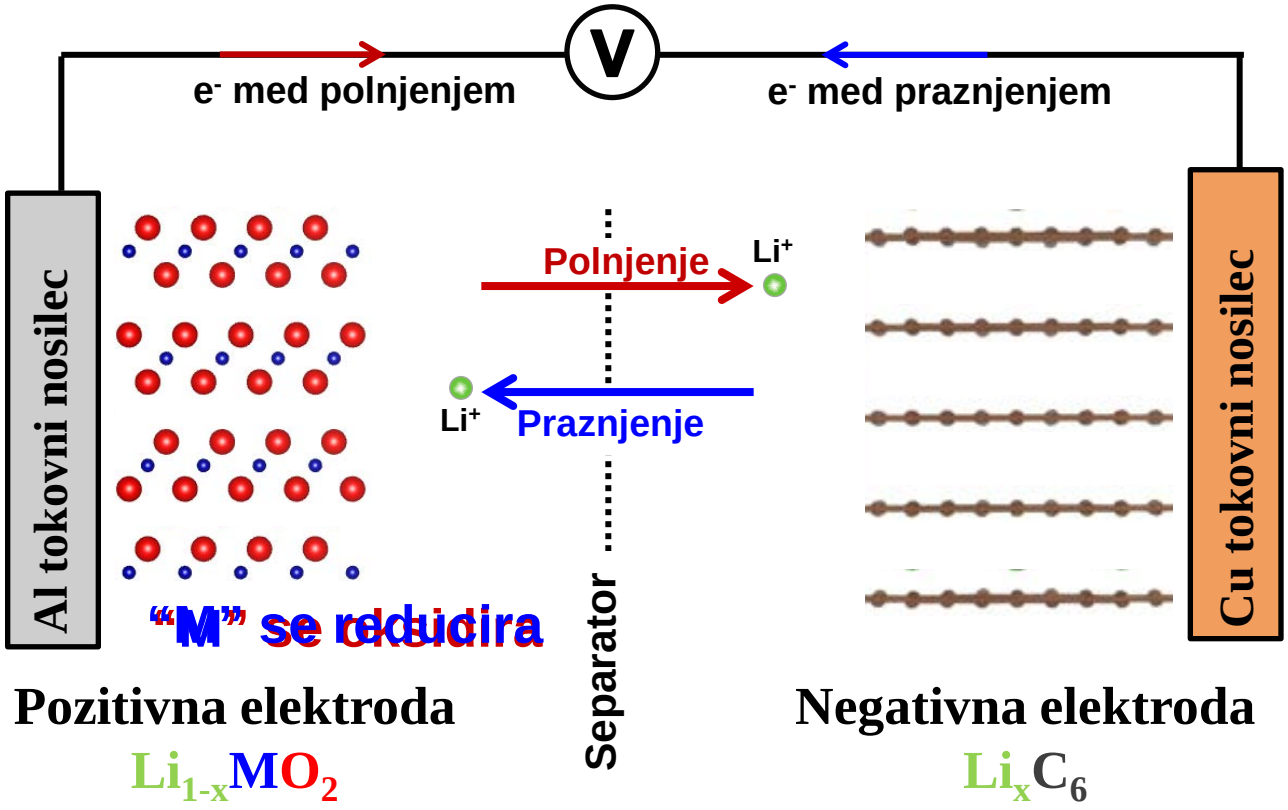
AAAS

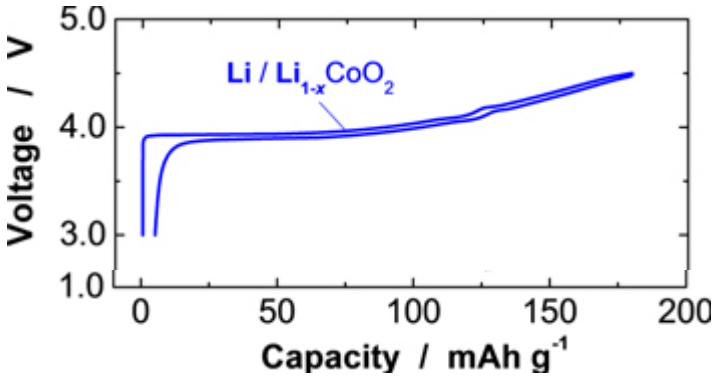
Komercialni Li-ionski akumulatorji

Energija je produkt napetosti in kapacitete

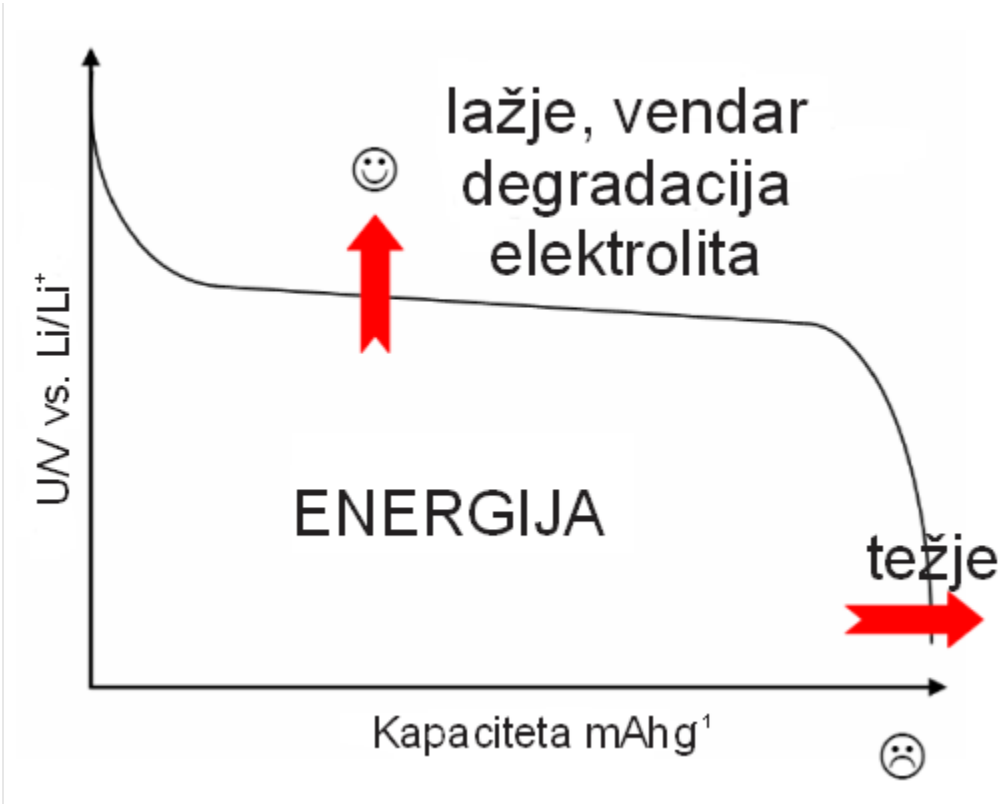
Pozitivna elektroda: približno 150 mAh/g pri 3.9 V

Negativna elektroda: 300 mAh/g za grafit





Kako povečamo energijsko gostoto



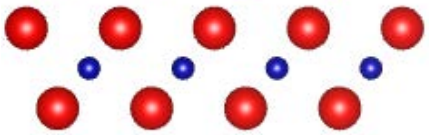
- Uporaba kovinskega litija kot anode
- 5V sistemi
- Katode z visoko kapaciteto (izkoriščanje > 1 elektron, kisik)

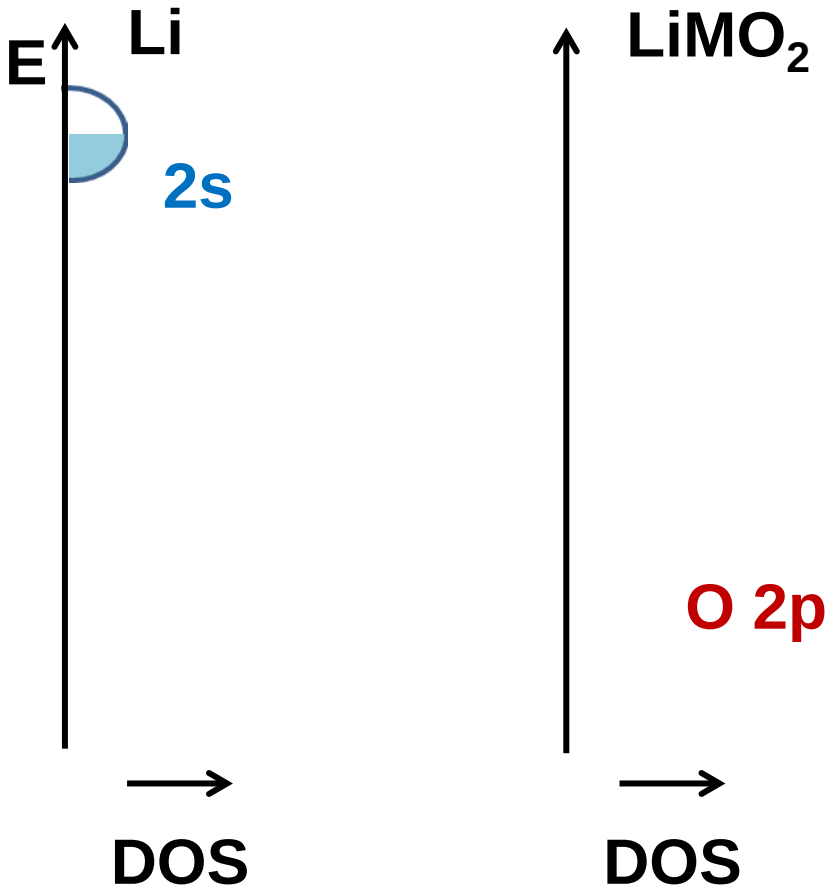
Kako povečamo energijsko gostoto

Povečanje kapacitete => več litija in multi elektron sistem

Višja napetost => odvisna od koordinacije, moči vezi in prehodne kovine

Prehodne kovine so oktaedrično koordinirane z O^{2-}





Kim and Goodenough, Chem. Mater 2010

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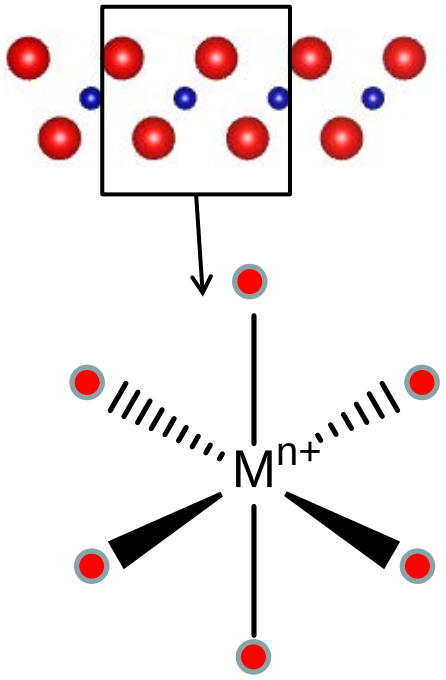

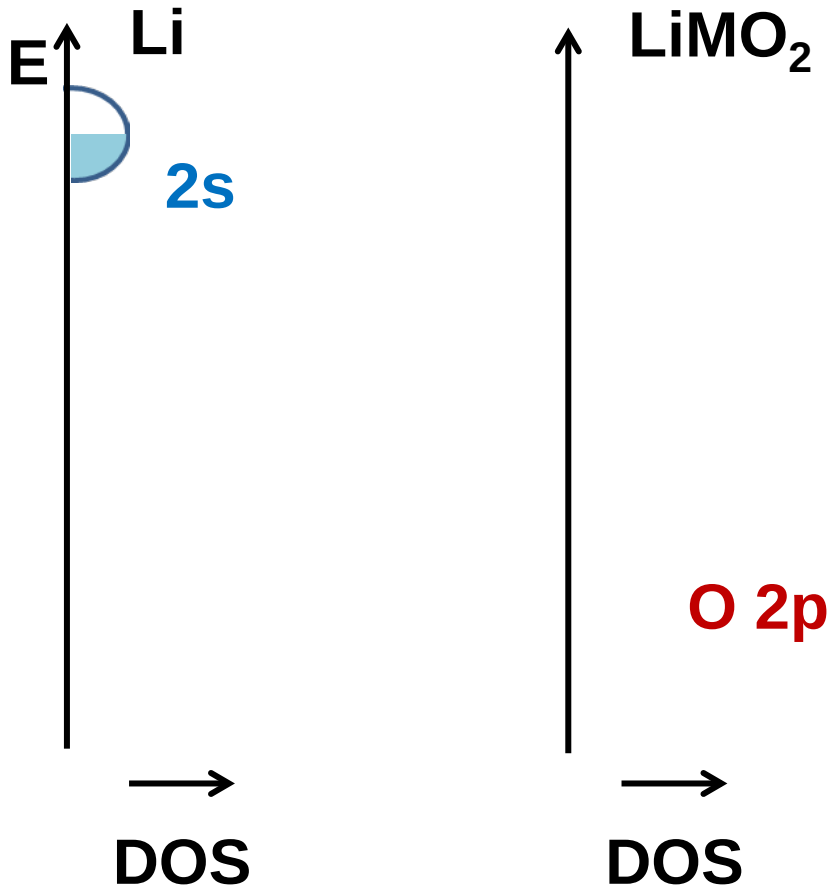

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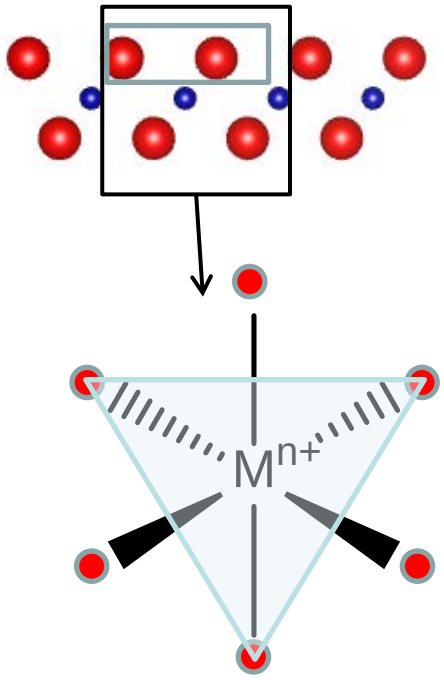

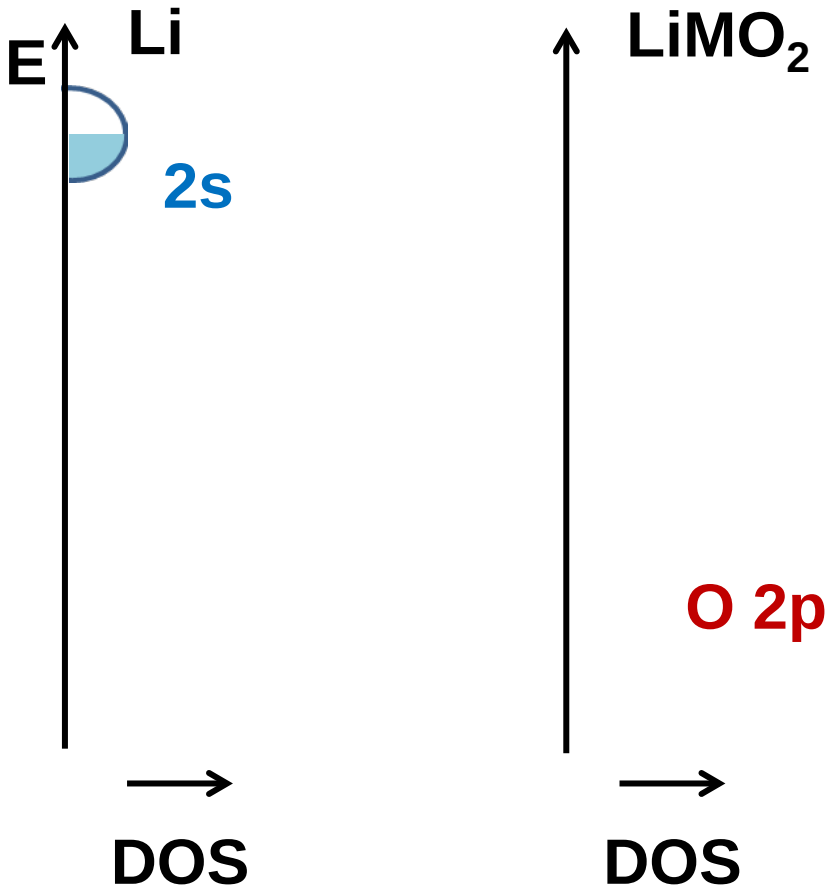

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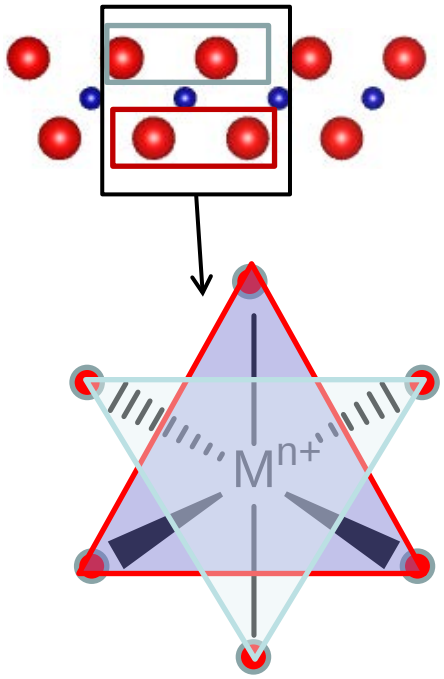

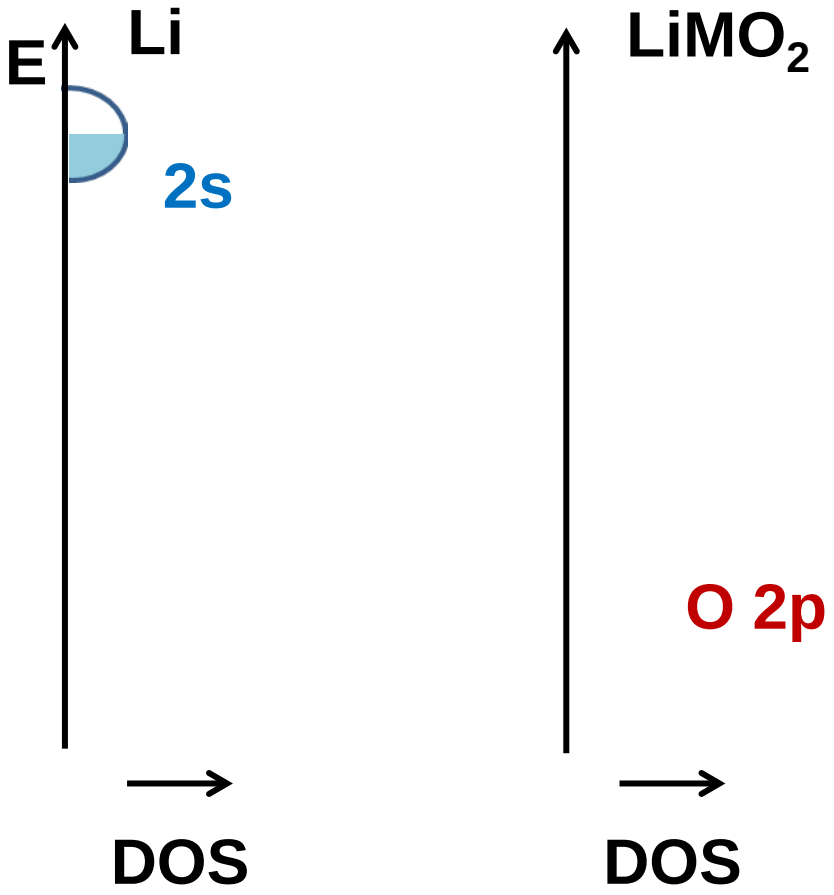

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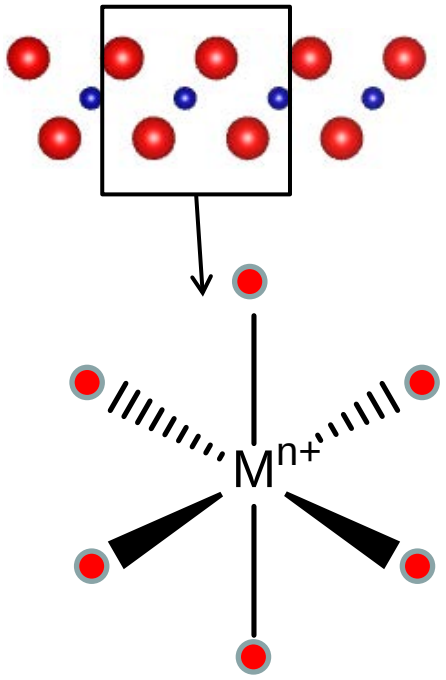

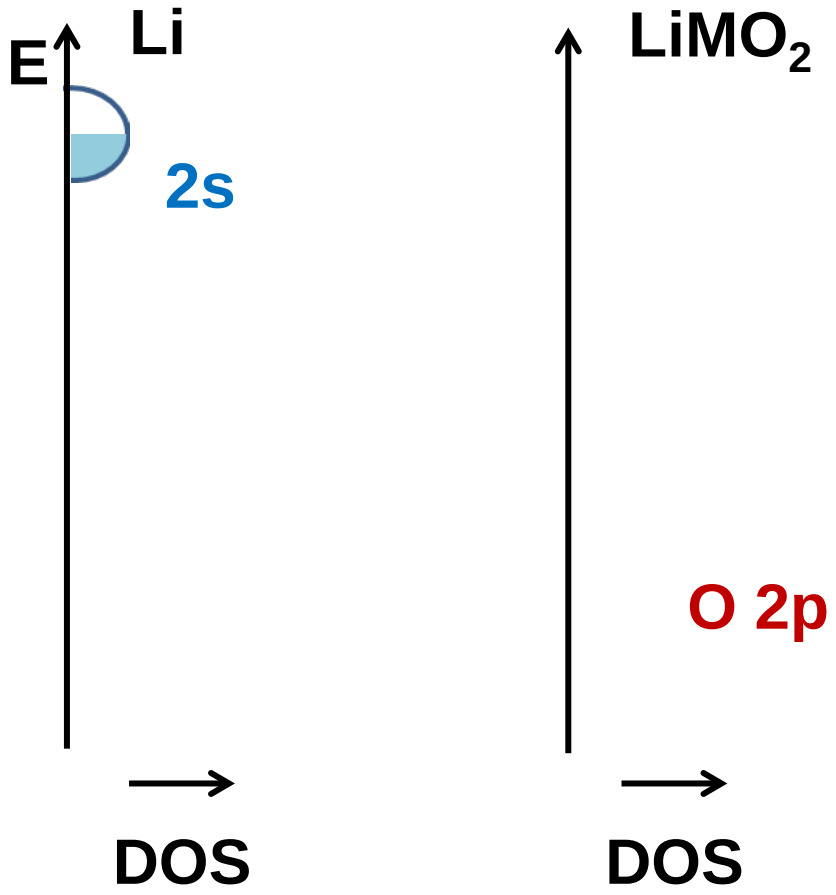

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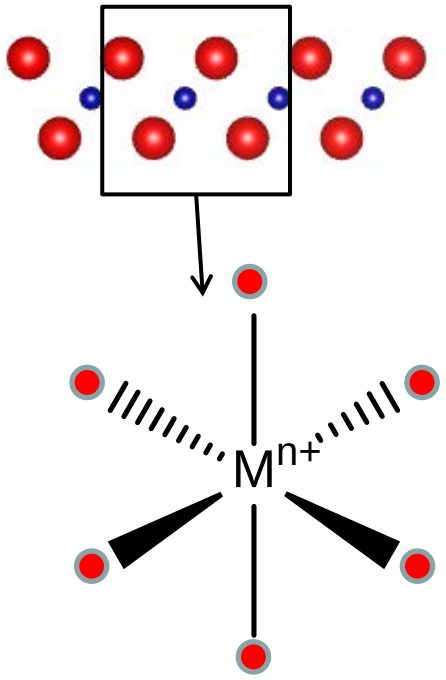

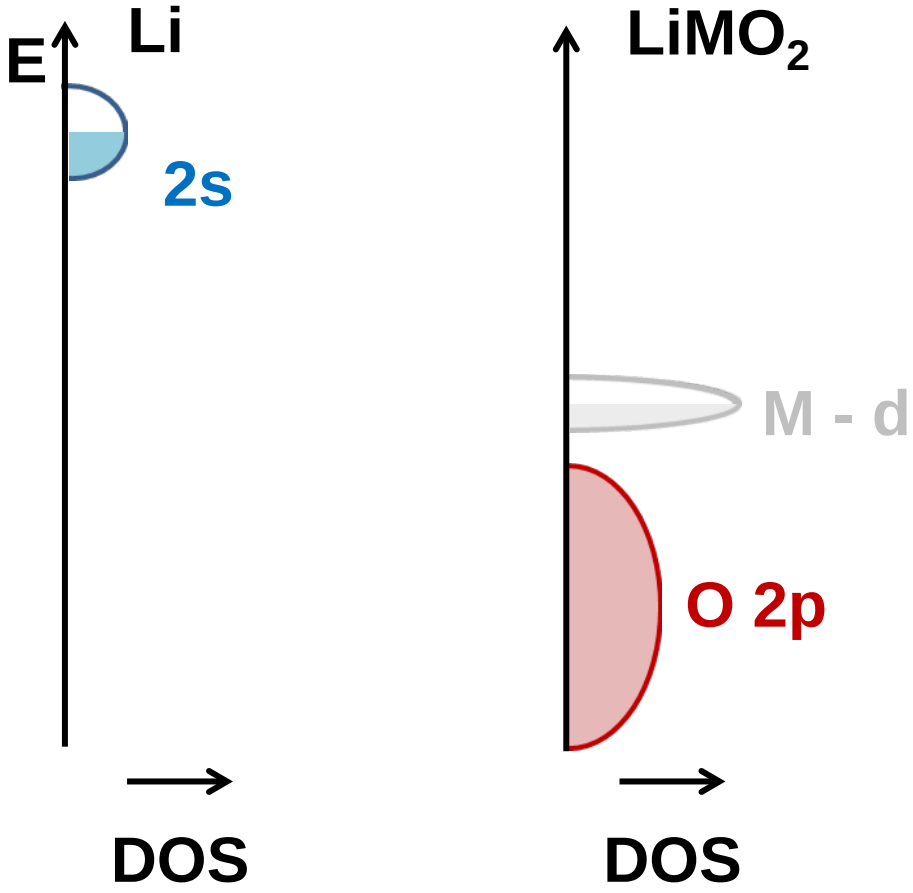

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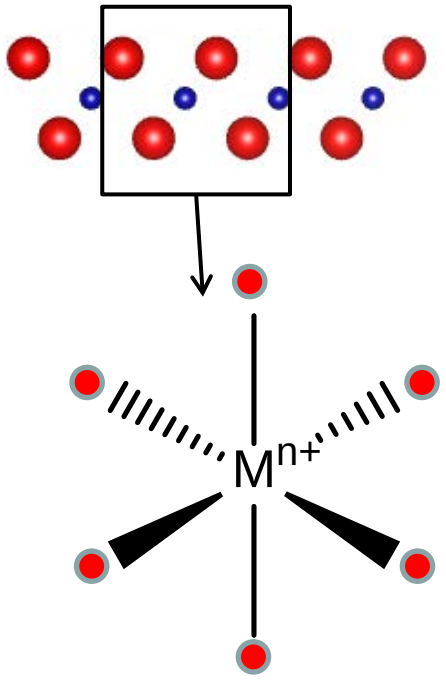

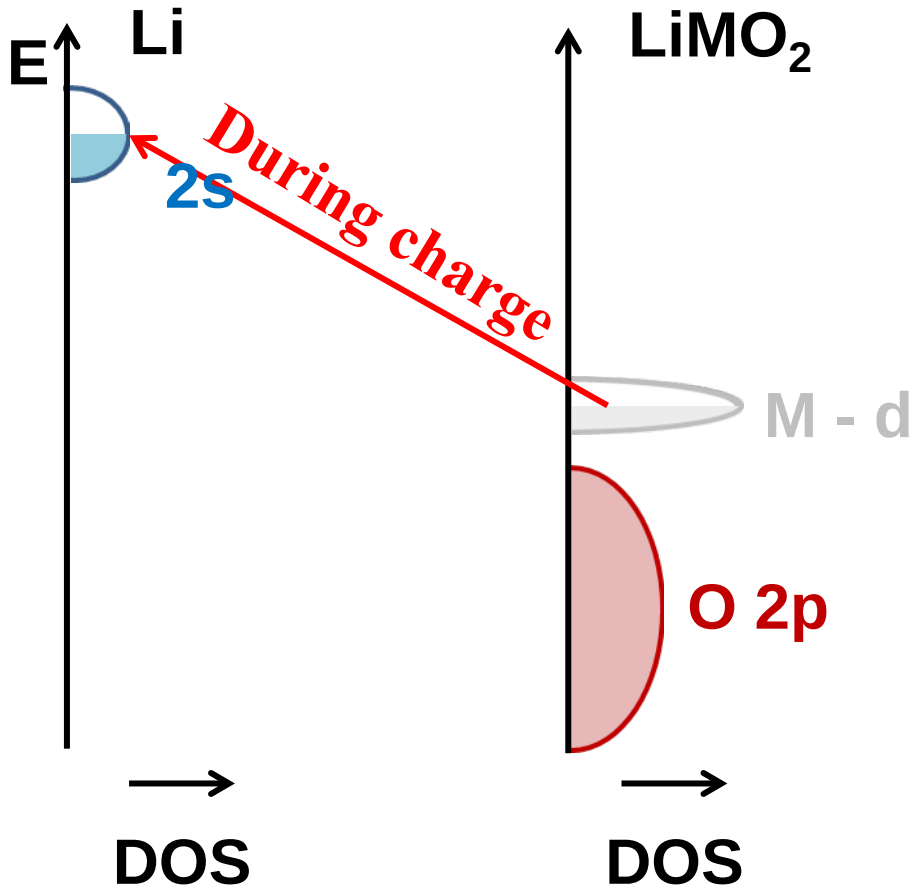

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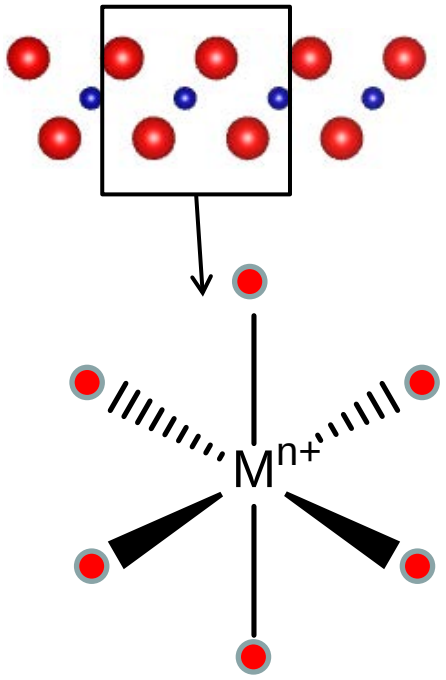

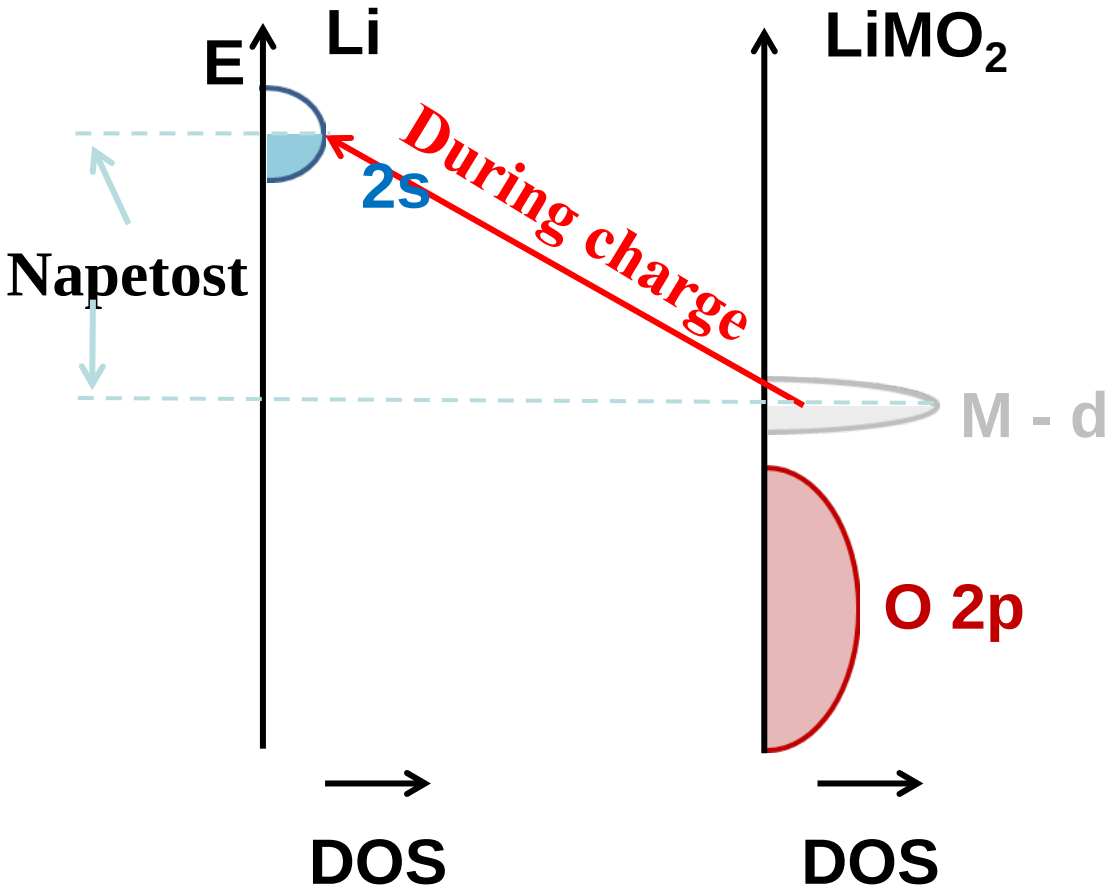

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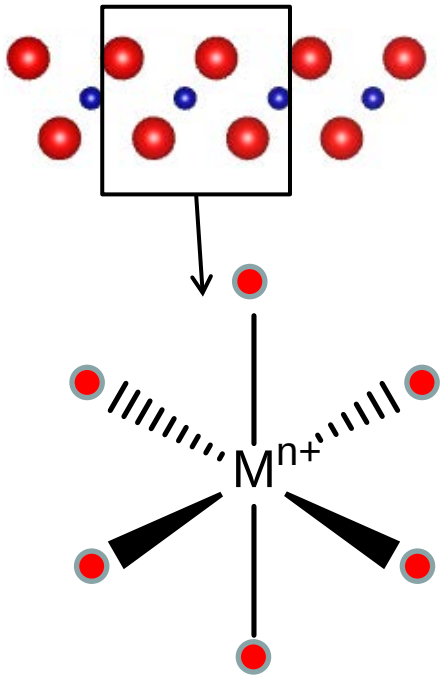

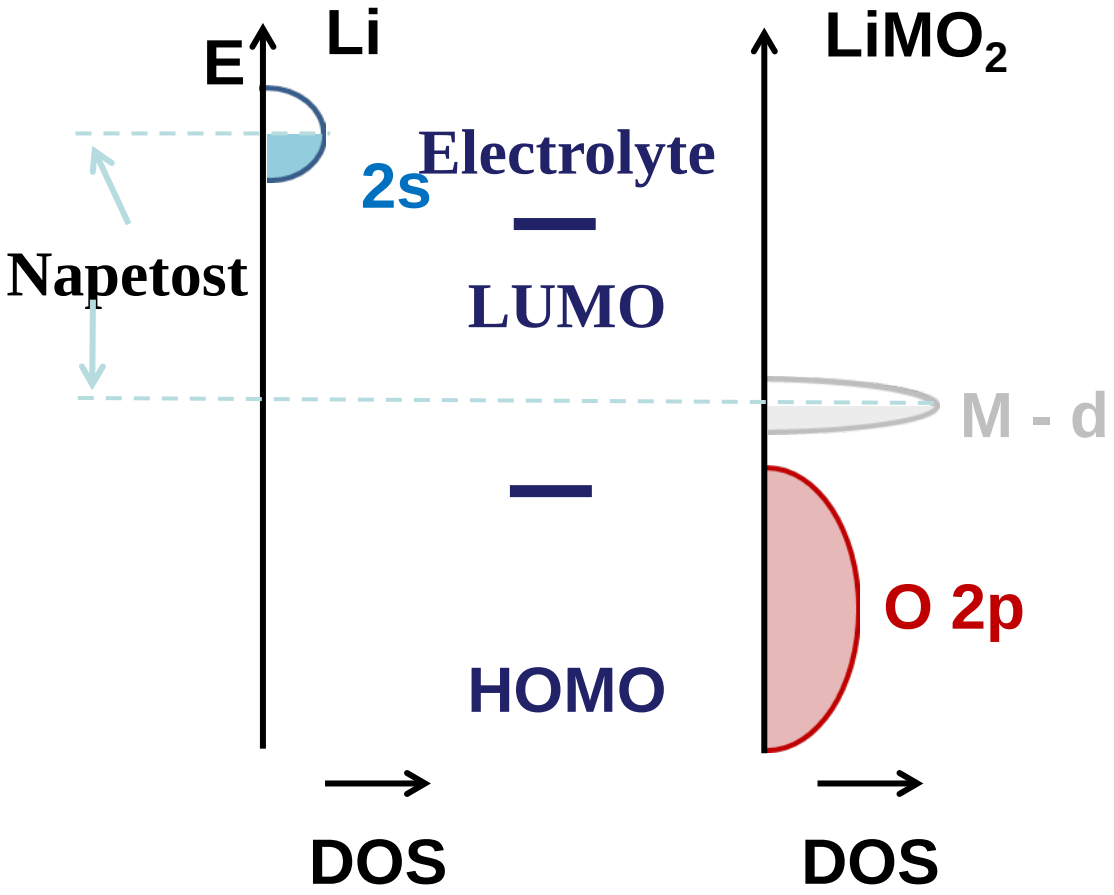

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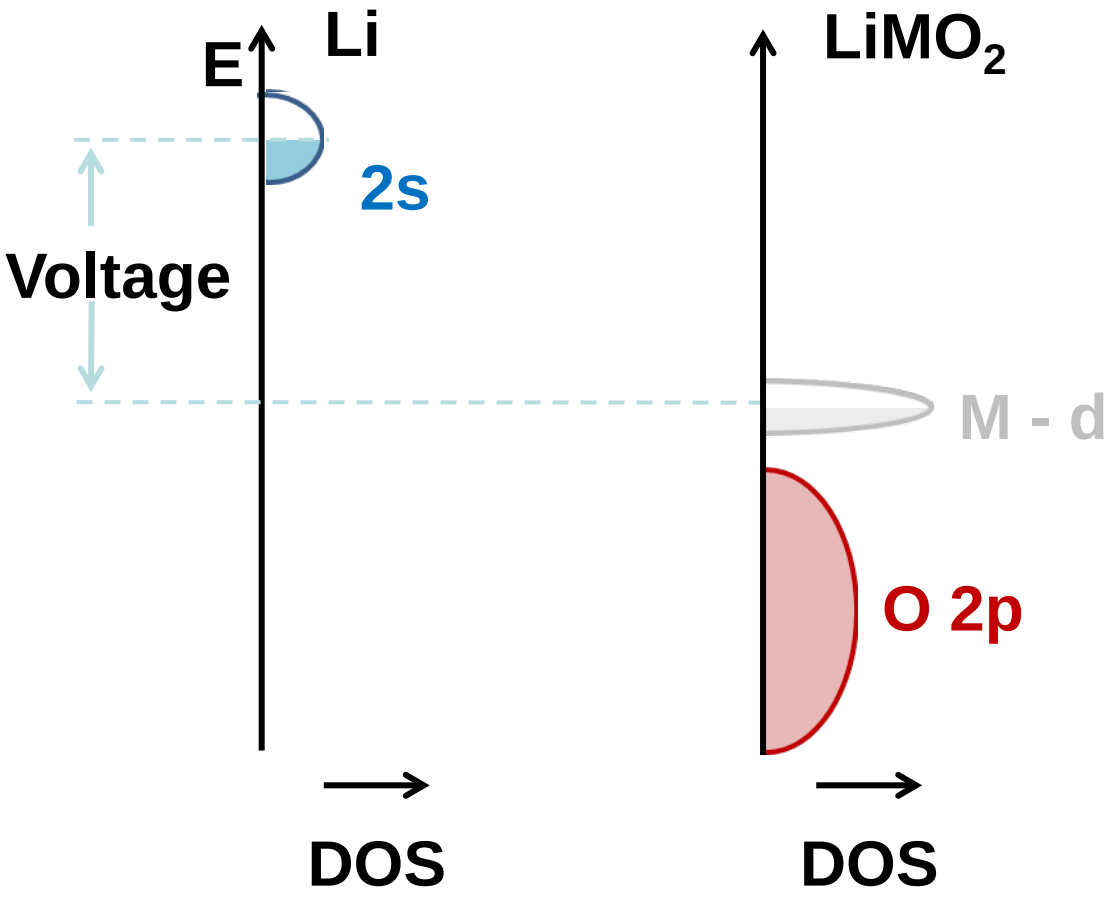
Kaj se dogaja med polnjenjem?

Ko elektronegativnost prehodne kovine narašča => Kisik se vključi v redoks reakcijo

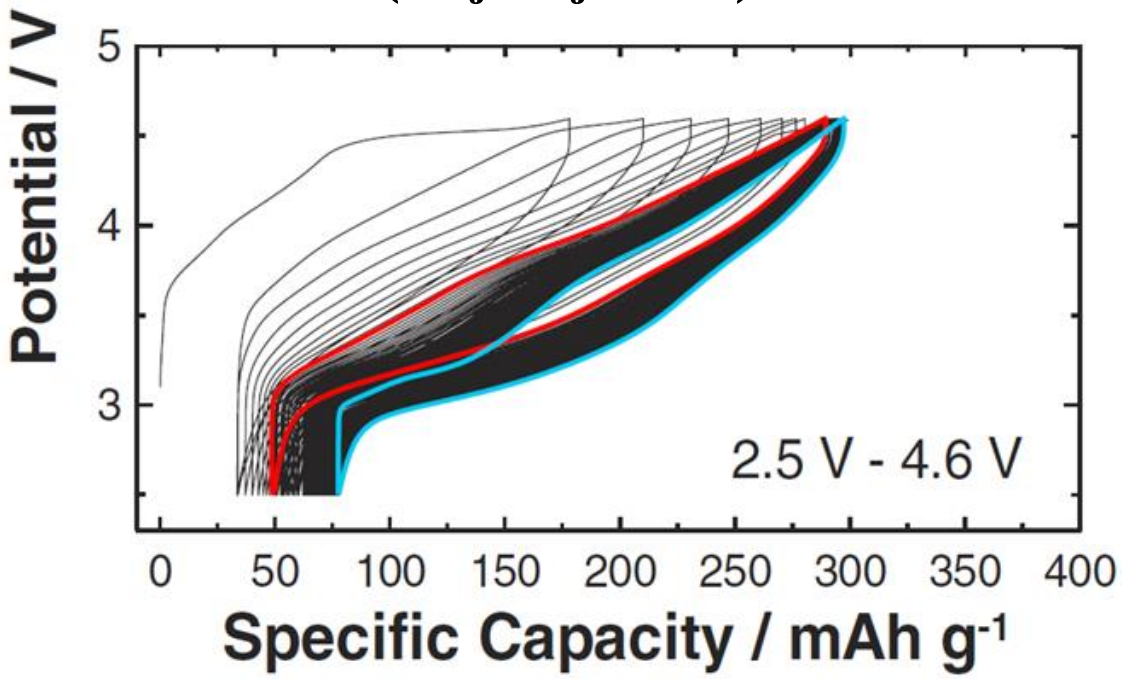


Litijirani oksidi prehodnih kovin

$Li[Li_{0.16}Ni_{0.12}Mn_{0.65}]O_2$

$Ni^{2+} \rightarrow {}^{4+}$ kapaciteta 100 mAh/g zaradi spremembe oksidacijskega stanja na niklju.

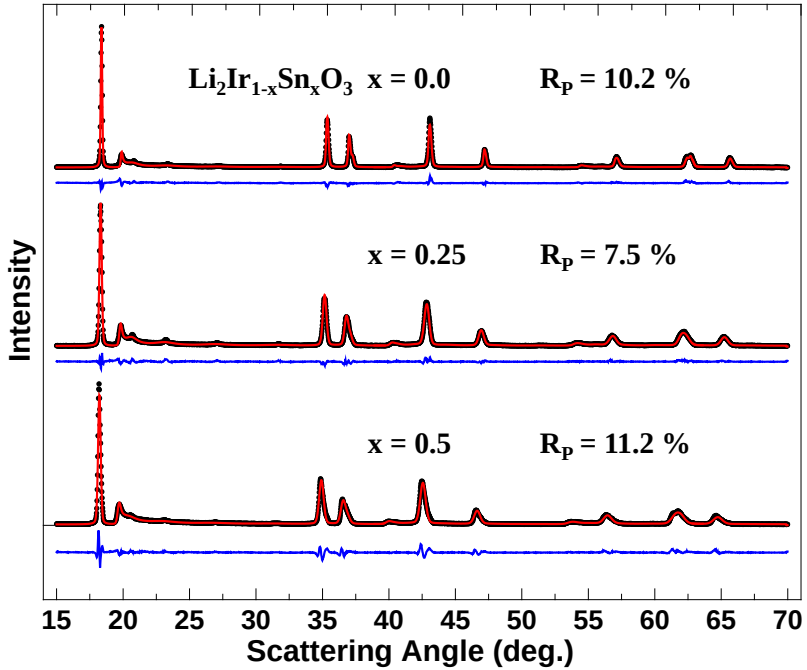
Celokupna reverezibilna kapaciteta 200 mAh/g (vključuje kisik)



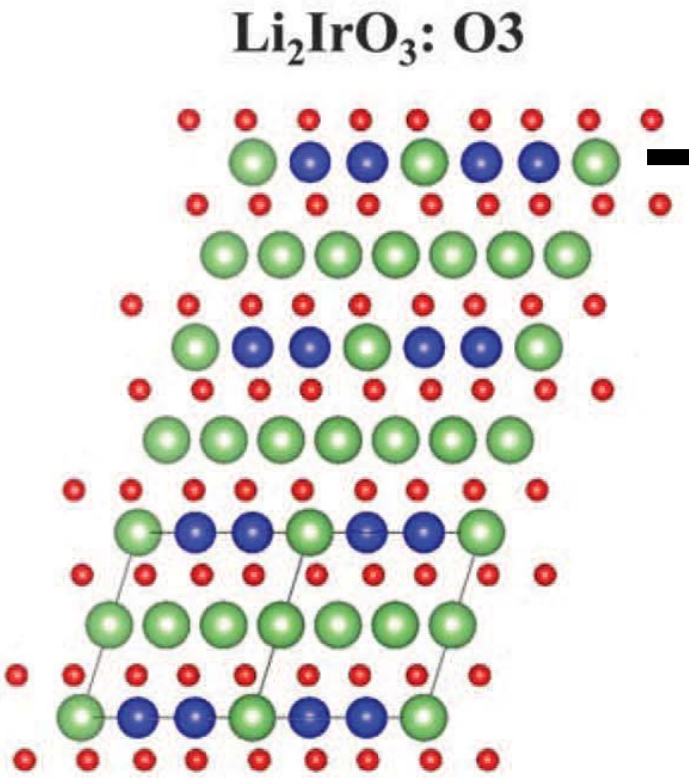
Degradacija: Padec kapacitete in sprememba napetosti.
Nastanek kisikovih radikalov, ki reagirajo z elektrolitom.

Solid state sinteza Li_2IrO_3

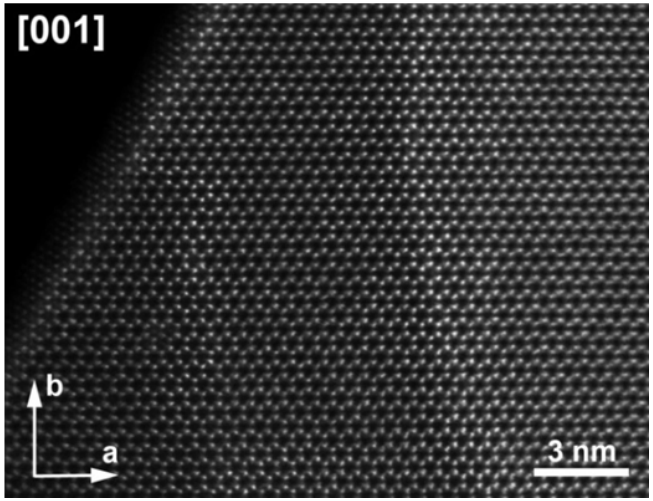
Mix IrO_2, SnO_2, in Li_2CO_3	Visoko energijsko mletje > 40 minut	Peletke	Sinteza (900°C, 15 h)



Li_2IrO_3

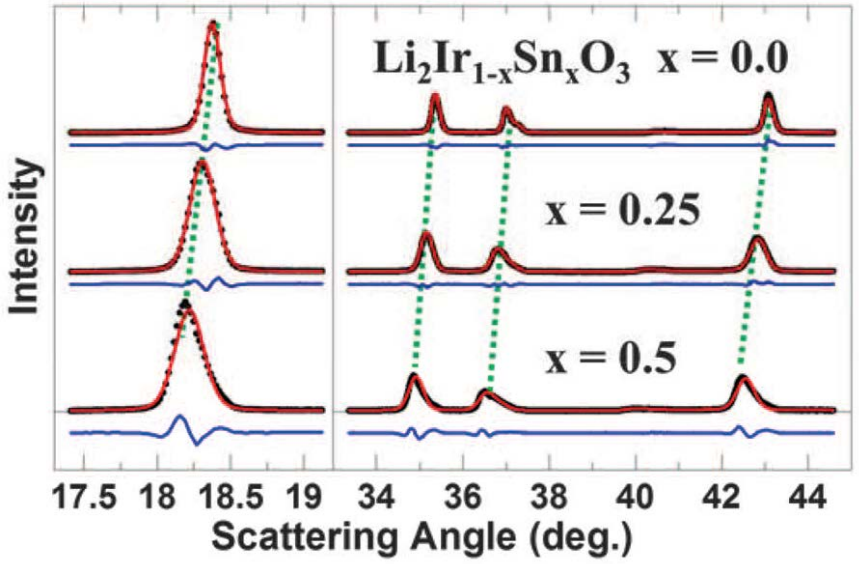


$Li_{1/3}Ir_{2/3}O_3$ hexagonalna koordinacija litija

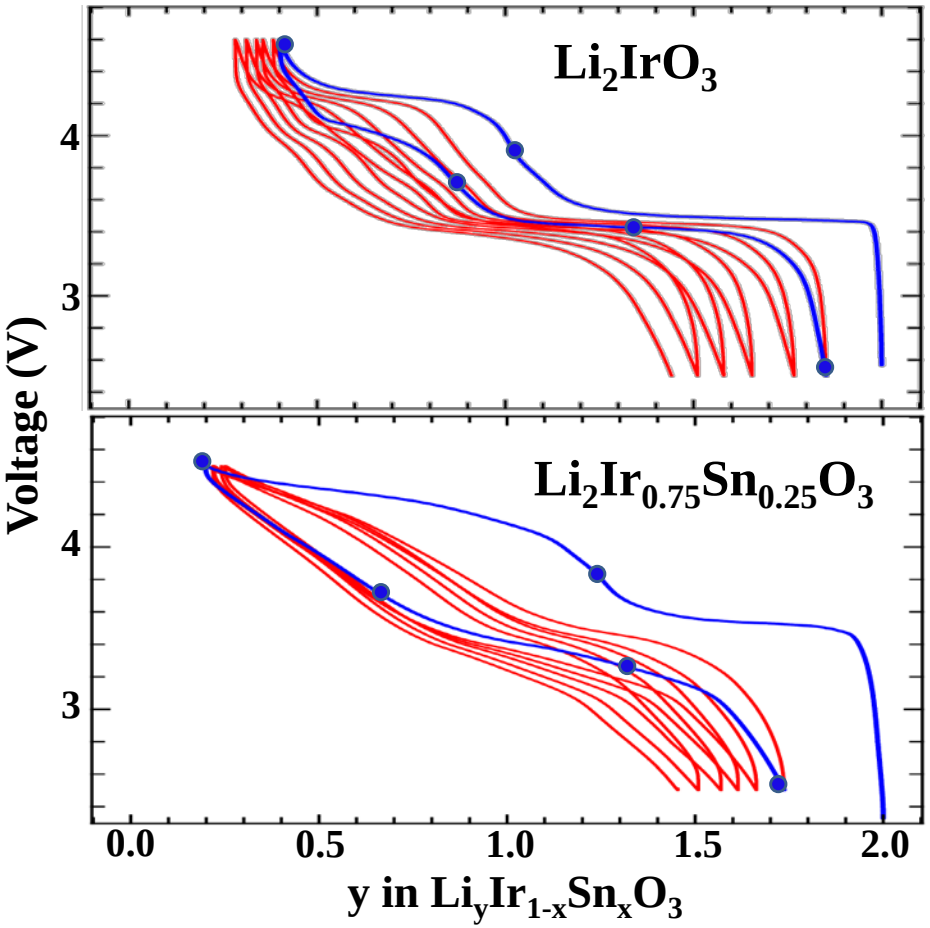


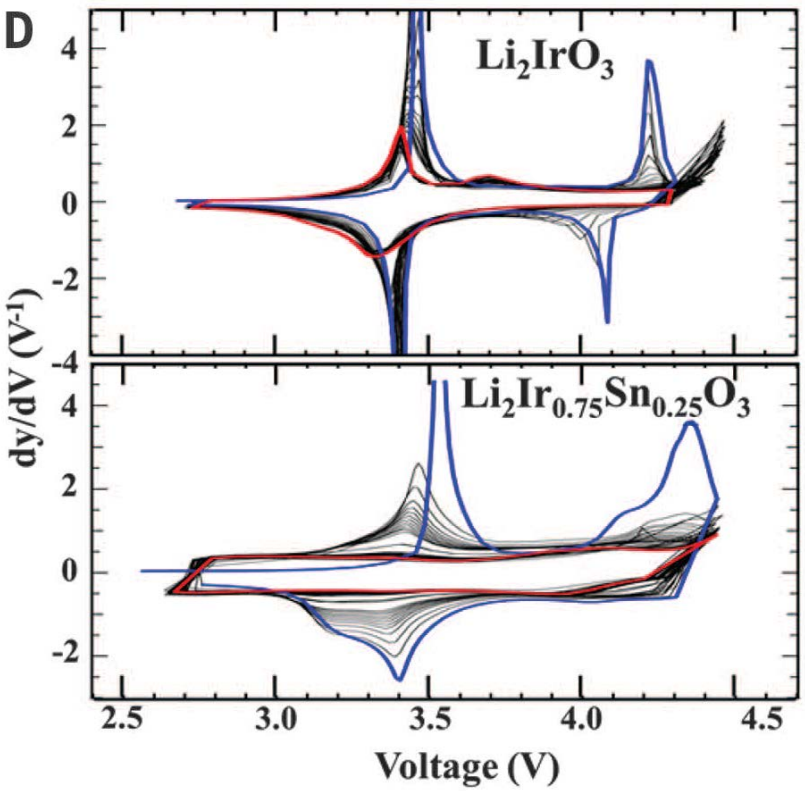
Ir – 5d orbitale

močna kovalentna vez –
minimalna kationska izmenjava



Li-Ir-Sn-O elektrokemija





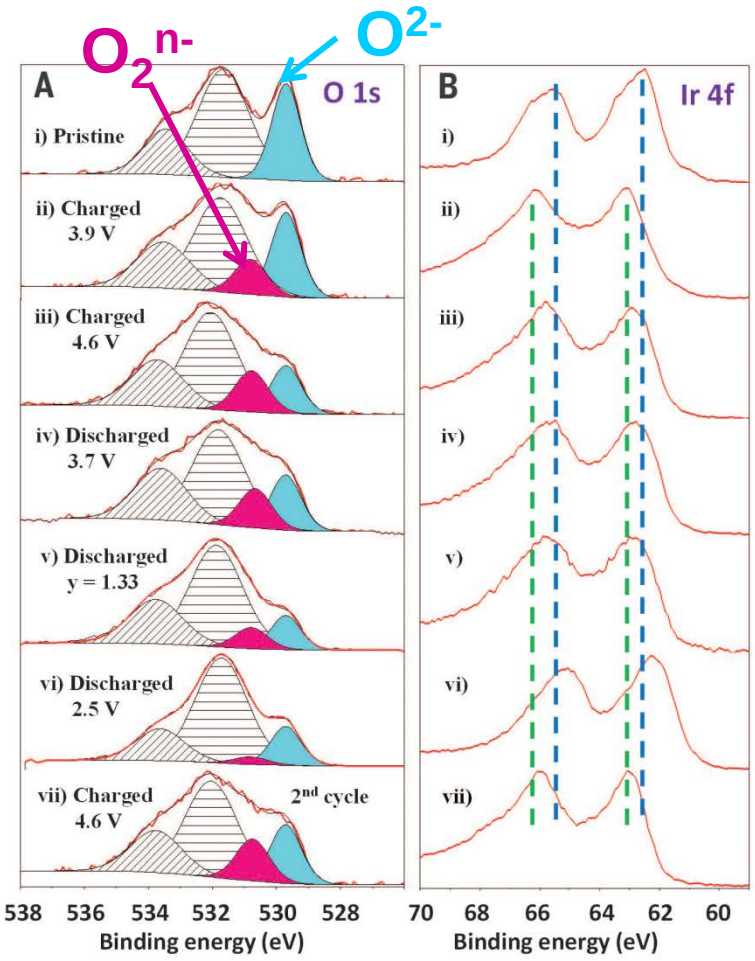
Izgradnja in vgradnja litija v Li_2IrO_3 poteka pri dveh različnih napetostih

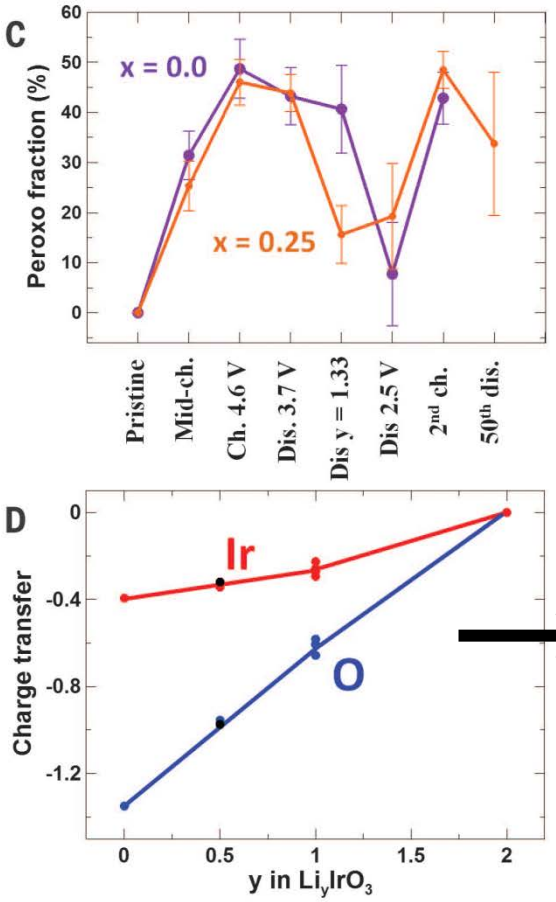
Količina naboja ustreza spremembi cca. 1.5 elektrona v molekuli

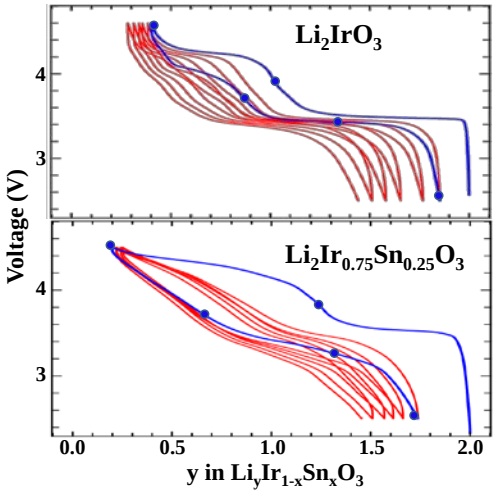
Li-Ir-Sn-O elektrokemija

Kisikova podmreža je udeležena v redoks reakciji že od začetka

V najbolj oksidiranem stanju je približno polovica kisika v O_2^{n-} stanju



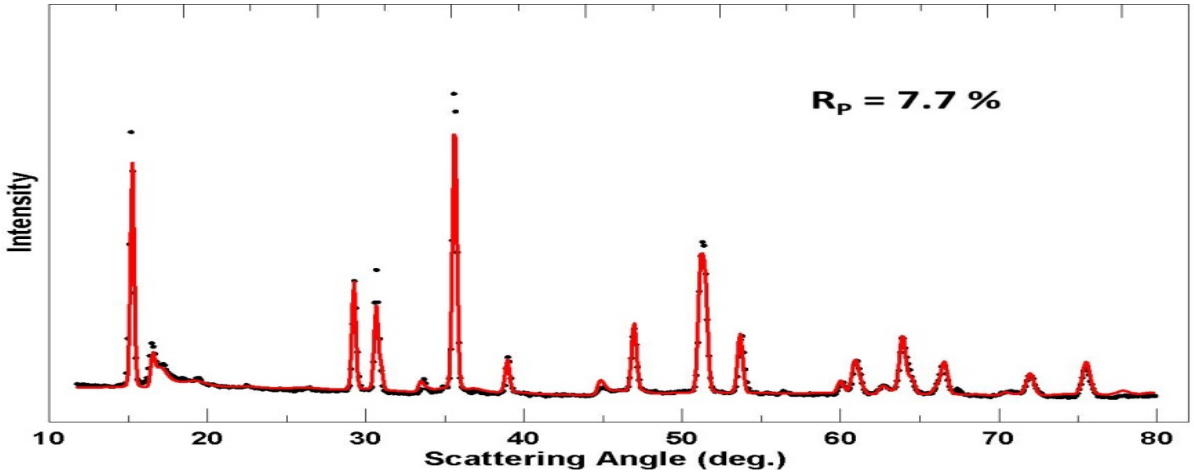


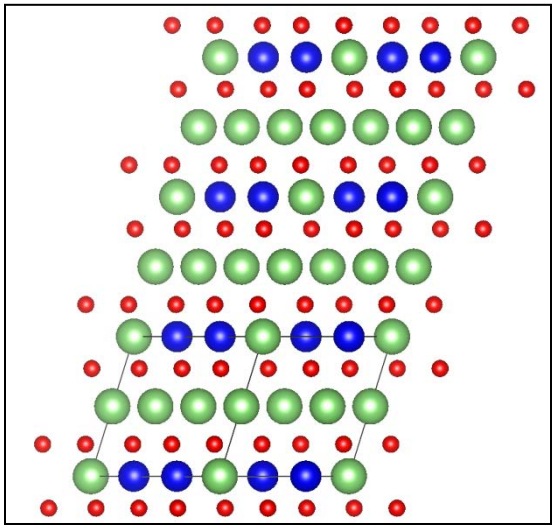


→ Bader charge DFT

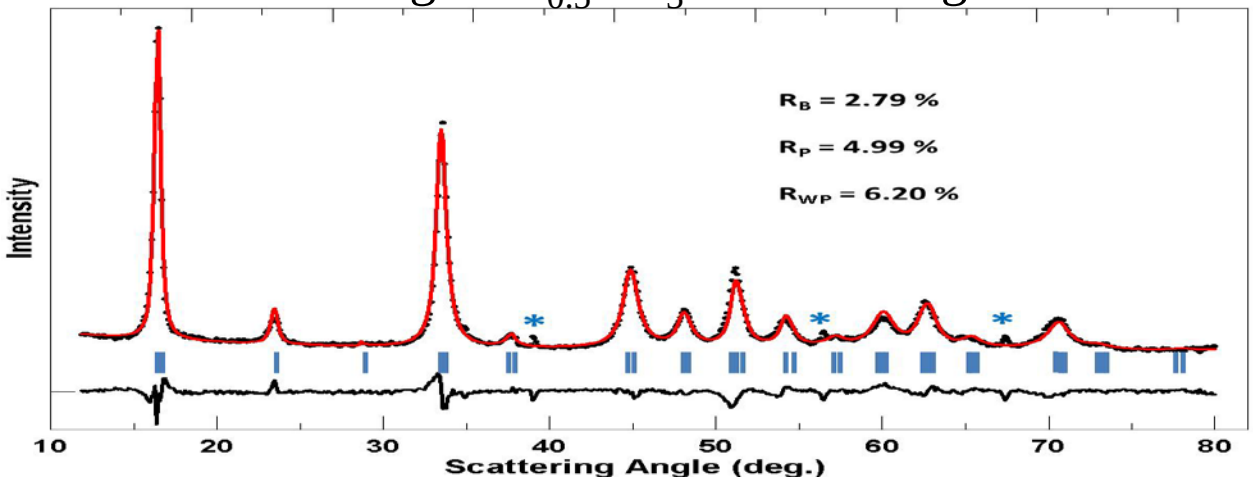
Strukturne spremembe

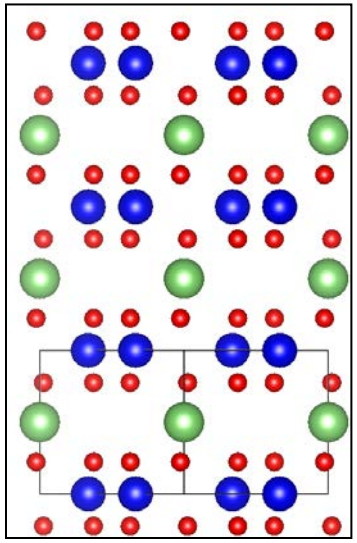
Pristine Li_2IrO_3: O3 stacking





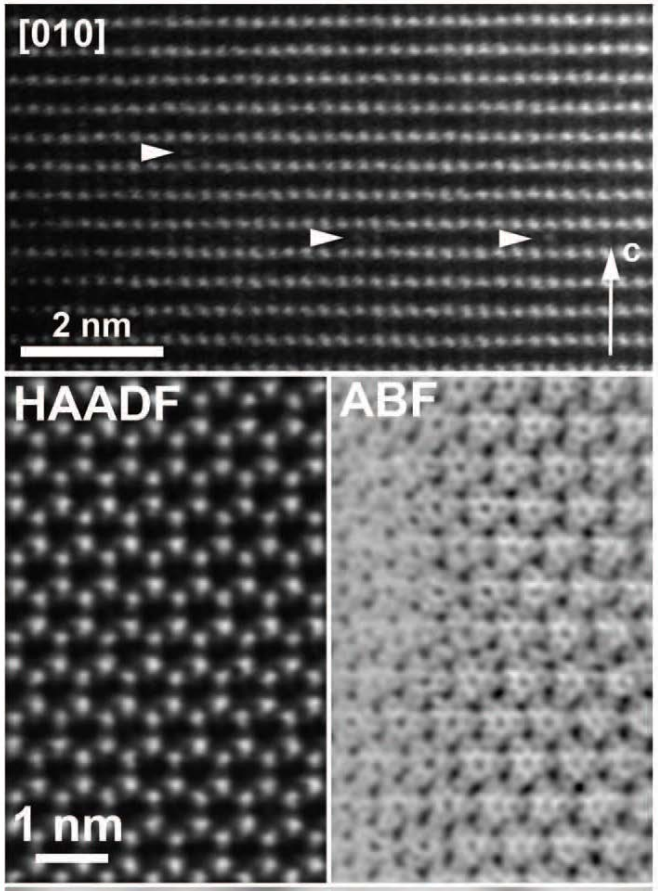
Charged $Li_{0.5}IrO_3$: O3 stacking





HR TEM mikroskopija $Li_{0.5}IrO_3$

Struktura oksidiranega vzorca vzdolž in prečno na „c“ os



Kljub izgradnji litija je iridijevi atomi ostanejo na originalnih kristalografskih mestih
HAADF pokaže nekaj intersticijskih Ir atomov

ABF-STEM Določitev pozicij lahkih elementov (Li, O)
Dve različni dolžini za vez Ir-O

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in annular bright field STEM (ABF-STEM)

Vizualizacija O-O dimerov z TEM

O-O razalje:

TEM:

1.56 Å in 1.83 Å

Neutron:

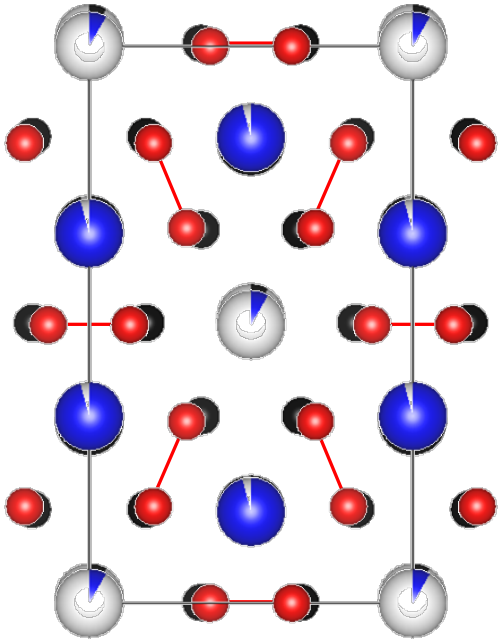
1.42 Å in 1.86 Å

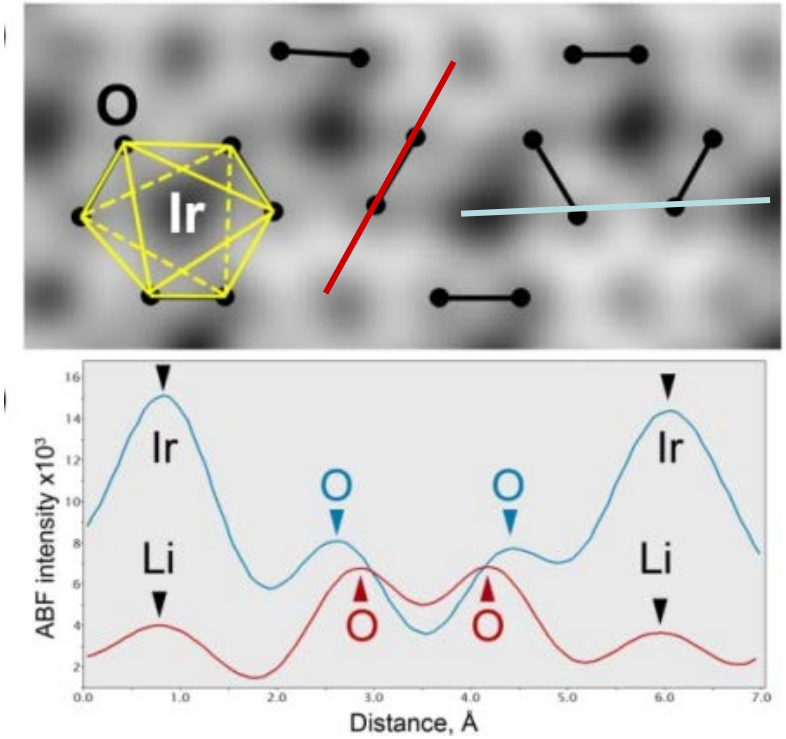
DFT:

1.51 Å in 1.88 Å

stanju

Modro: iridium



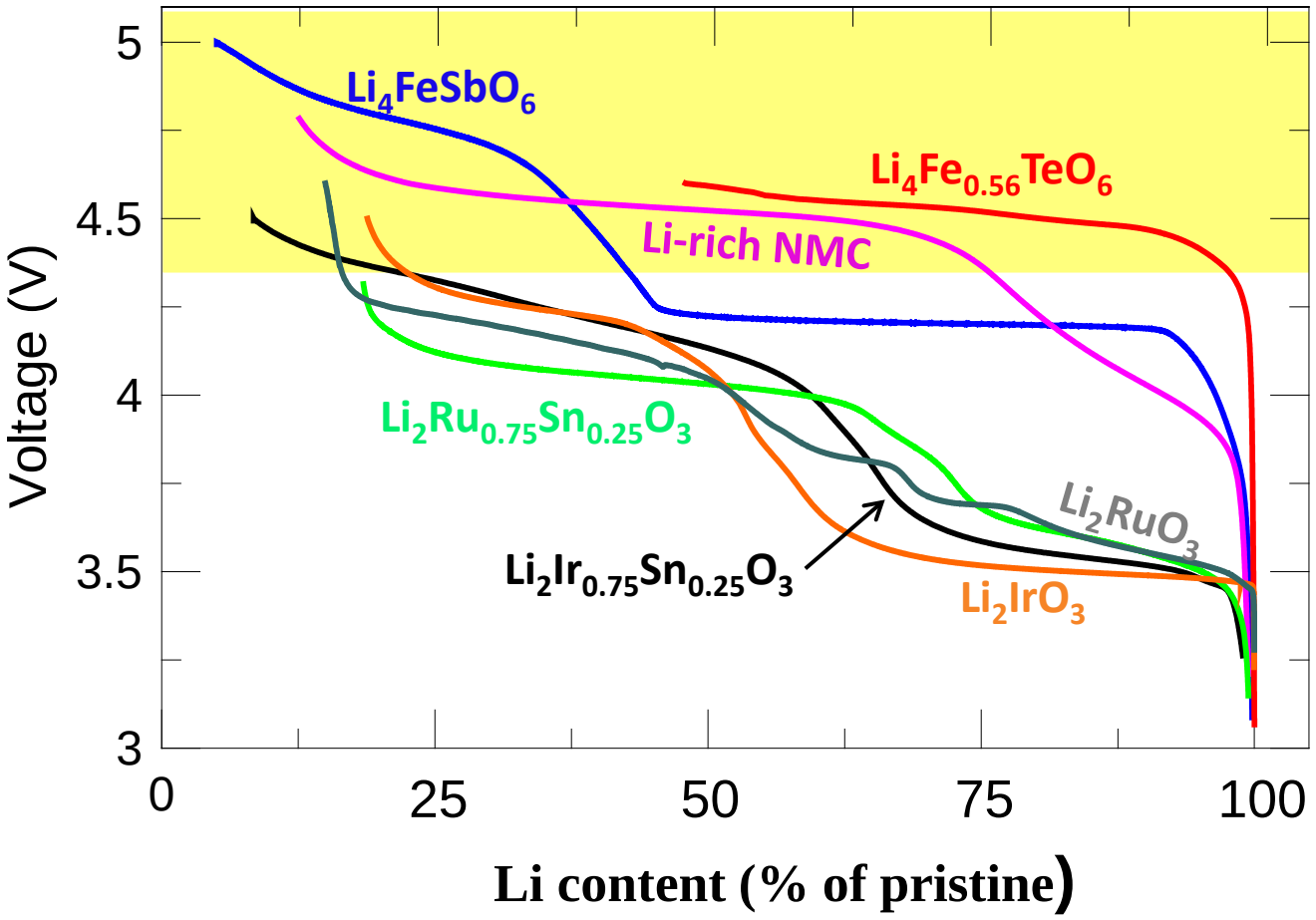


Li_2IrO_3: stabilna struktura in koordinacija Ir atomov onemogoča nastanek kationskega nereda – elektrokemijska krivulja ne spremeni oblike

$Li_2Sn_xIr_{1-x}O_3$: Sn v strukturi omogoča lokalen nered in s tem spremembo oblike elektrokemijske krivulje

Povzetek

Nastanek kisikovih dimerov je potreben pri napetostih pod 4.3V vs. Li



M - kovina:

- ⇒ **Ru**
- ⇒ **Ru, Sn**
- ⇒ **Ru, Mn**
- ⇒ **Ir**
- ⇒ **Ir,Sn**
- ⇒ **Ni,Mn,Co**
- ⇒ **Fe, Sb**
- ⇒ **Ni, Te**
- ⇒ **Ni, Sb**
- ⇒ **Mn**
- ⇒ **Fe, Te**

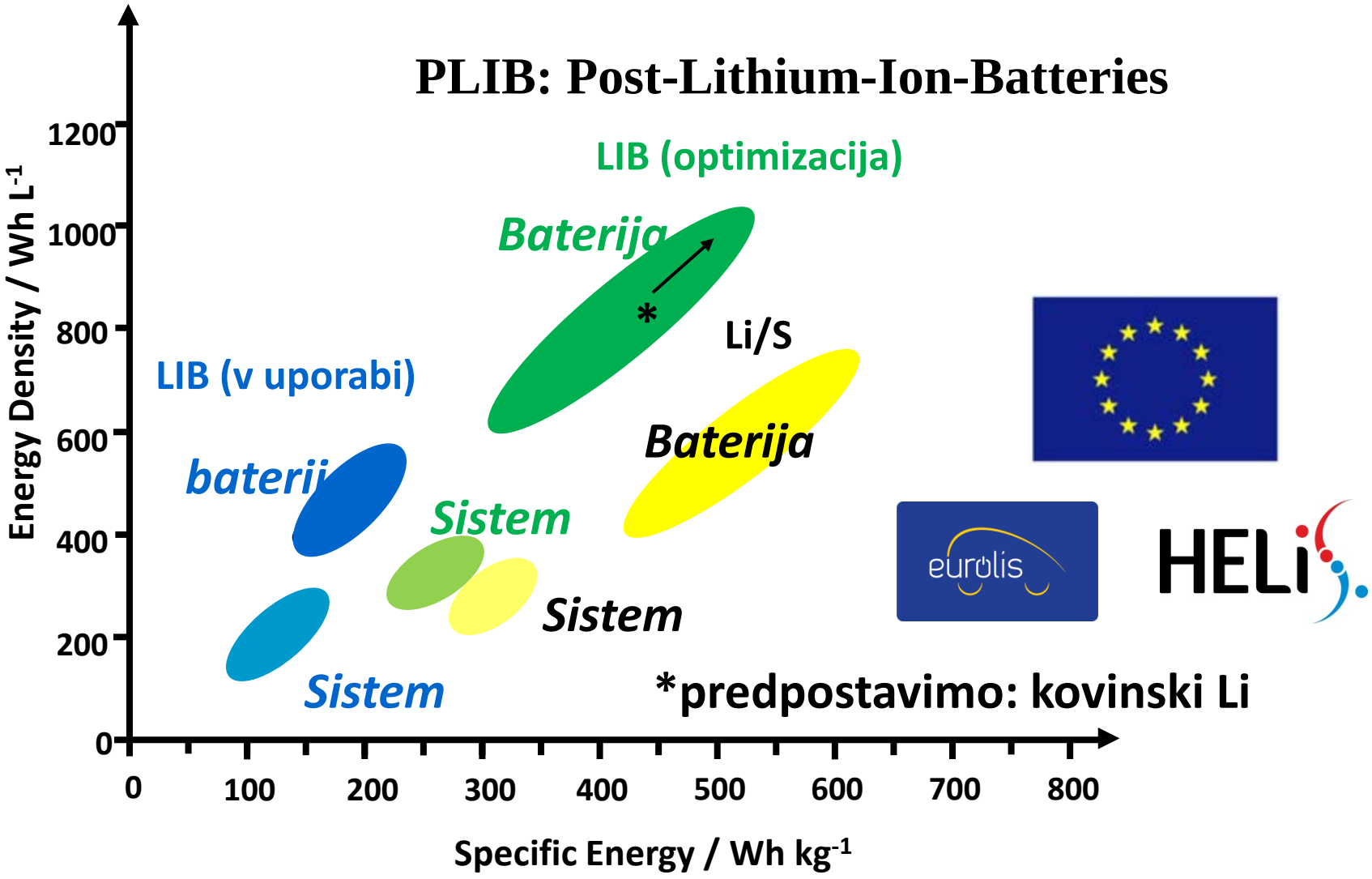
Nice

Mix

Bad

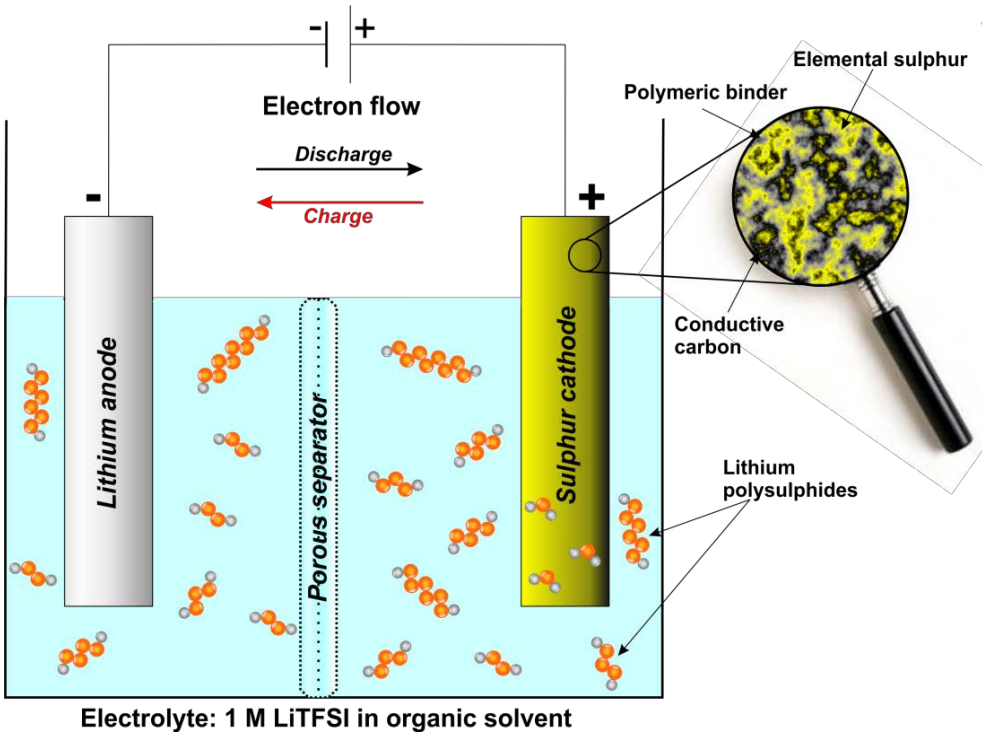
Močna kovalentna vez M-O

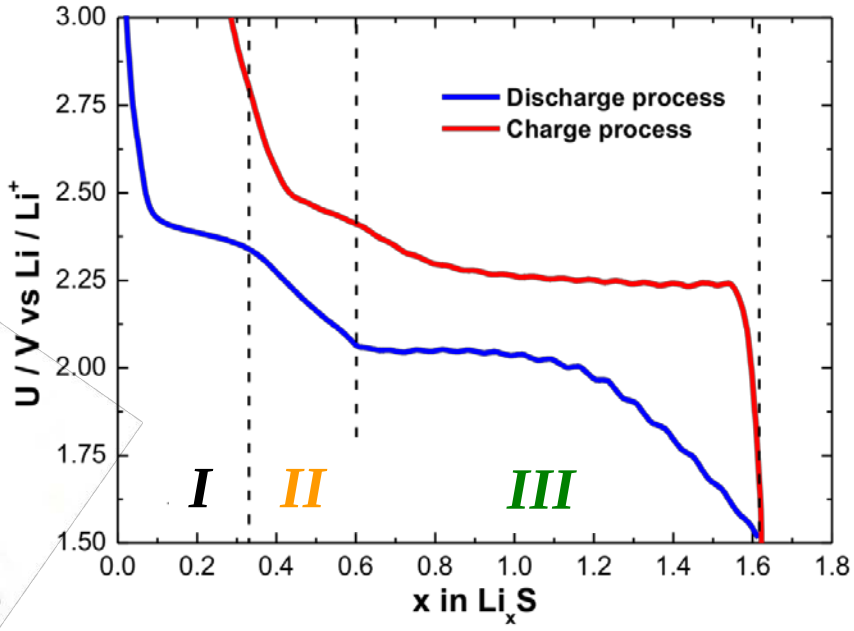
Energijska gostota (LIB vs. PLIB)



Litij žveplov akumulator

Shematična predstavitev Li-S akumulatorja:





Področje I: $S_8 \longrightarrow S_x^{2-}$; x ~ 6–8

Področje II: $S_x^{2-} \longrightarrow S_y^{2-}$; y ~ 3–4

Področje III: precipitacija Li_2S

R. Dominko, M. U.M. Patel, V. Lapornik, A. Vizintin, M. Koželj, N. N. Tušar, I. Arčon, L. Stievano, G. Aquilanti, *J. Phsy. Chem. C*, 2015, *119*, 19001-19010

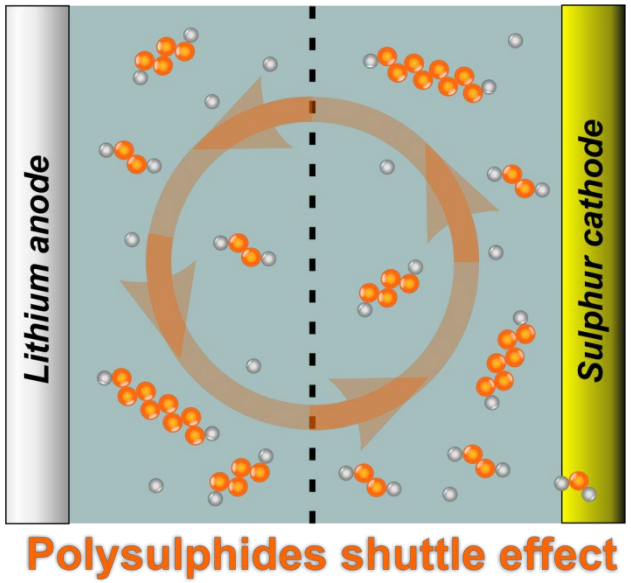
Litij žveplov akumulator

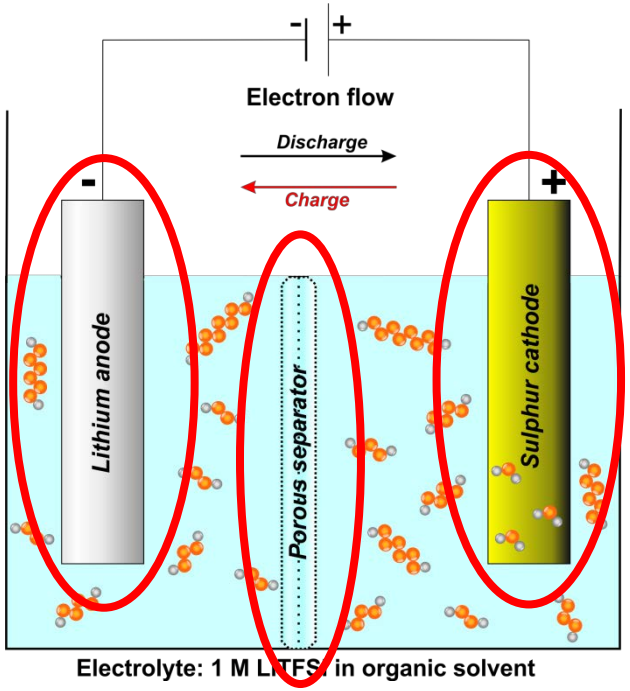
Slabosti ☹

- Prevodnost žvepla
- Volumske spremembe
- Samo praznjenje
- polisulfidi

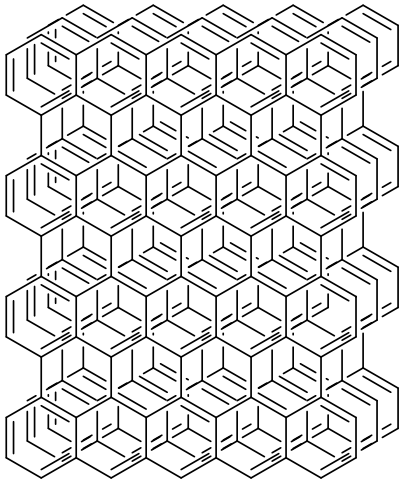
Možne rešitve ☺

- Nanostrukturirani materiali
- separator
- Zaščita litija



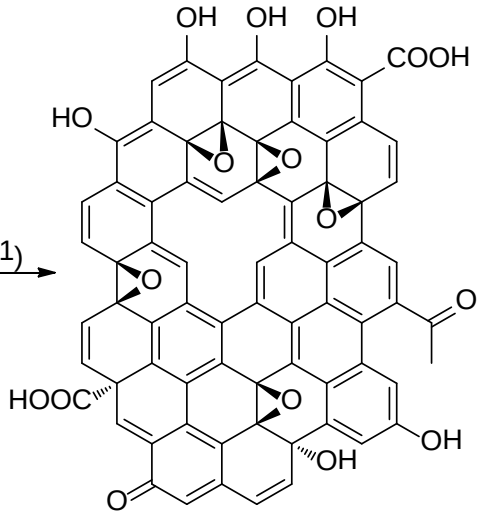


Sinteza GO in rGO



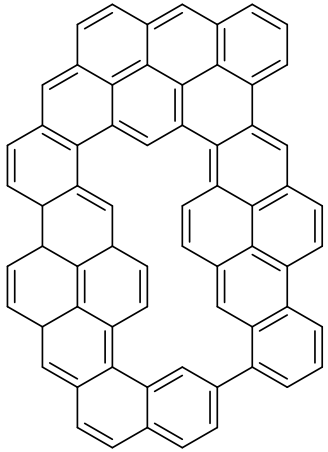
Graphite

$KMnO_4$, H_2SO_4 : H_3PO_4 (9:1)
rt, 12 h



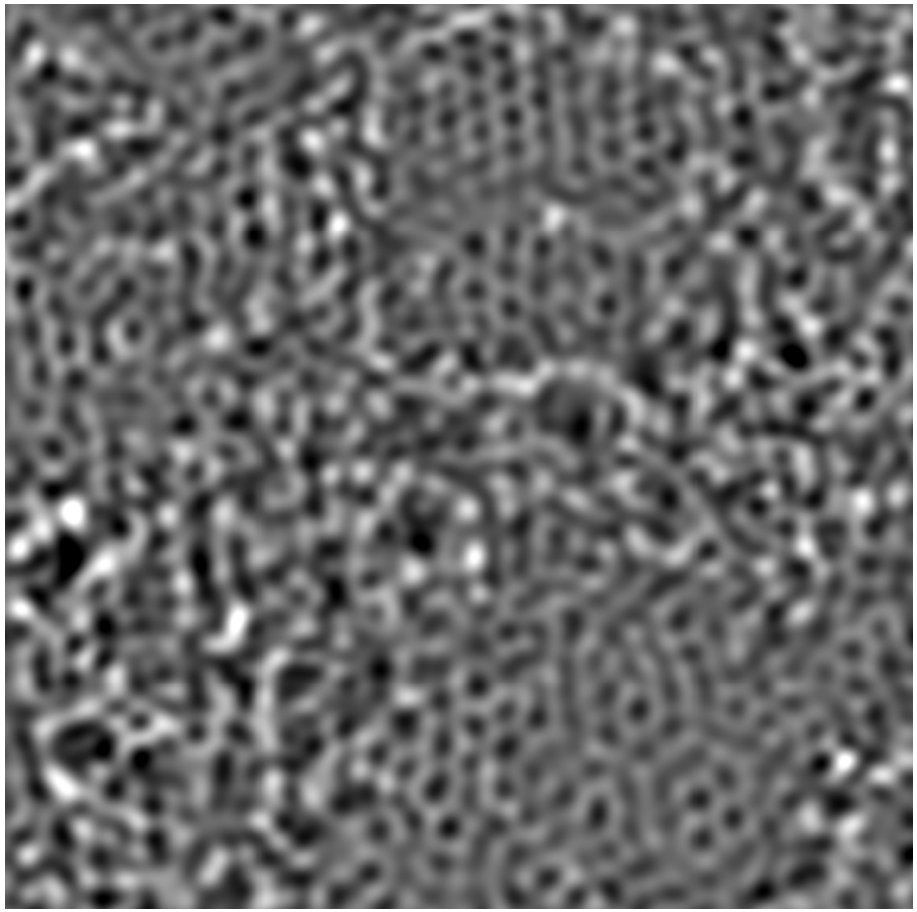
Graphene Oxide

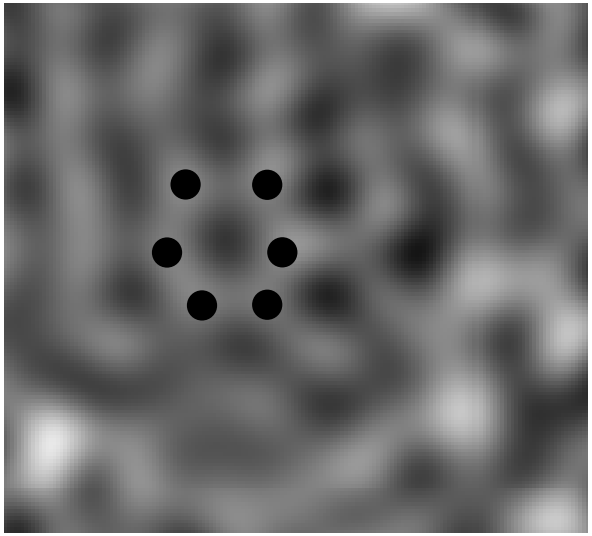
NH_2NH_2 (aq)
90 °C, 24 h



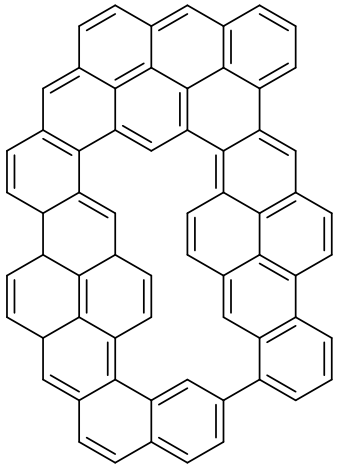
Reduced Graphene Oxide

Vizualicacija GO plasti





Fluoriran rGO

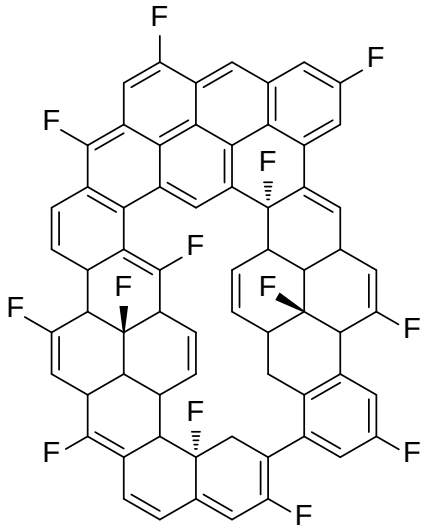


Reduced Graphene Oxide

a) XeF_2 (catalyst BF_3) in aHF, 25 days

b) F_2 in aHF, 3 days

c) F_2 in aHF, 51 days

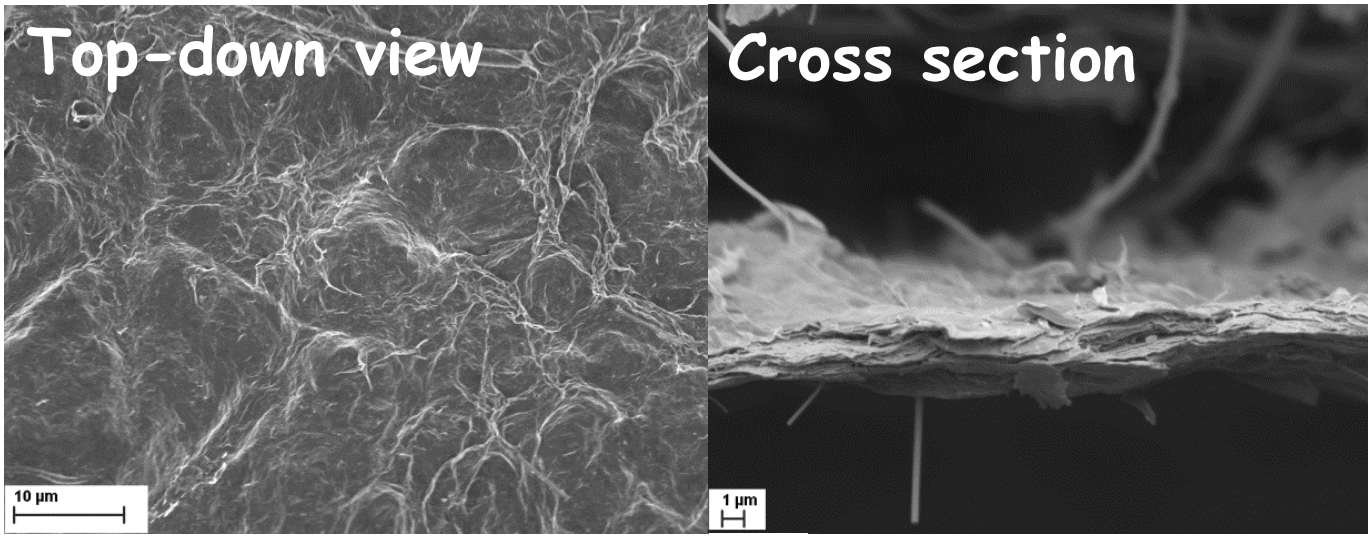


Fluorinated Reduced Graphene Oxide

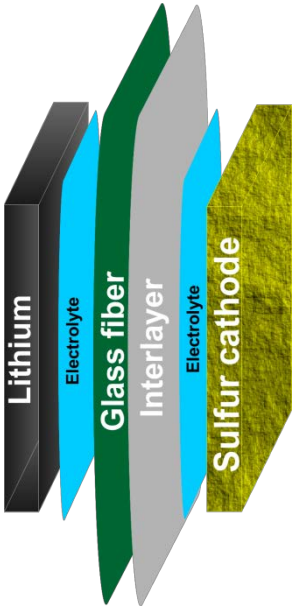
a) **F-rGO–1**;
b) **F-rGO–2**;
c) **F-rGO–3**

Priprava rGO sloja na separatorju

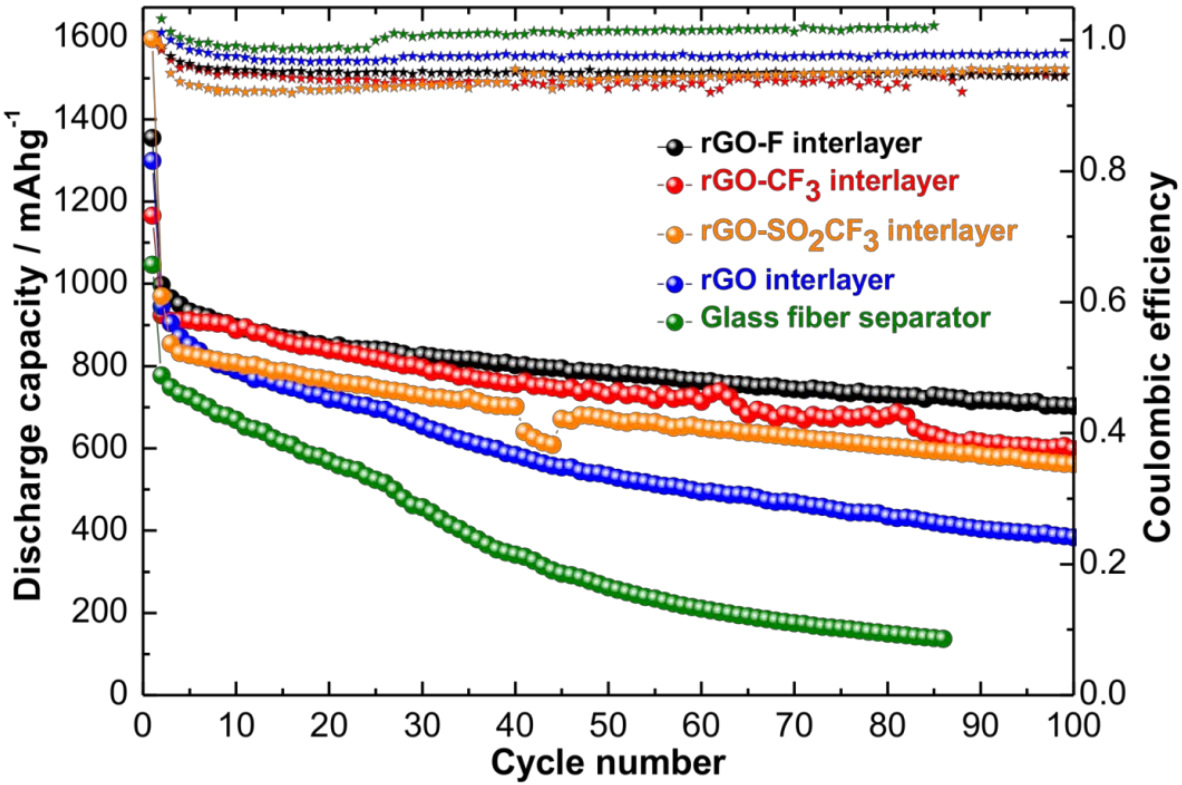
Površino separatorja smo prekrili z rGO-X

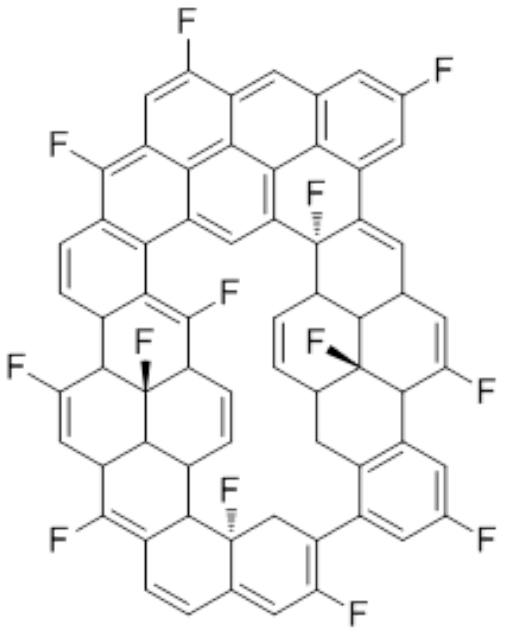


Konfiguracija baterije



Elektrokemija

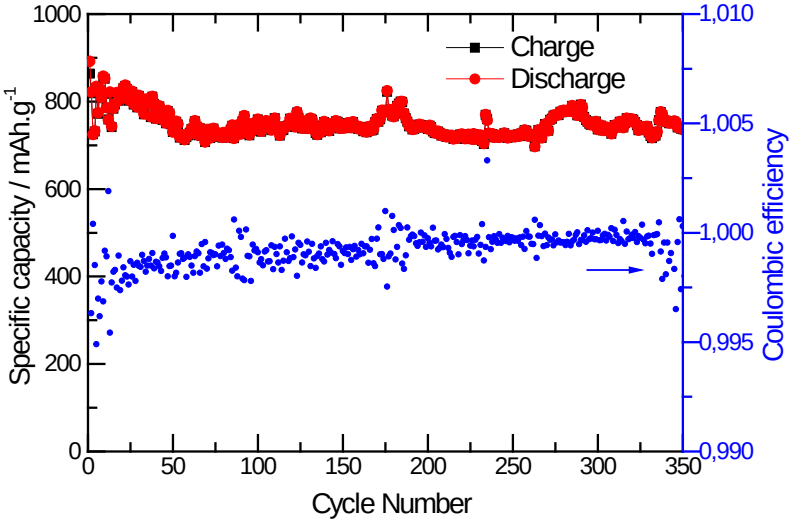


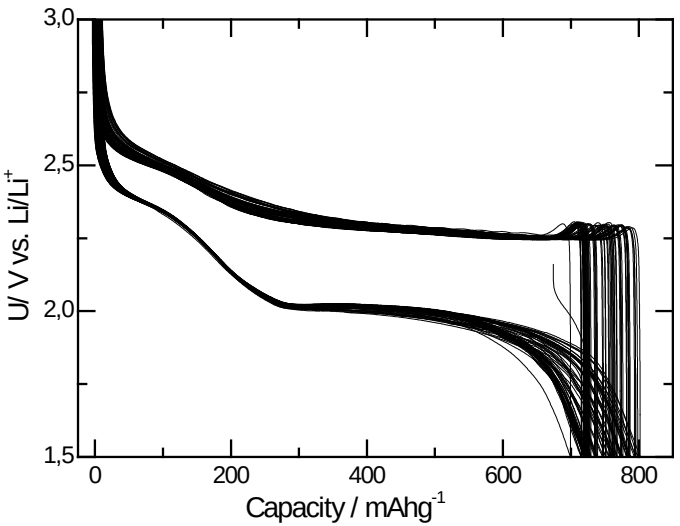


Hidrofoben efekt ustavi difuzijo polisulfidov skozi separator

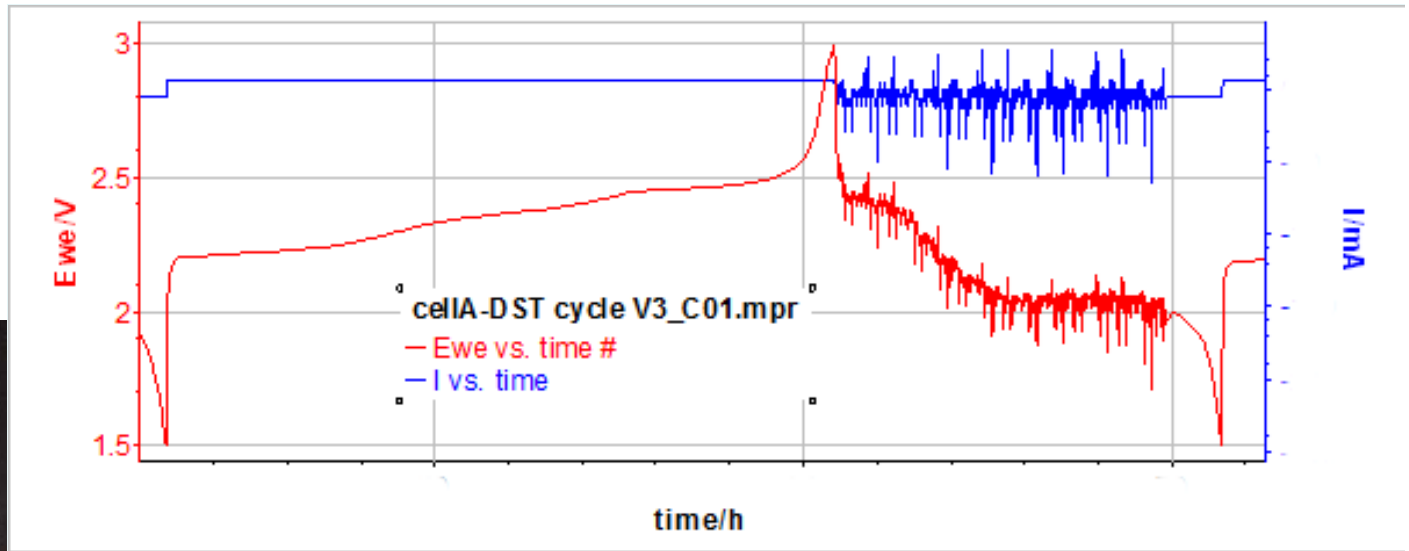
Delovanje Li-S akumulatorja

Delovanje Li-S akumulatorja v laboratoriju

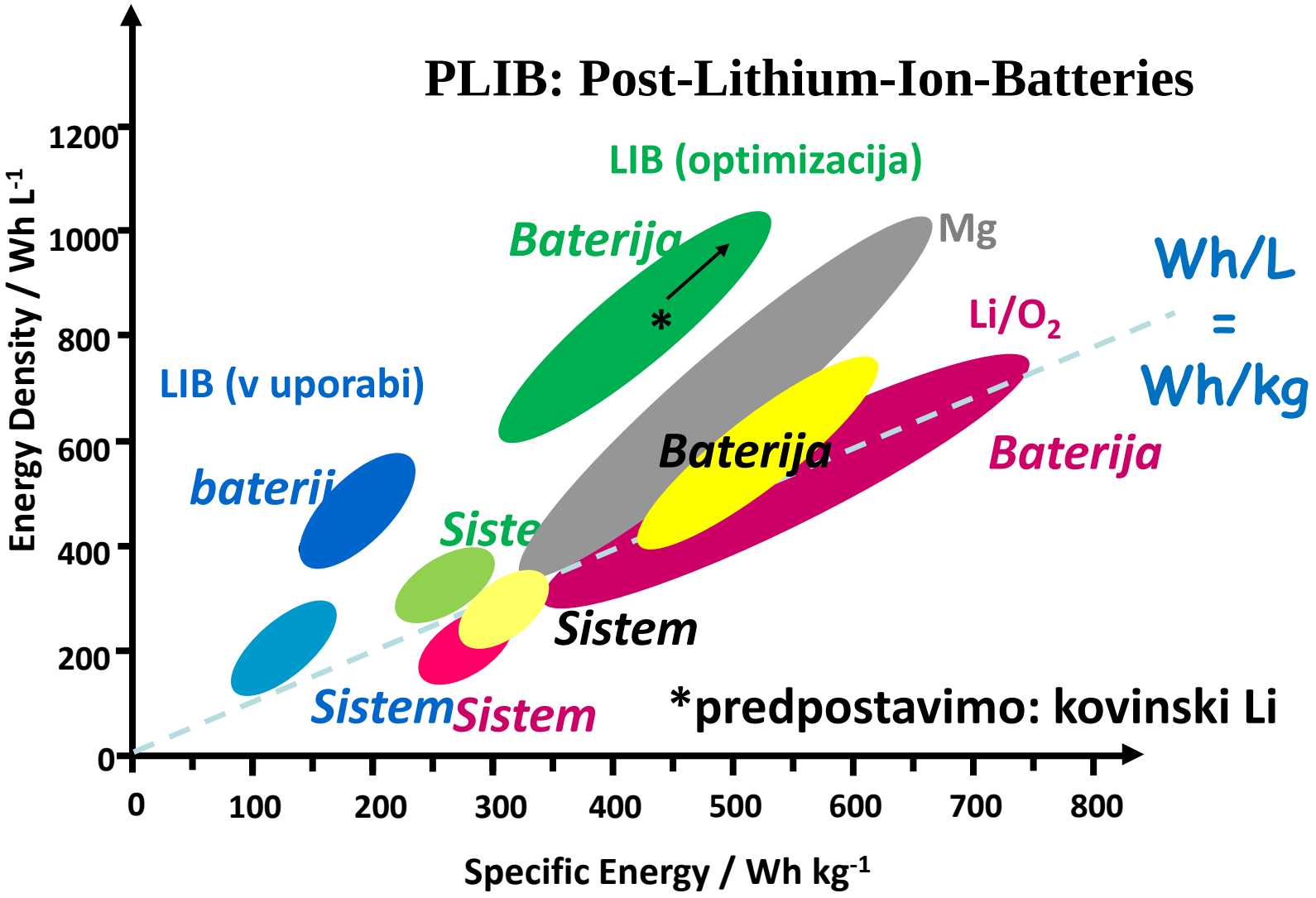




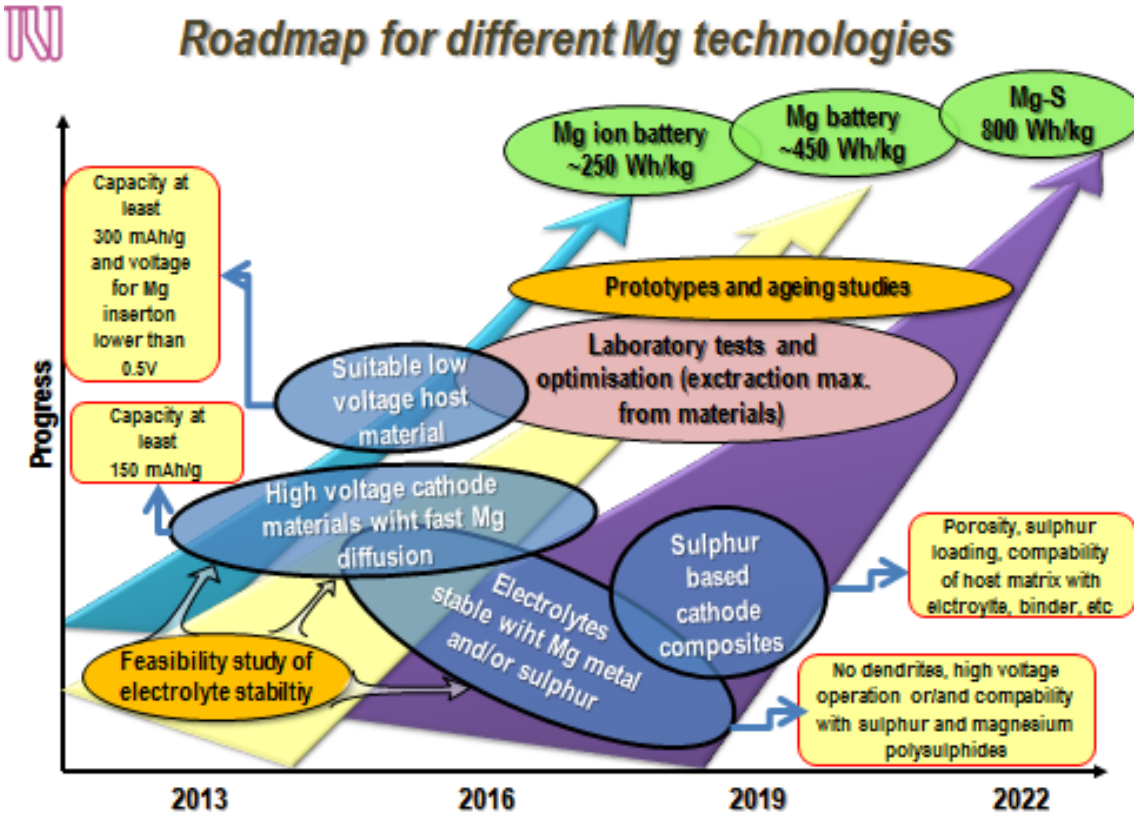
Delovanje prototipne celice po protokolu „Dynamic Stress Test“ – simulacija vožnje



Energijska gostota (LIB vs. PLIB)



Mg akumulatorji



Največja nahajališča litija so v Južni Ameriki

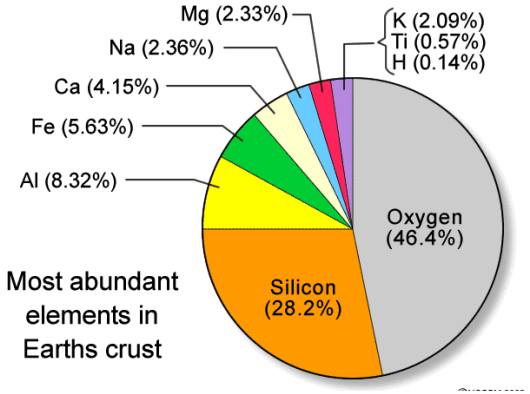
Neenakomerna porazdelitev litija za komercialno pridobivanje – GEOPOLITIČNO NERAVNOTEŽJE

Mg Donat Za zdravlje

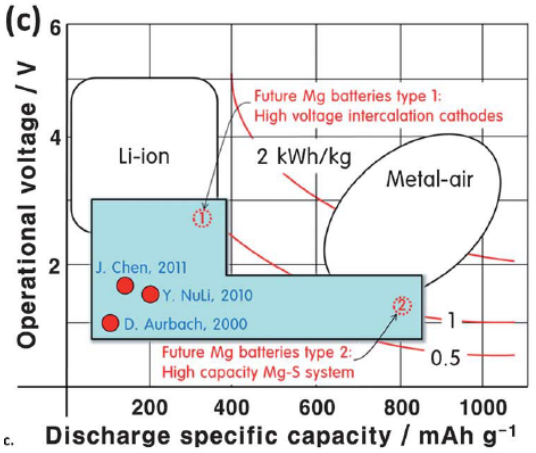
Lastnosti magnezija

- Mogoče uporabiti kovinski Mg

- Magnezij je zelo razširjen in približno 20 krat cenejši



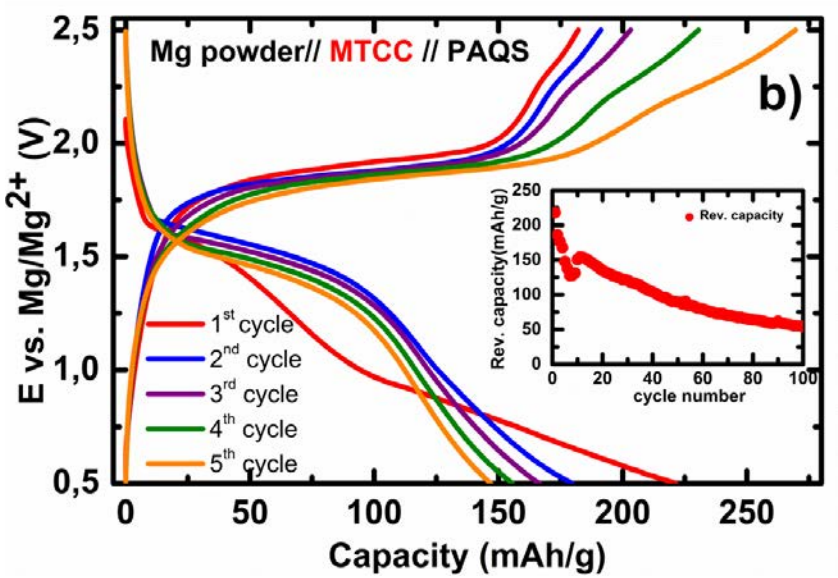
- Visok redoks potencial -2.36 V in dva elektrona v reakciji kar zagotavlja visoko energijo

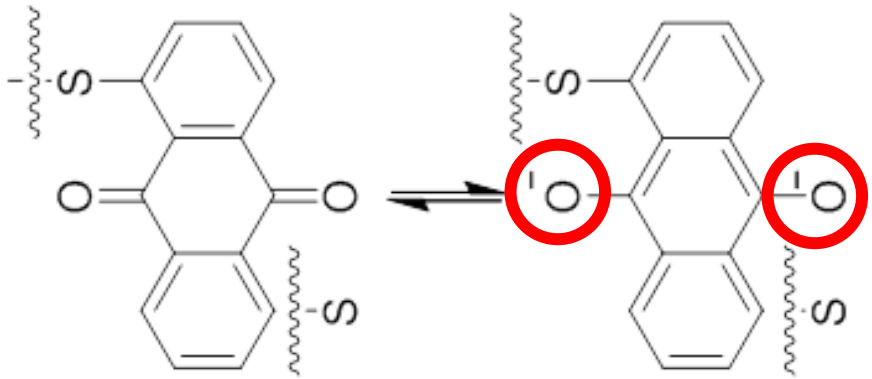


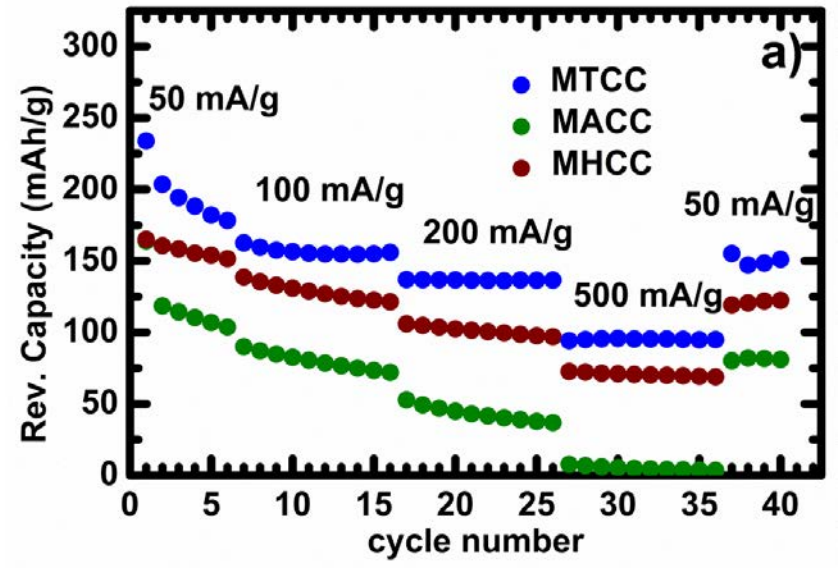
H. D. Yoo, et al, Energy Environ .Sci., 2013, 6, 2265-2279

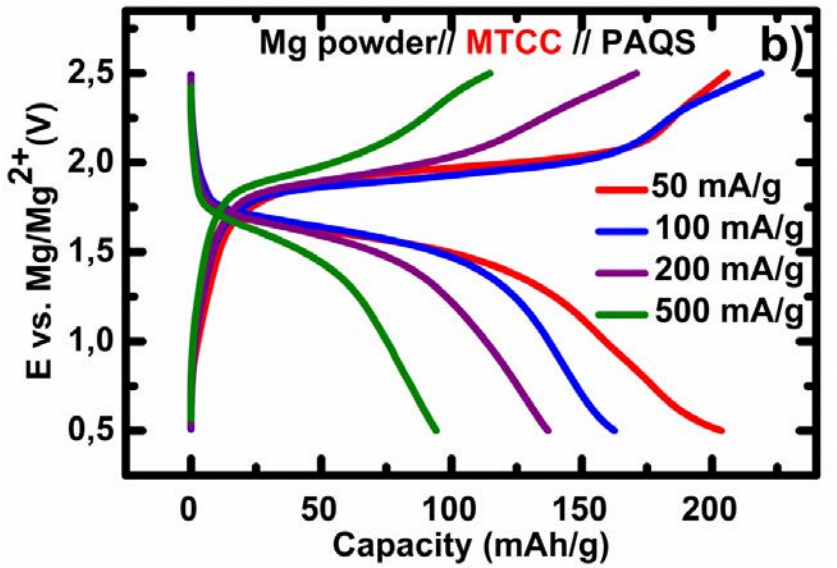
Organski Mg akumulatorji

Akumulatorji z napetostjo 1.8 - 2.3V na celico

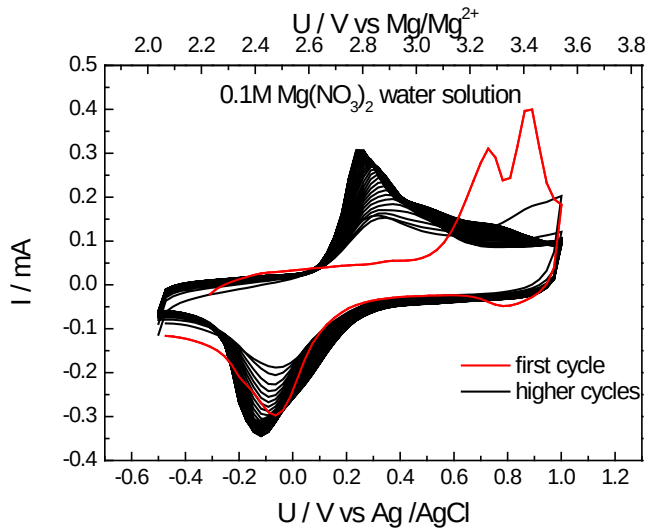


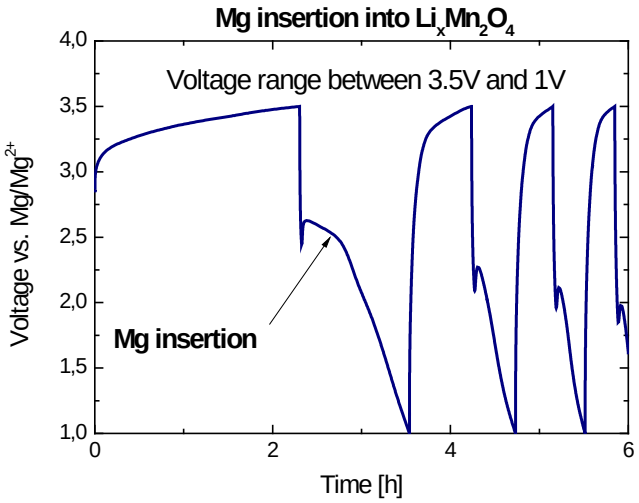




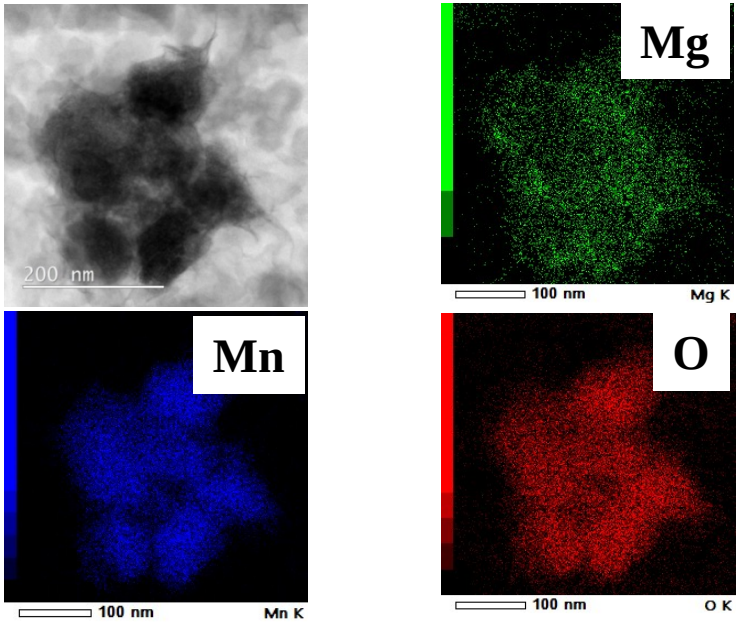


Vgradnja magnezija v spinel

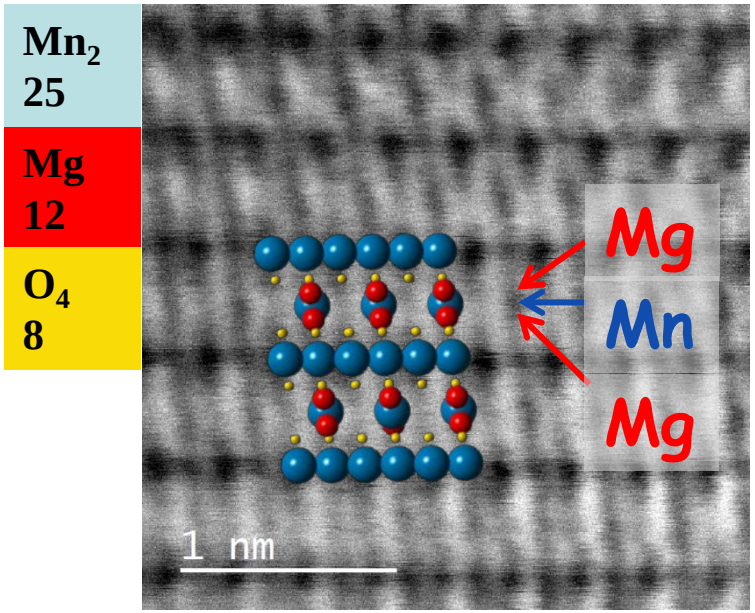




EDX

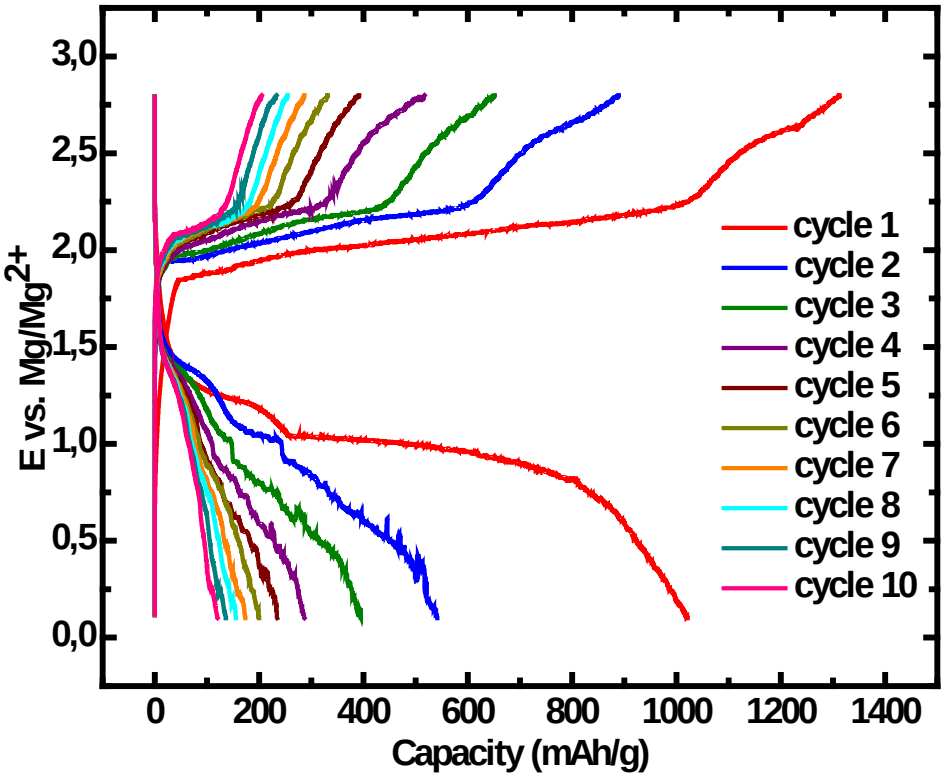


STEM-Annular Dark Field Image (ABF)



Magnezij žveplo akumulator

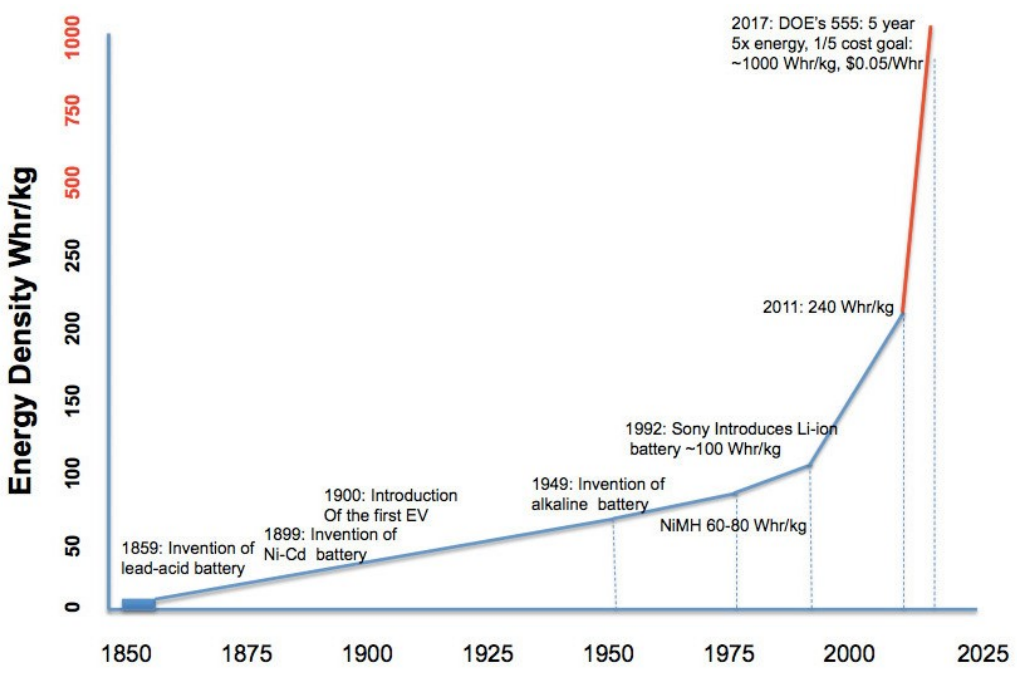
Kombinacija Mg in S elementov zagotavlja okoljsko vzdržnost, obenem pa se energijska gostota približuje potrebam za najbolj zahtevne uporabnike.

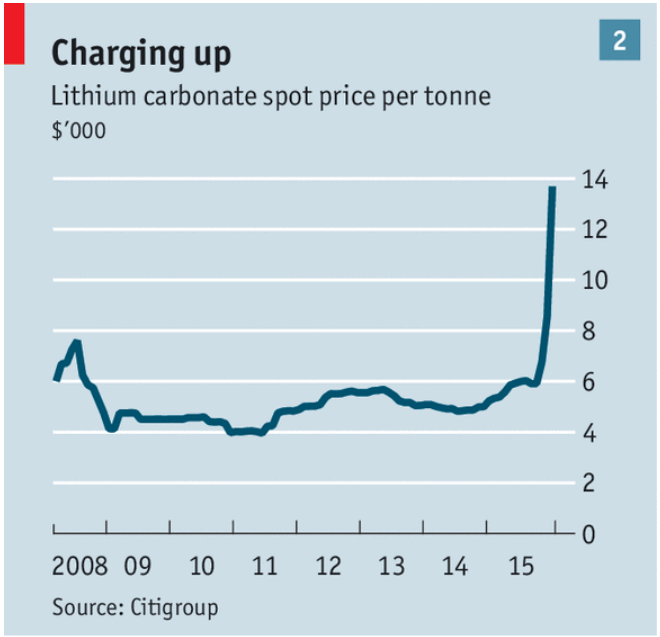


SUPERBATERIJA prihodnosti???

Kje so meje zmogljivosti baterij?

»Misliš že, da si dosegel meje svojih zmožnosti, in glej, pritečejo nove sile. Prav to je življenje.« Franz Kafka





http://www.economist.com/news/business/21688386-amid-surge-demand-rechargeable-batteries-companies-are-scrambling-supplies

»Pred nami so nova obzorja, za katerimi se skrivajo novi koncepti, ki bodo nam ali novim generacijam nadomestili fosilna goriva.«

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Program, projekt in mladi raziskovalci

Znanost na cesti

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