



Center for Energy Materials and Storage Devices

Tayfur Öztürk

Middle East Technical University



ENDAM in Brief

2004-2006 DPT Project on Energy Materials-Phase –I
2005-2010 NESSHY (EU FP6 Project)
2008-2012 DPT Project on Energy Materials –Phase-II
2010-2014 Yiğit Akü-METU Project
2011-2015 COST-MP1103 and COST- MP1004
2016 Ministry of Development - Project ENDAM
2018 The Center ENDAM established

Core personnel

[Kadri Aydinol](#), METU

[Simge Çınar](#), METU

[Emren Nalbant Esentürk](#), METU

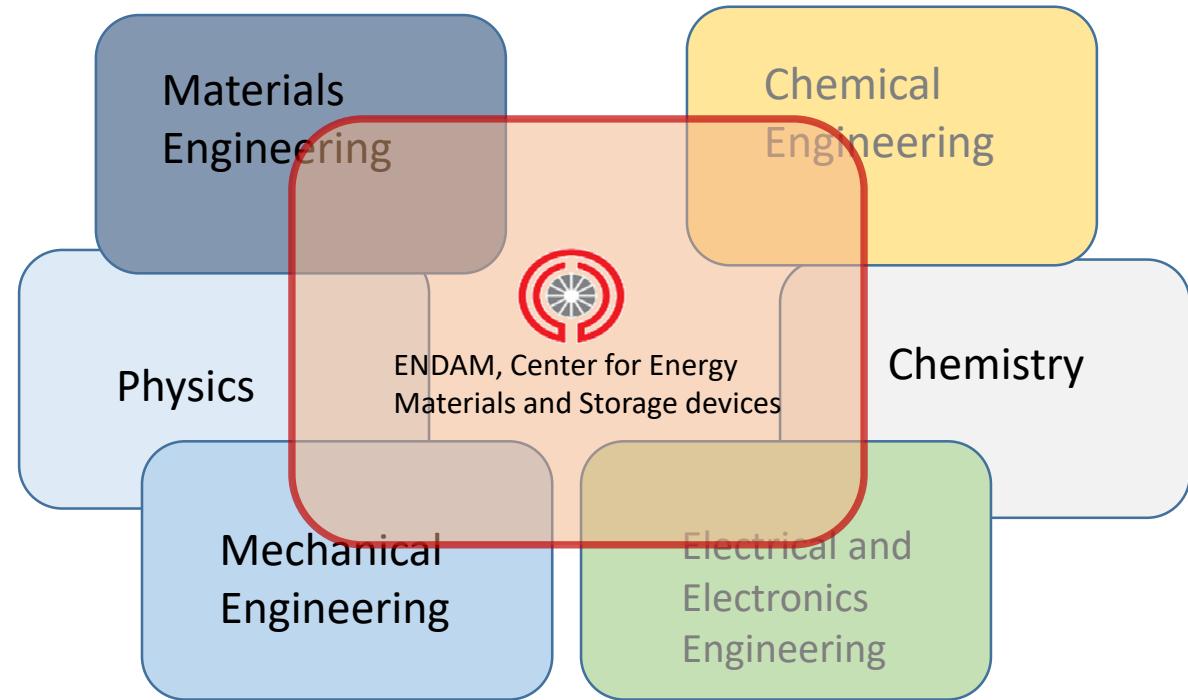
[Y Eren Kalay](#), METU

[Tayfur Öztürk](#), METU

[Damla Eroğlu Pala](#), Boğaziçi University

[Şaban Patat](#), Erciyes University

[Emrah Ünalan](#), METU



Research at ENDAM



Na-ion Batteries

Ayşe Şahin
Nur Şaşmaz
Eren Şimşek
Yusuf Taş

Gülhan Çakmak
Muğla Sıtkı Koçman Univ



Li-ion Batteries

Cansu Savaş Uygur
Mert Övün
Batuhan Kara
Mustafa Alp Yıldırım
Erdem Erkin Erdoğan

Berke Pişkin

Muğla Sıtkı Koçman Univ



Alkaline Batteries

N. Özgür Darıcıoğlu
Yiğit Akbaş
Emre Eren
Aylin Elçi



Supercapacitors

Alptekin Aydınlı
Batuhan Durukan
Farzaneh Hekmat
Kadir Özgün Köse



Li-S Batteries

Merve Can
Ayşegül Karakuş

TÜBİTAK 2244
Industrial Ph.D. Program

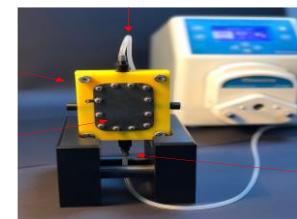
YÖK 100/2000

TÜBİTAK 1001/1003

TÜBİTAK 2232
Outstanding Researchers Program

SAN-TEZ

DPT/Ministry of Development



Flow Batteries

Yasemin Aşkar
Berfu Karlı
Bayram Yıldız



Zn-air Batteries

Burcu Arslan Hamat
Hayriye Aşina Pamuk

Infrastructure at ENDAM – Active Material Synthesis

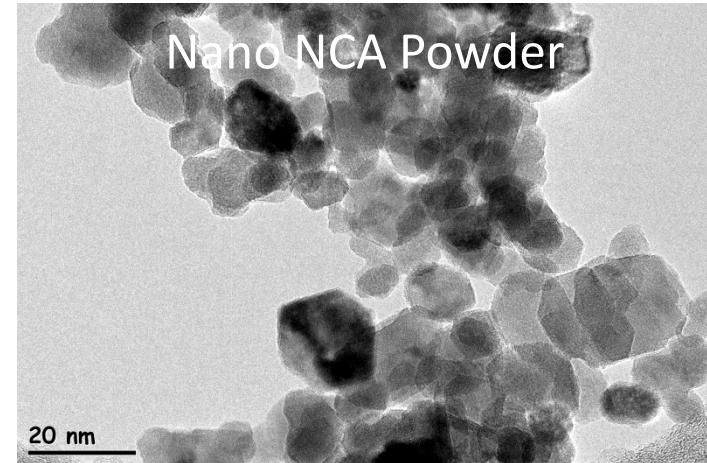
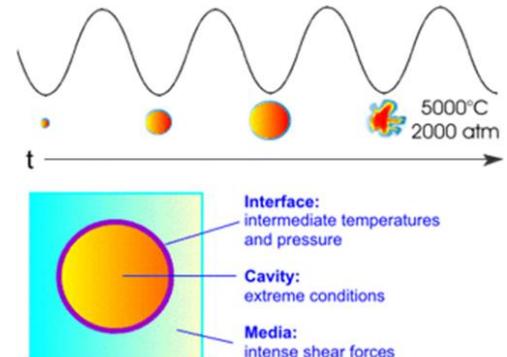
- Sonochemical Synthesis



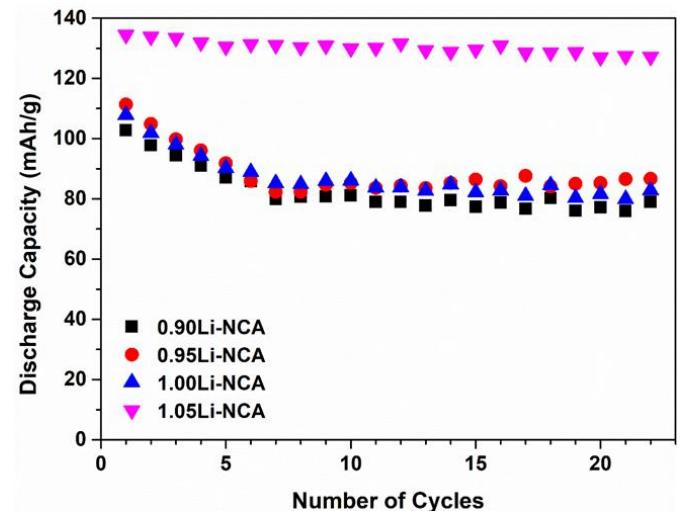
Equipment:
Hielscher UIP2000HD

Features

- increase in reaction rate
- increase in reaction output
- more efficient energy usage
- smaller particles
- narrower particle size distribution



Sonochemical processing of Li-rich nano NCA powder



Infrastructure at ENDAM – Active Material Synthesis

- Microwave Synthesis



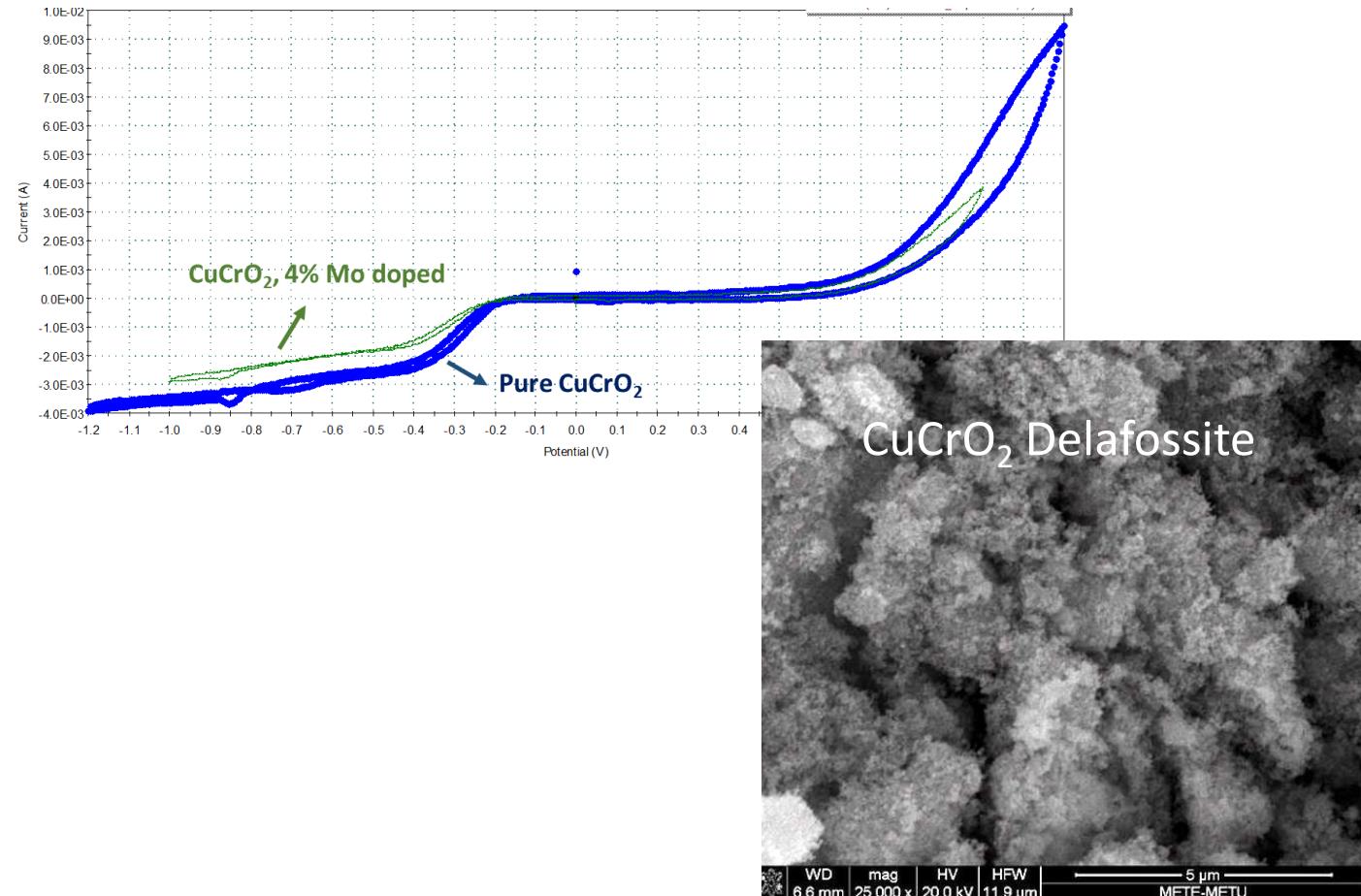
Features

- cleaner and more eco-friendly synthesis
- Direct heating of compounds
- Less or no use of solvents
- Reduced reaction time

Equipment:

Anton Paar Multivawe Pro

Microwave synthesis of Cu based delafossite type ORR/OER catalyst



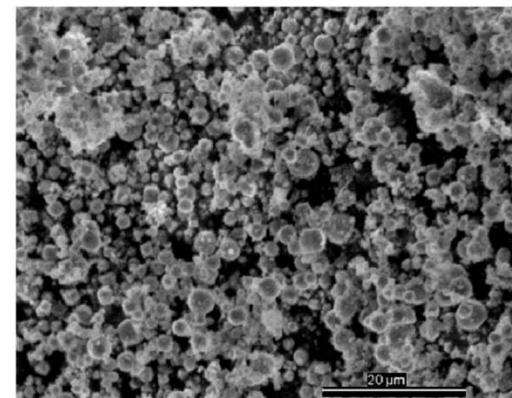
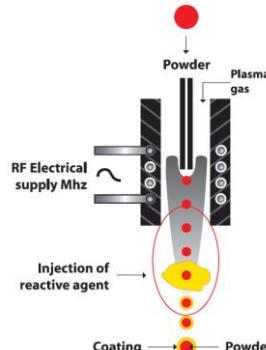
Infrastructure at ENDAM – Active Material Synthesis

- Thermal Plasma Synthesis

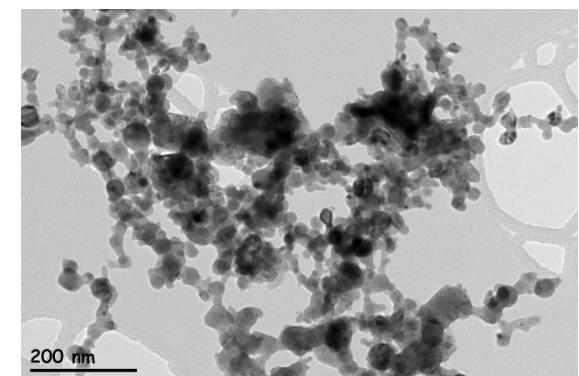


Applications(so far)

- Plasma Black (100 up to 300 m²/g)
- Bifunctional electrocatalyst (LaSrCoO₃)
- Carbon coated Mg



Carbon coated Mg



LaSrCoO₃

Çakmak et al. Continuous synthesis of graphite with tunable interlayer distance, in press
Livan et al. Carbon encapsulation of elemental particles J Mat. Sci. 2018 14350-14360,
Aktekin et al. Carbon coating of Magnesium, J Alloys and Compounds, 720 (2017) 17-2

Device Fabrication

ENDAM has access to facilities at Yiğit AKÜ

- Pouch Type Li-ion Batteries (Two sizes are available)

175x200 mm up to 20 Ah capacity

Cathode: LFP
Anode: Graphite
Electrolyte: EC:DEC 1M LiPF6
Separator: Celgard 2223



43x67 mm up to 3 Ah capacity

Cathode: NCA
Anode: Graphite
Electrolyte: EC:DEC 1M LiPF6
Separator: Celgard 2400



Infrastructure at ENDAM – Testing and Characterization

- Active Material Testing

Electrochemical Characterization (@ -40 to +60 °C)

- Galvanostatic charge/discharge
- Capacity determination
- Cycle life determination
- Rate capability measurements
- LSV, CV, EIS, PITT,GITT measurements



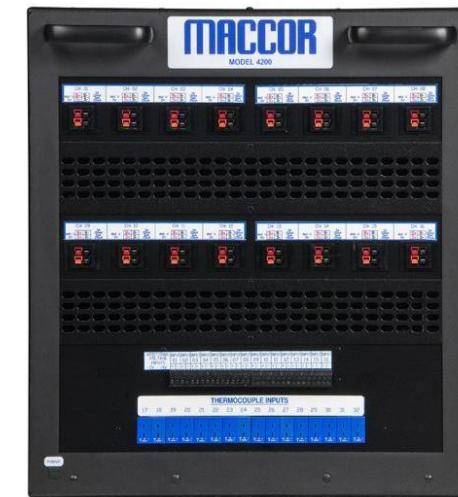
Equipment:

Biologic MPG 2
(max. 100 mA, 40 channels)

- Battery Testing

Electrochemical Characterization (@ -40 to +60 °C)

- Galvanostatic charge/discharge
- Capacity determination
- Cycle life determination
- Rate capability measurements



Equipment:

Maccor 4200
(max 5 A, 16 Channels)

Infrastructure at ENDAM – Testing and Characterization

- Battery Testing

Calorimetric Characterization

- Heat capacity determination
- Accelerating rate adiabatic calorimetry (battery safety tests)
 - nail penetration test, crush test, thermal abuse, overcharge, overdischarge, external short circuit
- Thermal runaway determination

Chamber Size: 25X50 cm Temperature: Up to 450°C

Equipment:

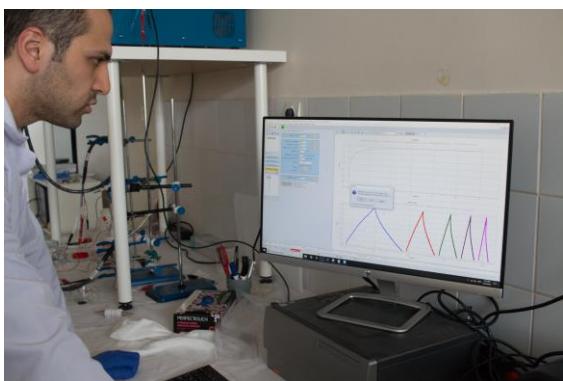
THT EV-ARC



Supercapacitors

Development of nanostructured active materials for Supercapacitors

Current efforts at ENDAM are centered on the development of binary and ternary nanocomposite supercapacitor electrodes and devices using carbonaceous materials (i.e. graphene, CNTs), metal oxide nanoparticles and conducting polymers. Capacitive deionization performance of the fabricated electrodes are also determined.



Patents

- G. Amaratunga, H. Wang, H. E. Unalan, M.A.K. Rouvala, D. Wei, "High Efficiency Energy Conversion and Storage Systems Using Carbon Nanostructured Materials" (US9406985B2).
- H. E. Unalan, N. L. Rupesinghe, G. Amaratunga, "Process for Producing Carbon Nanostructure on a Flexible Substrate, and Energy Storage Devices Comprising Flexible Carbon Nanostructure Electrodes" (US 2010/0178568 A1).
- D. Wei, A. Colli, M.A.K. Rouvala, H.E. Unalan, P. Hiralal, G. Amaratunga, N. Rupesinghe, "Process for Producing Carbon Nanostructure on a Flexible Substrate, and Energy Storage Devices Comprising Flexible Carbon Nanostructure Electrodes" (US 2010/0216023 A1).
- P. Hiralal, H.E. Unalan, H. Wang, G. Amaratunga, D. Wei, M.A.K. Rouvala, "Nano-Structured Flexible Electrodes, and Energy Storage Devices Using the Same" (US9786444B2).

Publications

- Paper Based, Expanded Graphite/Polyppyrrole Nanocomposite Supercapacitors Free from Binders and Current Collectors, R. Yuksel, N. Uysal, A. Aydinli, H.E.Unalan, J. Electrochim. Soc. 165 (2018) A283.
- Chemical and structural optimization of ZnCl₂ activated carbons via high temperature CO₂ treatment for EDLC applications, Kose, K; Piskin, B; Aydinol, MK . International Journal of Hydrogen Energy 43 (2018) 18607-18616
- Flexible, Silver Nanowire Network Nickel Hydroxide Core-Shell Electrodes For Supercapacitors, R. Yuksel, S. Coskun, Y. E. Kalay, H. E. Unalan, J. Power Sources 328 (2016) 167-173.
- Cobalt Oxide Nanoflakes on Single Walled Carbon Nanotube Thin Films for Supercapacitor Electrodes, M. B. Durukan, R. Yuksel, H. E. Unalan, Electrochimica Acta 222 (2016)1475-1482.
- Coaxial Silver Nanowire Network Core Molybdenum Oxide Shell Supercapacitor Electrodes, R. Yuksel, S. Coskun, H. E. Unalan, Electrochim. Acta 193 (2016) 39-44.
- Ternary nanocomposite SWNT/WO₃/PANI thin film electrodes for supercapacitors, R. Yuksel, C. Durucan, H. E. Unalan, J. Alloys. Compd. 658 (2016) 183-189.
- All-organic electrochromic supercapacitor electrodes, R. Yuksel, S. C. Cevher, A. Cirpan, L. Toppare, H. E. Unalan, J. Electrochim. Soc. 162 (2015) A2805-A2810.

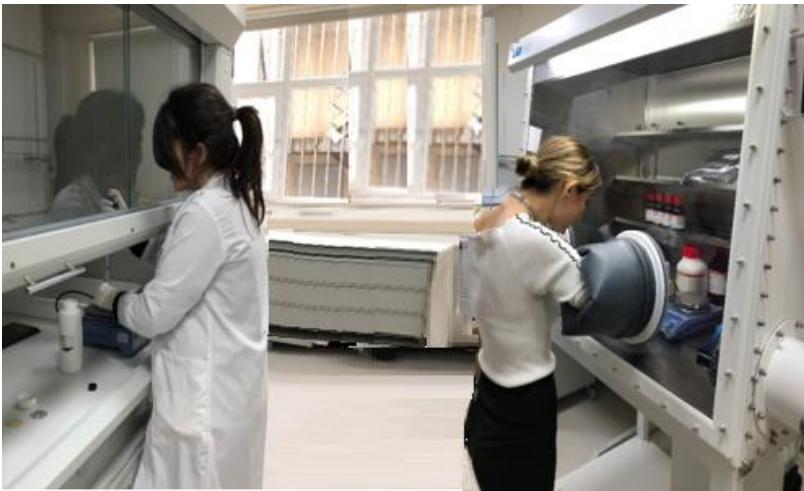


Li-S Batteries

Li-S Batteries: Materials-, Cell- and Systems Level Performance

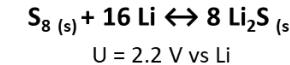
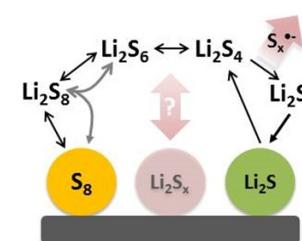
3501- 116M574

- Electrochemical modeling
- Electrochemical characterization
- Techno-economic modeling



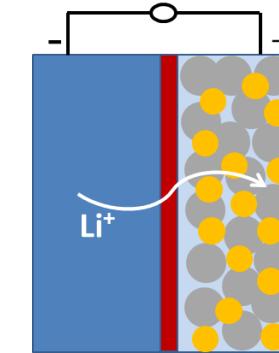
Please refer to Eroglu's presentation in this website

Materials-Level Reaction and Degradation Mechanisms



Surface area for e- transfer
Polysulfide surface concentration

Electrode-Level Design



C to S ratio in the cathode
E to S ratio in the cathode

Cell-Level Performance

Useable specific capacity
Capacity retention
Cycle life

Systems-Level Performance

Energy density
OEM cost

Emerce NB, Eroglu D. Effect of Electrolyte-to-Sulfur Ratio in the Cell on the Li-S Battery Performance. *J. Electrochem. Soc.*, in press.

Michaelis, C, Erisen, N, Eroglu, D, Koenig, GM. Electrochemical performance and modeling of lithium-sulfur batteries with varying carbon to sulfur ratios. *Int J Energy Res.* 2019; 43: 874–883.

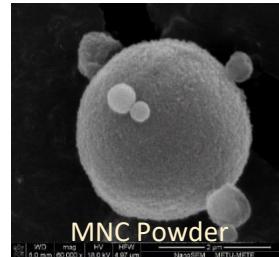
Erisen, N, Emerce, NB, Erensoy, SC, Eroglu, D. Modeling the effect of key cathode design parameters on the electrochemical performance of a lithium-sulfur battery. *Int J Energy Res.* 2018; 42: 2631– 2642.



Li-ion Batteries

Development of infrastructure for active material synthesis for Li-ion Batteries

Current efforts at ENDAM are generally centered on layered transition metal oxide material development due to their desired kinetic properties. On the other hand, thermal and structural stability problems of these compounds have to be addressed, because of which is often alloyed to obtain $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC) and $\text{Li}(\text{NiCoAl})\text{O}_2$ (NCA) compounds. Research programs carried out to optimized chemistry for NCA and NMC.



Patents

A. Büyükbürç ve M.K. Aydinol, "Yeniden Doldurulabilir Lityum İyon Bataryalar İçin W ve M Alaşımı LiCoO₂ ve Bunun Üretim Metodu" Türk Patent Enstitüsü No: TR 2014 00051B, 2016.

Gerbrand Ceder, Yet-Ming Chiang, Donald R. Sadoway, Watertown, Mehmet K. Aydinol, Young-II Jang, Biying Huang, "POLYMER ELECTROLYTE, INTERCALATION COMPOUNDS AND ELECTRODES FOR BATTERIES", US 2005/0181280 A1.

Anne M. Mayes, Gerbrand Ceder, Yet-Ming Chiang, Donald R. Sadoway, Mehmet K. Aydinol, Philip P. Soo, Young-II Jang, Biying Huang, "Non-crosslinked, Amorphous, Block Copolymer Electrolyte For Batteries", US 7,026,071 B2.

Cansu Savaş Uygur, Berke Pişkin ve Mehmet Kadri Aydinol, Synthesis of $\text{Li}_{x}(\text{Ni}0.80\text{Co}0.15\text{Al}0.05)\text{O}_2$ Cathodes with Deficient and Excess Lithium Using Ultrasonic Sound Assisted Co-Precipitation Method for Li-Ion Batteries, Bulletin of Materials Science, in press.

H. Sahan, H Goktepe, S. Yıldız, C. Caymaz Ş. Patat A novel and green synthesis of mixed phase $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ anode material for lithium ion batteries, IONICS 25, 2019, 447-455

M. Kunduracı, C. Savaş Uygur and M.K. Aydinol, "Activation of Manganese Ions in Lithium-ion Battery Anode Materials via Nickel and Cobalt Doping". Journal of Electronic Materials, 47(11), 6420 (2018).

B. Pişkin, C. Savaş Uygur and M.K. Aydinol, "Mo doping of layered $\text{Li}(\text{NixMnyCo1-x-y-zMz})\text{O}_2$ cathode materials for lithium-ion batteries". International Journal of Energy Research, 42, 3888 (2018).

P. Livan, B. Miser, S. Altınok, C. Eyövge, M.K. Aydinol and T. Öztürk, "Carbon Encapsulated Silicon Nanoparticles as Anodes for Lithium Ion Batteries". ECS Transactions, 77(11), 373 (2017).

B. Pişkin and M.K. Aydinol, "Development and characterization of layered $\text{Li}(\text{NixMnyCo1-x-y})\text{O}_2$ cathode materials for lithium ion batteries", International Journal of Hydrogen Energy, 41, 9852 (2016)

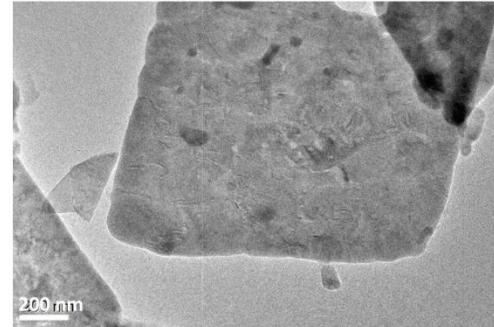
H. Goktepe, H Sahan, S Patat Effect of silver and carbon double coating on the electrochemical performance of LiFePO_4 cathode material for lithium ion batteries, International Journal Of Hydrogen Energy, 41,2016, 9774-9779.

Li-ion Batteries

Fabrication of 20Ah Lithium-ion Pouch Cell
for Electric Vehicles (Yiğit Akü)

Santez - 00714.STZ.2010-2

- To establish line for a pilot scale production of Li-ion Battery
- Cathode: LiMnPO_4 and LiFePO_4 composite
- Anode: Si/Graphite nanocomposites



LFP Nano Plate



Mixing (max. 60 L capacity)

Pilot Line for Li-ion Battery at Yiğit Akü



Coating (max. 5 m/min, max. 40 cm width) *Double sided gap coater*

Partners: Yiğit Akü

MIDDLE EAST TECHNICAL UNIVERSITY

Li-ion Batteries

Fabrication of 20Ah Lithium-ion Pouch Cell
for Electric Vehicles (Yiğit Akü)

Santez - 00714.STZ.2010-2

Cathode: LFP
Anode: Graphite
Electrolyte: EC:DEC 1M LiPF6
Separator: Celgard 2223



Pilot Line for Li-ion Battery at Yiğit Akü (cont.)



Calendering (40 tons)



Electrode cutting

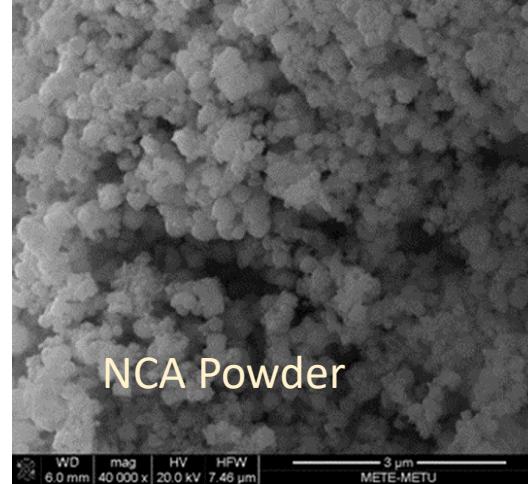


Electrode Stacking

Li-ion Batteries

Design, fabrication of Lithium-Ion Battery Group with Uninterruptible Power Supply Characteristics (Aselsan)

Santez - 0670.STZ.2014



The objective of this project was to develop a Lithium Ion battery light enough to be portable and is capable of providing the specified power. The battery group was able to charge its batteries by AC or DC sources, and will act as UPS for the system it is supplying. NCA type active material was synthesized and used in 2.7 Ah pouch type batteries.



Cathode: NCA
Anode: Graphite
Electrolyte: EC:DEC 1M LiPF6
Separator: Celgard 2400

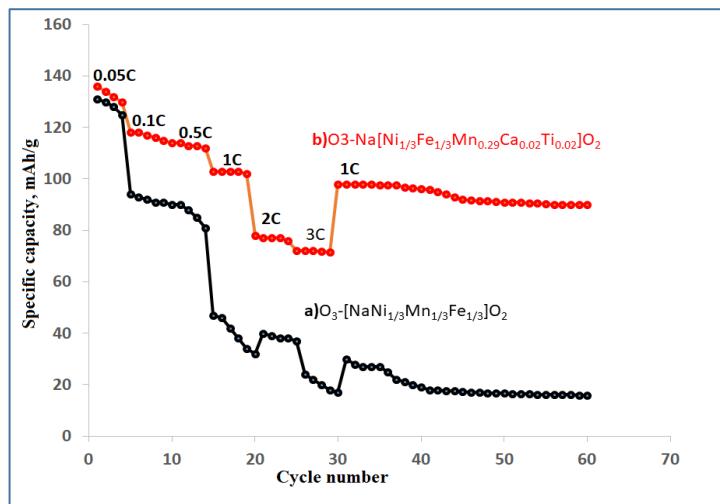
Partners: Gazi University(Coordinator) , Yiğit Akü, ASELSAN

Na-ion Batteries

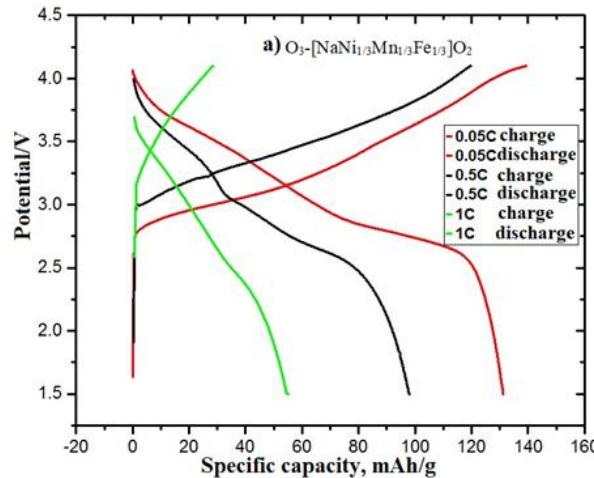
Cathodes with improved energy density and stability for Na-ion batteries

TUBITAK 1003 -118M077

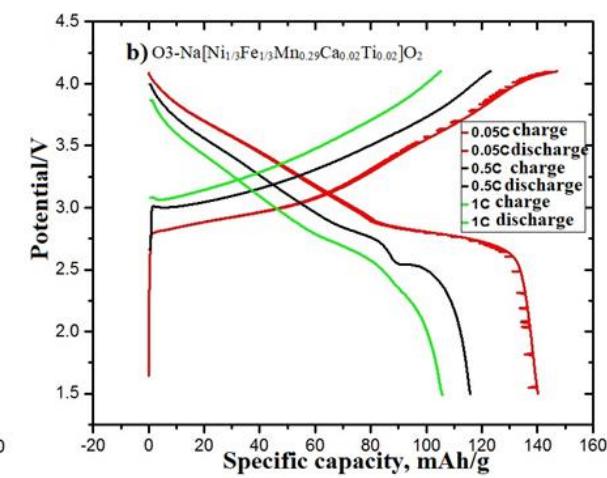
- Achieve a specific capacity 140 mAh/g or higher with
 - improved cycle life
 - improved electrode stability in air



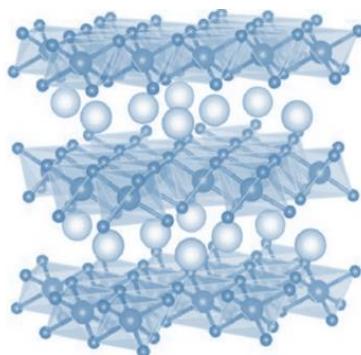
Rate performance and capacity retention achieved



O₃-[NaNi_{1/3}Mn_{1/3}Fe_{1/3}]O₂
NaClO₄, EC-DEC (1:1 by w/w)
Na



O₃-Na[Ni_{1/3}Fe_{1/3}Mn_{0.29}Ca_{0.02}Ti_{0.02}]O₂
NaClO₄, EC-DEC (1:1 by w/w)
Na

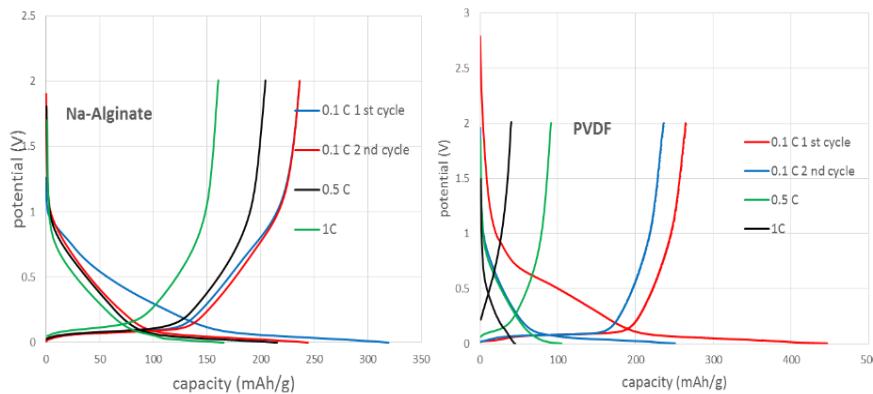


- Ş. Patat , S. Yıldız, N. Özdemir, A. Ülgen High Performance Layered O₃-NaMx1My2Mz Mk Ml Mm O₂ CathodeMaterials for Sodium-Ion Batteries mESC-IS2017 Int. Symp on Materials for Energy Storage and Conversion 26-28 Sept 2017 Ortahisar Nevşehir

Na-ion Batteries

Anodes for Na-ion batteries

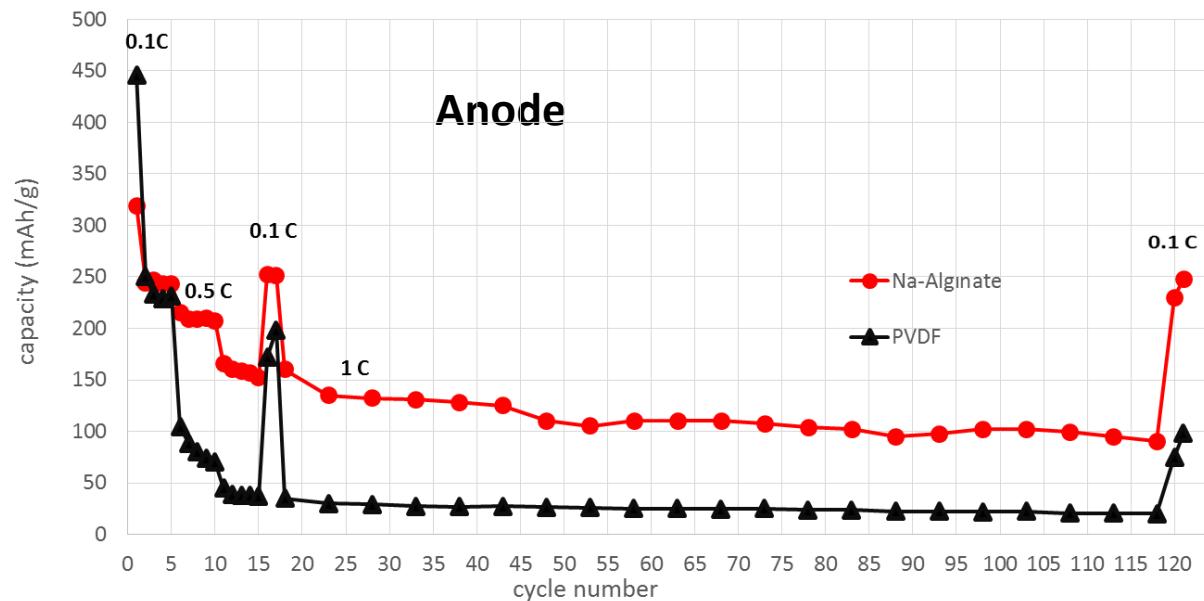
TUBITAK 1003 -118M076



Hard carbon with PVdF and Na-alginate binders at 0.1C, 0.5C and 1.0C current densities

Ş. Patat, A. Ülgen, S. Yıldız, A. R. Türkmen , T. Öztürk "Wood derived hard carbon anode material for low-cost sodium-ion batteries towards practical application for grid energy storage"

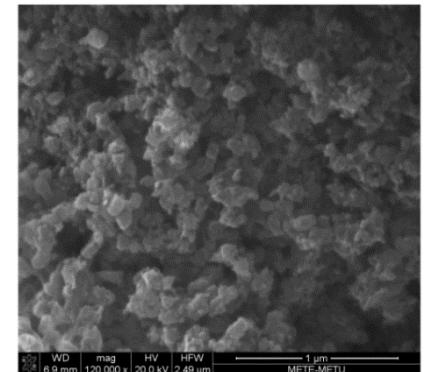
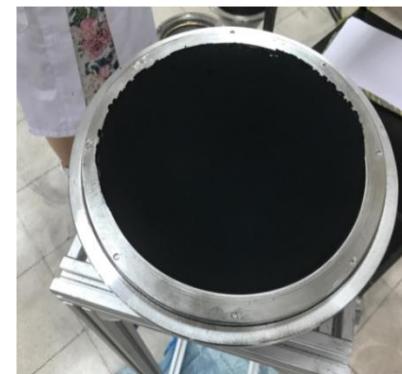
G.Çakmak T.Öztürk, Continuous synthesis of graphite with tunable interlayer distance, Diamond and related Materials, in press



Cycling performance of the hard carbon electrodes with PVdF and Na-Alginate binders

Continuous synthesis of graphite with tunable interlayer distance

3.338 Å < $d(002)$ < 3.758 Å



Alkaline Batteries

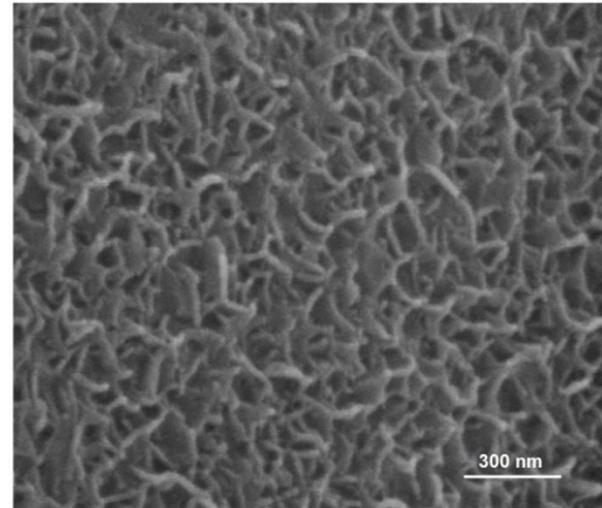
Development of encapsulated nanoparticles for energy storage

1001-113M193 –COST MP1103

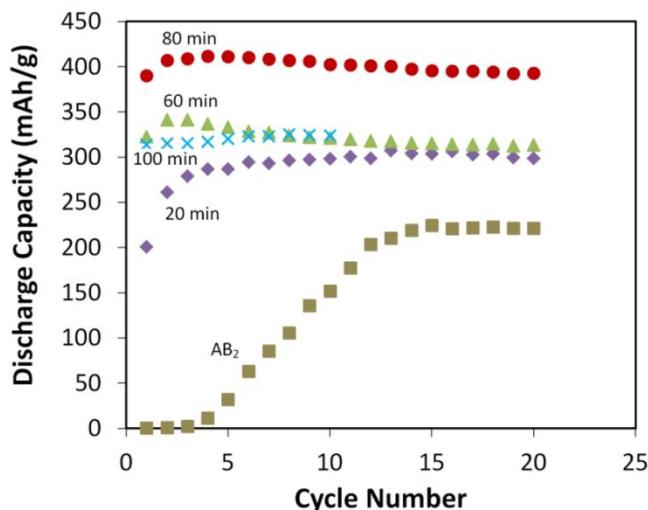
- Rare-Earth Free MH
- Fast activation
- Improved Discharge Capacity

- S Tan, Y Shen, E.O. Sahin , Dag Noreus , T. Ozturk, Int. J Hydrogen Energy 41 (2016) 9948-9953
- C. Eyovge and T.Ozturk, Journal of the Electrochemical Society, 165 (10) A2203-A2208 (2018)

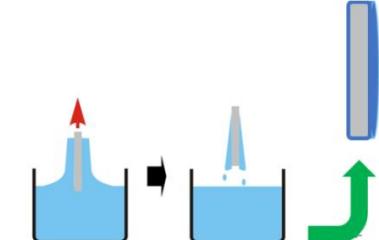
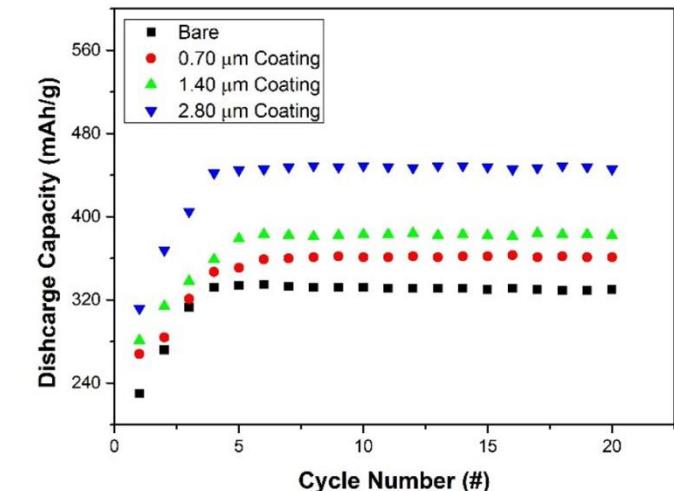
Collaboration
Dag Nerous, Stockholm University



Surface Modification
 $(\text{TiZr})_x (\text{V Ni Mn Cr})_2$



Encapsulated electrode
Mg50Ni50

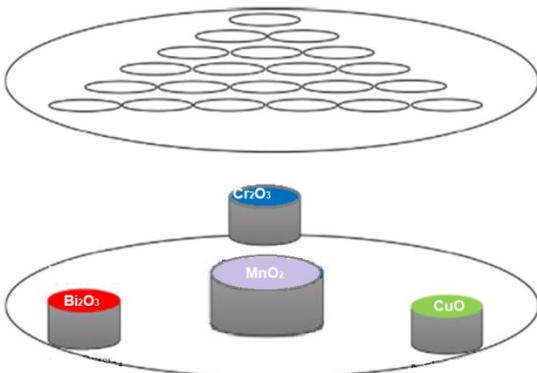


Alkaline Batteries

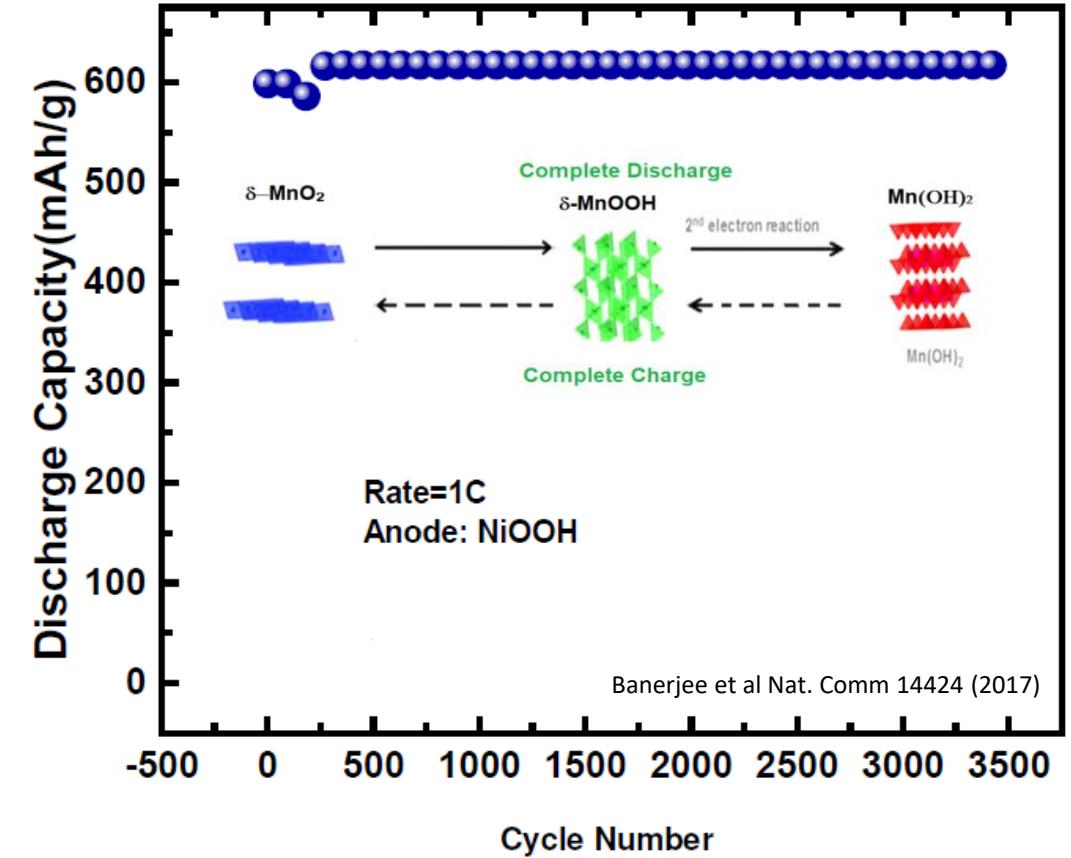
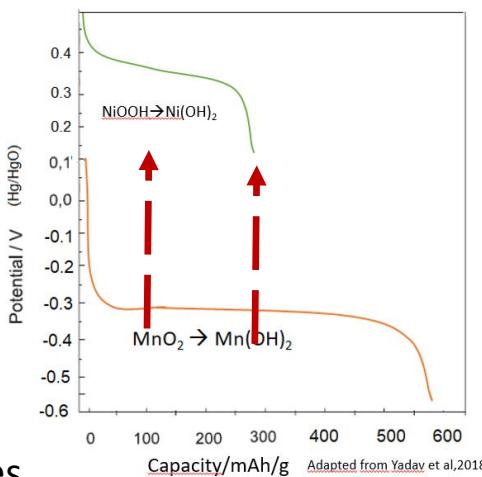
Development of δ -MnO₂ based cathode materials for rechargeable alkaline batteries:

1003-118M076

- Zn-MnO₂ Rechargeable Battery
- Improved 2e⁻ rechargeability
- Improved voltage profile



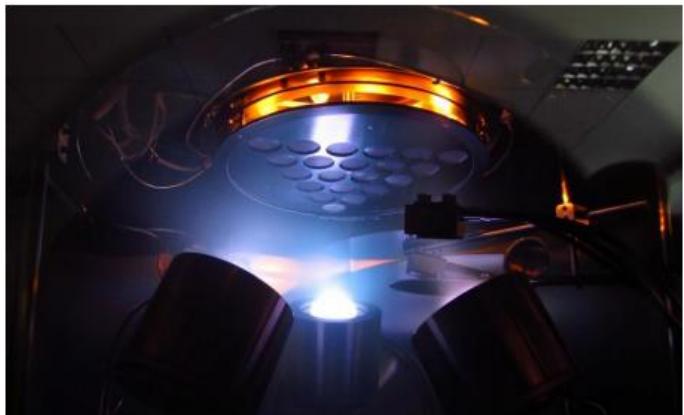
Combinatorial deposition of cathodes



Combinatorial search for improved battery chemistry

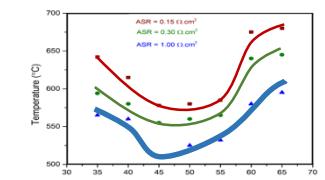
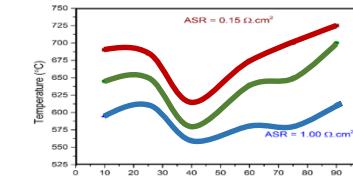
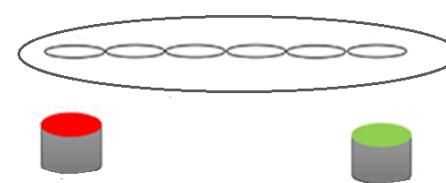
Development of layered cathode materials for rechargeable alkaline batteries:

1003-118M076



- 36 cathodes in a single experiment
- Fast initial electrochemical screening

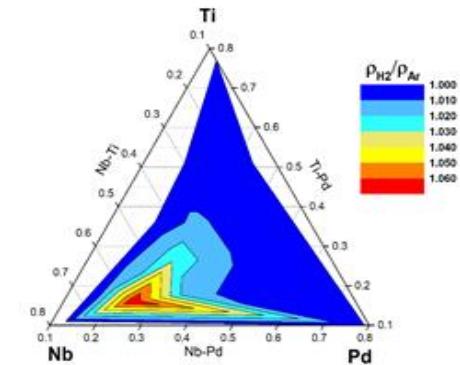
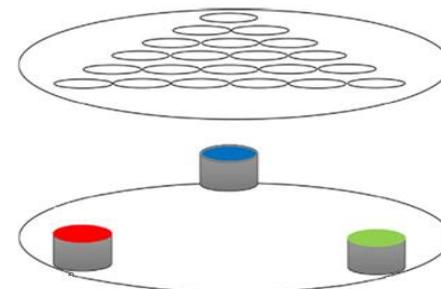
Binary



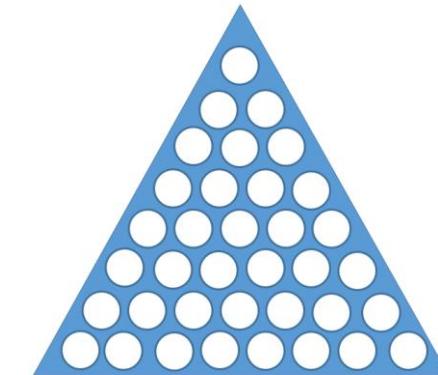
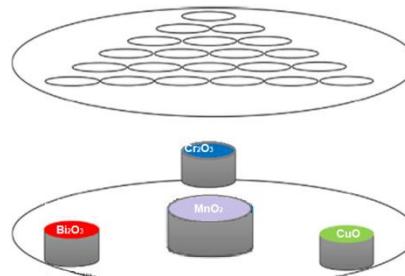
Combin. development of of electrocatalysts for ORR

D Sari, F Piskin, ZC Torunoglu, B Yasar, YE Kalay, T Ozturk Solid State Ionics 326 (2018) 124–130

Ternary



Multi- Component



Ongoing Research Themes

- Combinatorial Discovery of Improved/new Battery Chemistry
- Cathode Materials for Li-ion Batteries (specifically Ni and Li rich layered oxides and TM sulphides)
- Fast Ion Conductors for Solid State Li-ion Batteries (Computational DFT Approach)
- Anode Materials for Aqueous Li Batteries (Titanates)
- Improved anodes for Na-ion Batteries

- Redox Active Organic Materials for Organic Flow Batteries (Quinone based)
- Suspension Flow Battery (SFB) Technology

- Pseudocapacitive Materials for Supercapacitors (TM phosphides)
- Metal Nanowires for Flexible Supercapacitors
- Ultrasonic Spray Coating for Nanostructured Electrodes

- Electrocatalysts for ORR/OER
- MnO₂ based cathode materials for alkaline batteries
- Co free cathodes for alkaline batteries





Tayfur Öztürk
ENDAM,
Center for Energy Materials and
Storage Devices,
Middle East Technical University
6800 Ankara
endam@metu.edu.tr