Exceptional Energy and New Insight with Sodium – Selenium Battery based on Carbon Nanosheet Cathode and Pseudographite Anode

David Mitlin[1], Jia Ding[2]

[1] Clarkson University, Chemical & Biomolecular Engineering and Mechanical Engineering, 8 Clarkson Avenue, Potsdam NY 13699

[2] Materials Science and Engineering, State University of New York, Binghamton, New York, 13902, USA

COVER: Energy and Environmental Science, 2017, 10, 153-165.

Acknowledgement

Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-SC0018074.

Energy Storage --
The “Missing Link” in Renewable Energy

How to Provide Power when :

No sun? No wind?

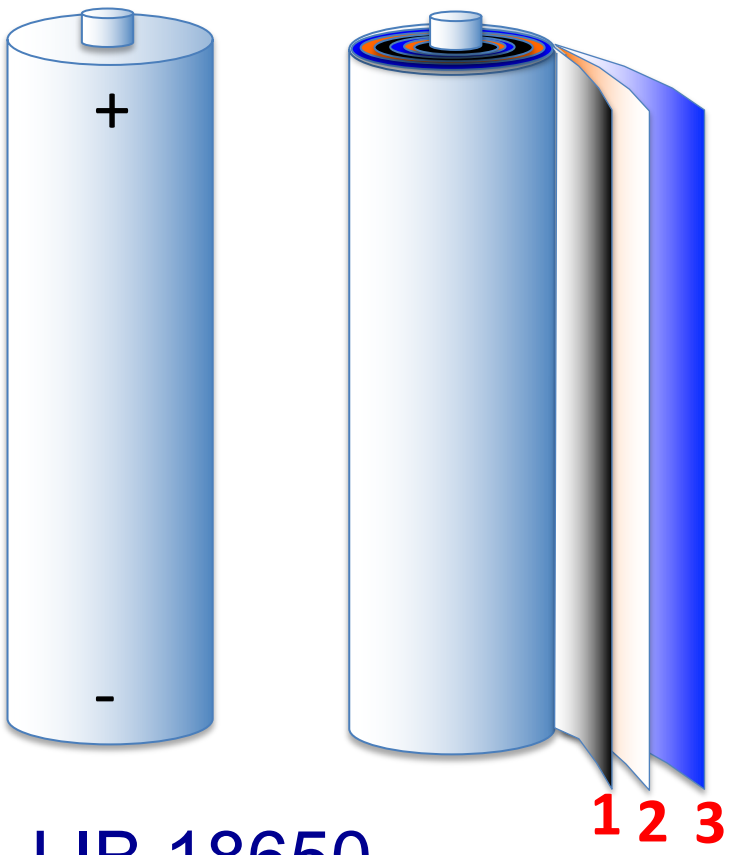
Key Forms of Storage: Lithium Ion Batteries (LIBs)
Electrochemical Capacitors
Battery – Capacitor Hybrids (HICs)

LIB Market
~ $ 30 Billion

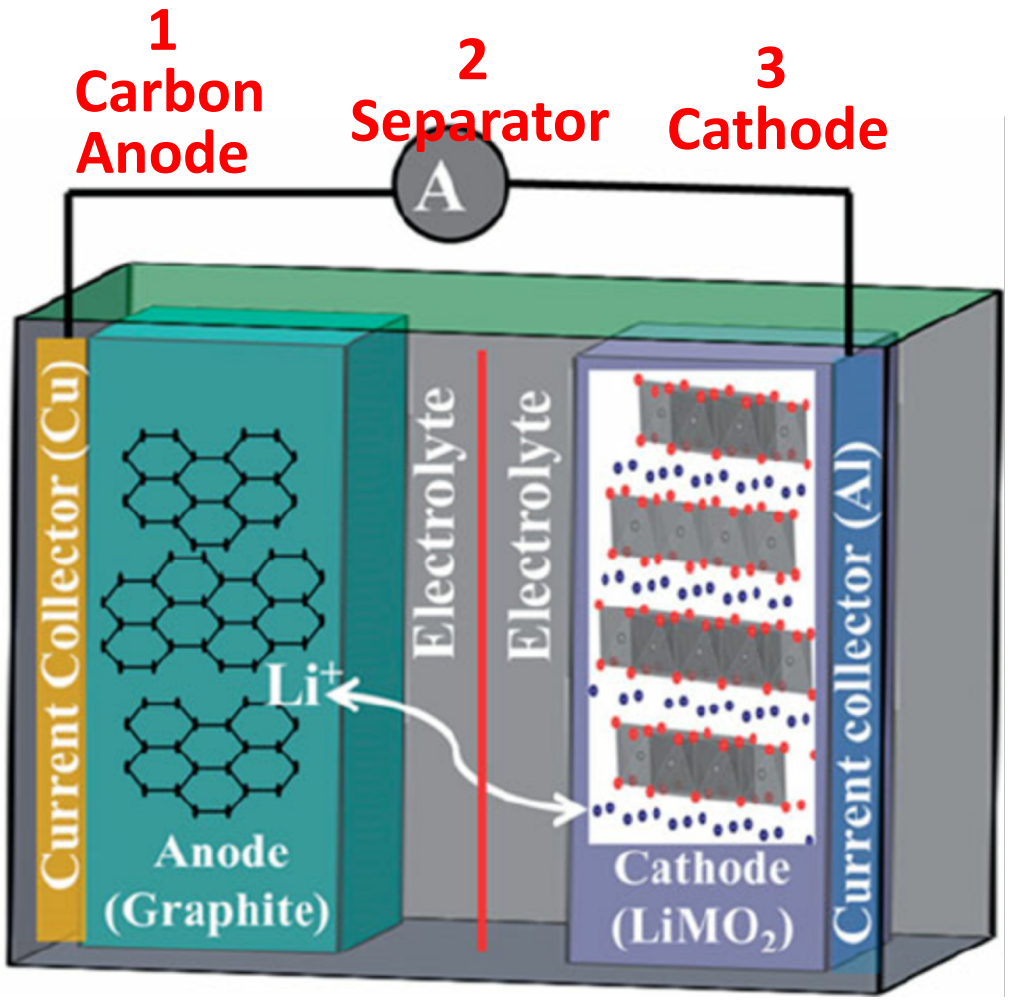
Ultracap Market
(power, cyclability)
~ $ 1 Billion

Grid Storage Market
Many $ Billions

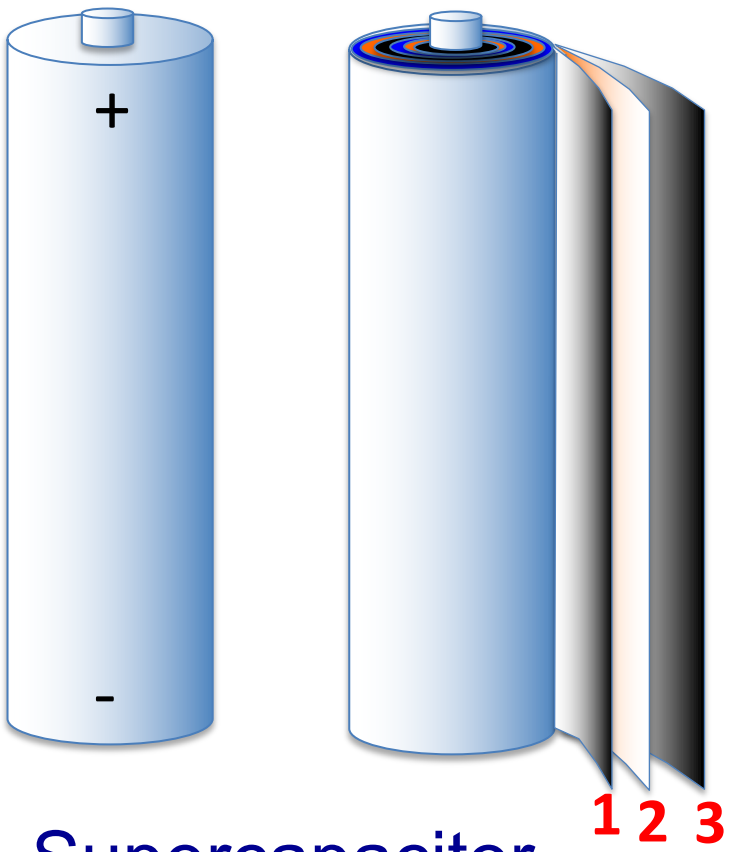
Carbon Electrodes - the Universal Anode for Ion Batteries, Host for Next Generation S (Se) Cathodes



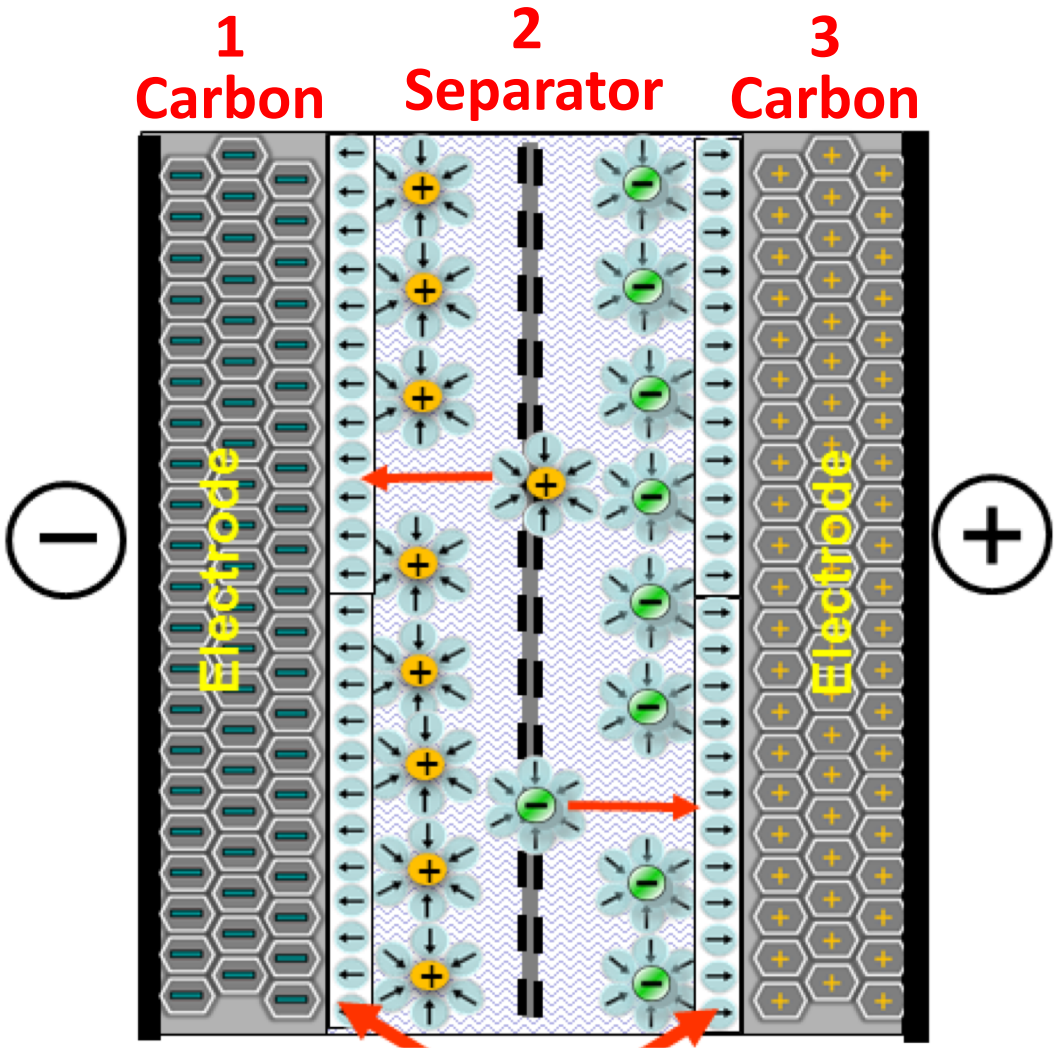
LIB 18650
Cylindrical Cell



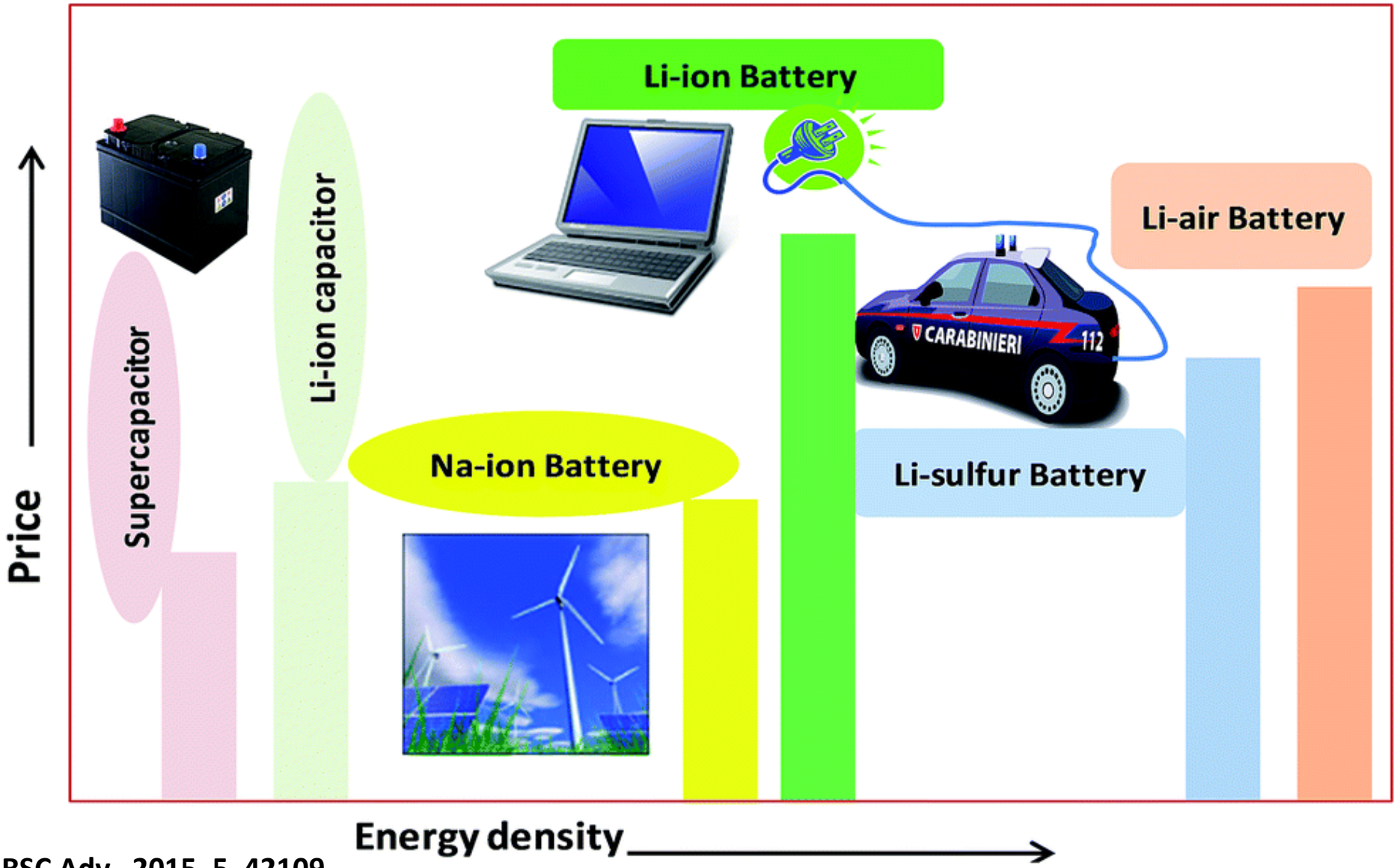
And….Carbon Electrodes--the Heart of an Capacitor and HIC – They Store Charge



Supercapacitor
Cylindrical Cell



Motivation for Sodium Ion Batteries and for Sulfur (Selenium) – Metal Batteries



RSC Adv., 2015, 5, 42109

Selenium Metal Batteries May be Useful for High Energy Grid Level Storage Applications

high purity 99.99 4N up selenium granule for selenium drum

FOB **Reference** Price: Get Latest Price

US $29-98 / Kilogram | 1 Kilogram/Kilograms (Min. Order)

Supply Ability: 300 Kilogram/Kilograms per Month

Port: Shanghai

Contact Supplier

Chat Now! Add to Favorites

- **Se vs. S electrical conductivity (1×10^{-11} S m^{-1} vs. 0.5×10^{-27} S m^{-1}) Much more reactive with Li/Na, less intermediate species**
- **Lower gravimetric capacity with Li/Na than sulfur (Na_2Se = 678 mAh/g, Na_2S = 1675 mAh/g)**
- **Comparable volumetric capacity (e.g. Na_2Se = 3250 mAh/cm^3, Na_2S = 3470 mAh/cm^3)**

Experimental

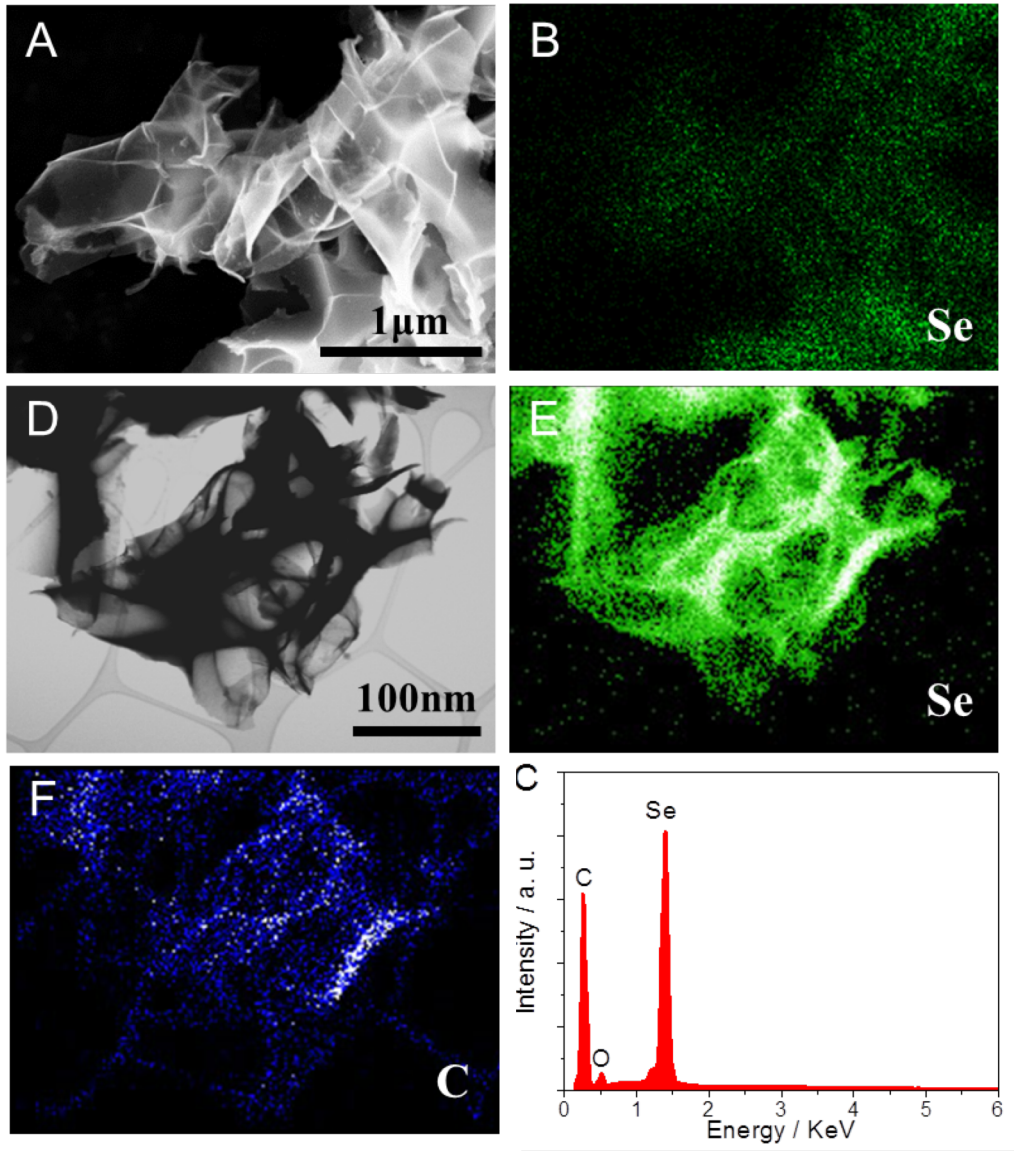
- Cellulose Nanocrystals as precursor for Carbon Nanosheets. Cellulose was carbonized and activated at 800°C for 1h with KOH.

- Se powder and carbon nanosheets were planetary ball milled under argon atmosphere.

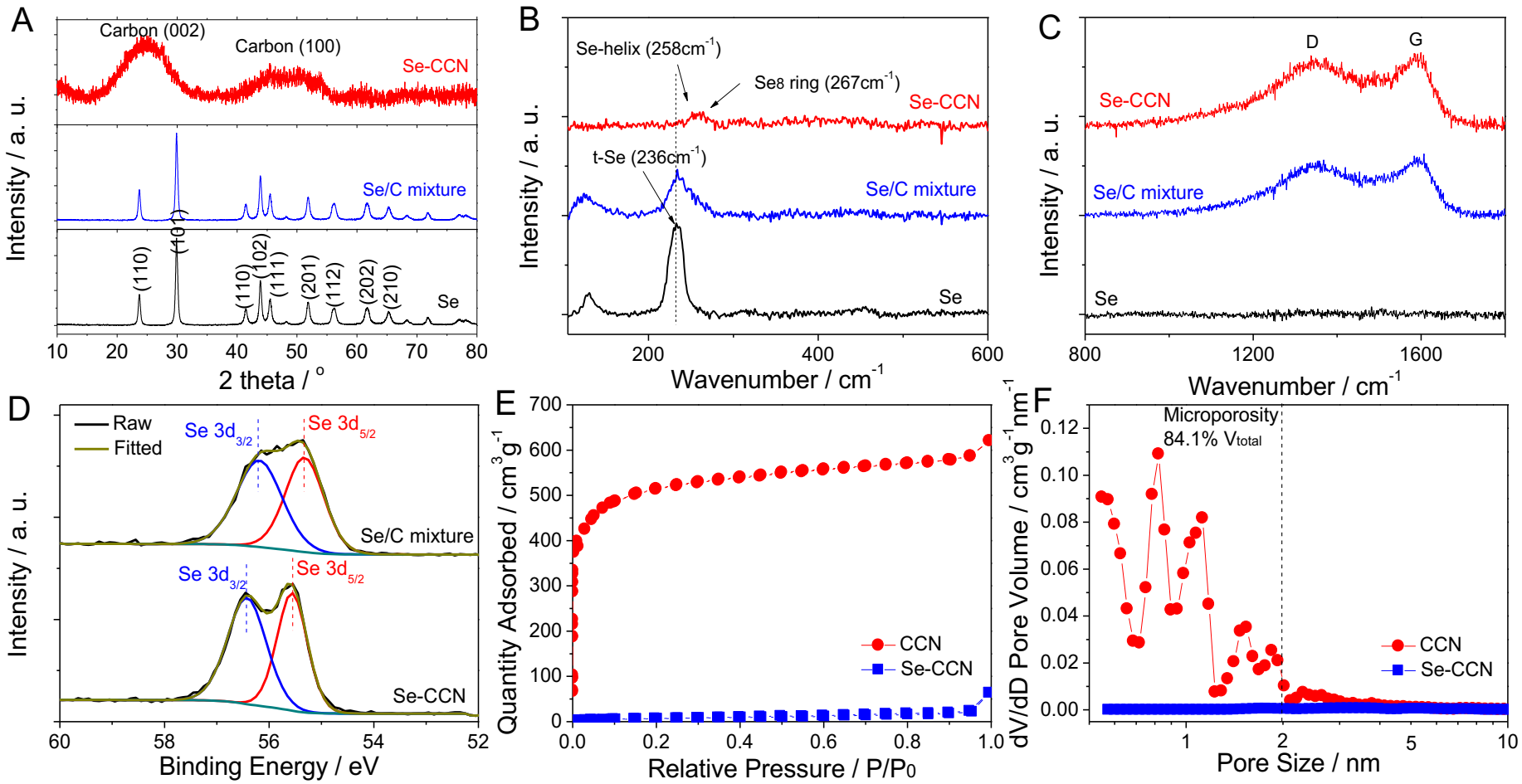
- The Se impregnation is two steps: 1) Se diffusion process which is conducted at 260°C for 12 h. 2) An Ar-filled glass tube containing powder is further soaked at 600°C for 3h

- Mass loading of Se is 53wt.%

- Se-Carbonized Cellulose Nanosheets Se-CCN as cathode.
- Pseudographitic carbon PGC as anode for full battery.



Se-Carbonized Cellulose Nanosheets Se-CCN as cathode: Structure

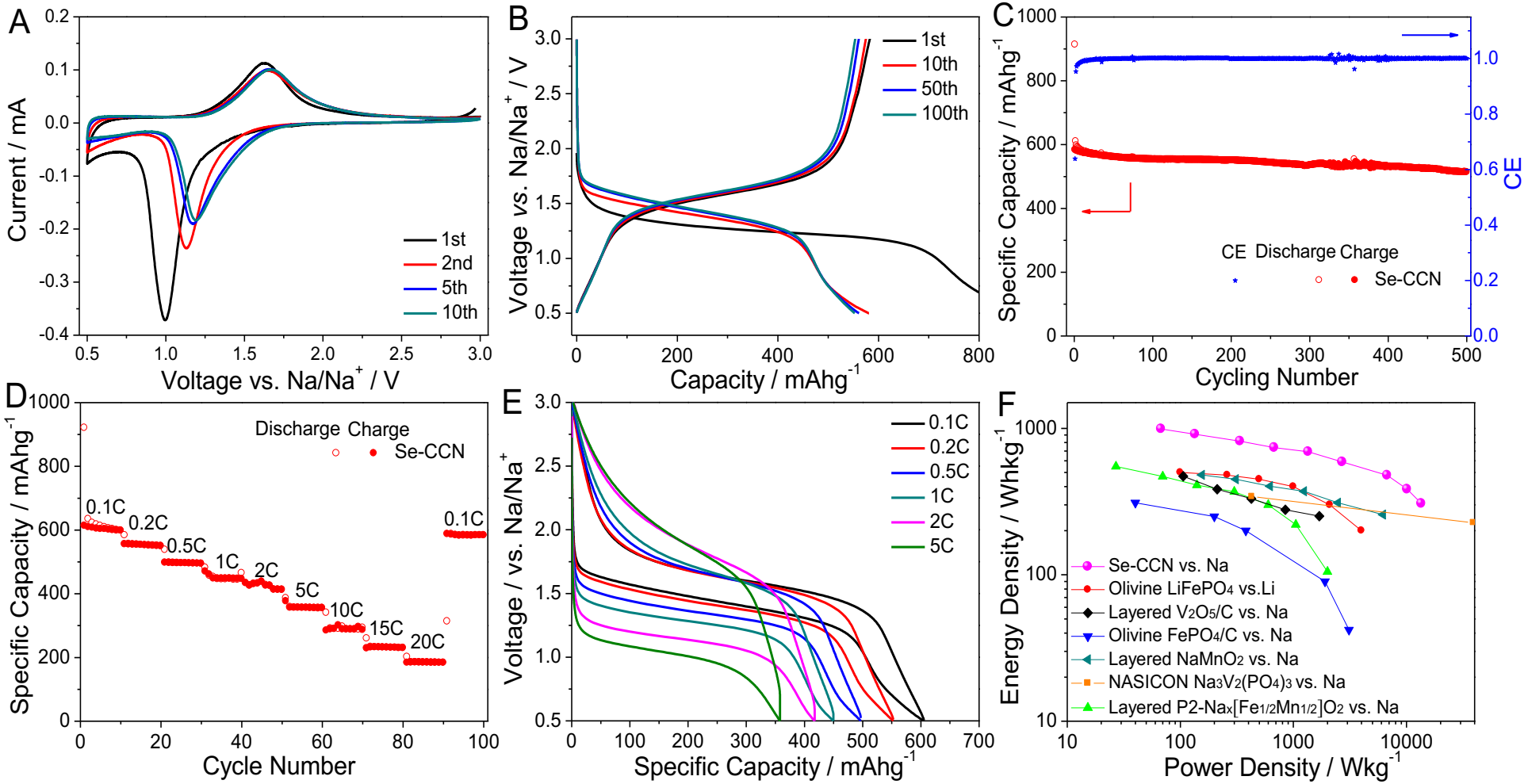


- **Se in Se-CCN is X-ray amorphous, with the only observed reflection being the broad (002) and (100) reflections associated with short-range ordering in the amorphous carbon matrix.**

- **Low-order Se is beneficial for cycling stability, due to inhibition of polyselenide formation that is known to be severe in crystalline Se and S electrodes against Li or Na.**

- **BET analysis shows that Se fills all the CCN pores. XPS shows bonding between Se and C.**

Se-Carbonized Cellulose Nanosheets Se-CCN as cathode

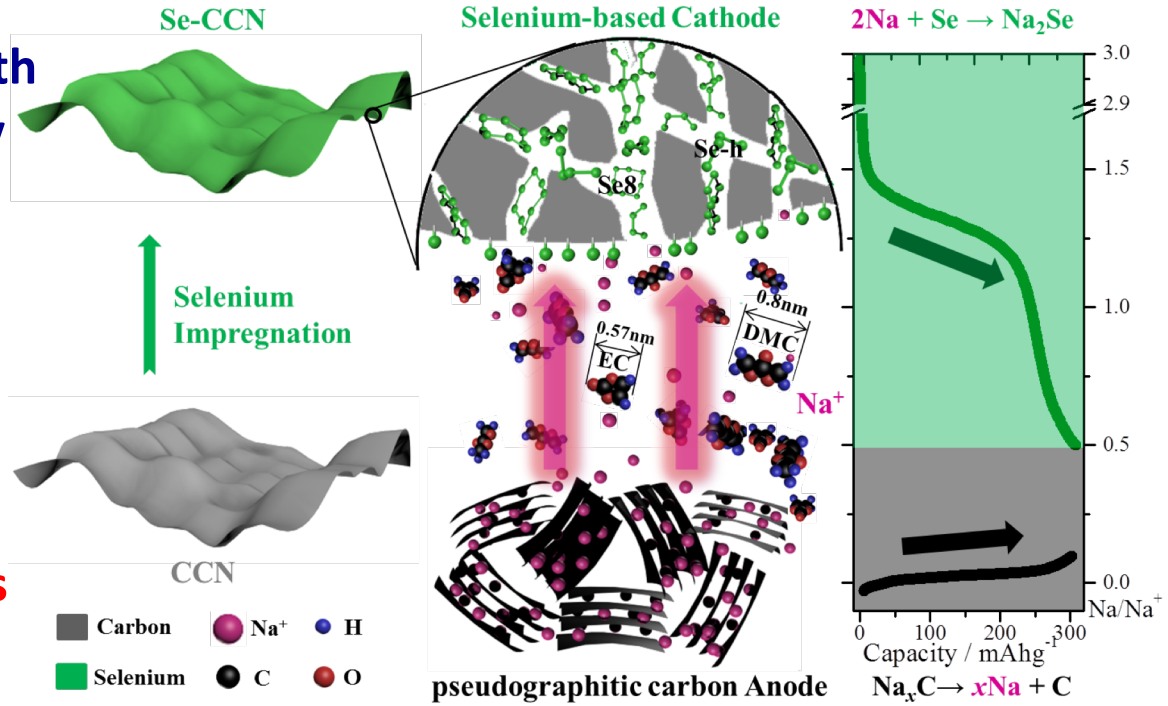


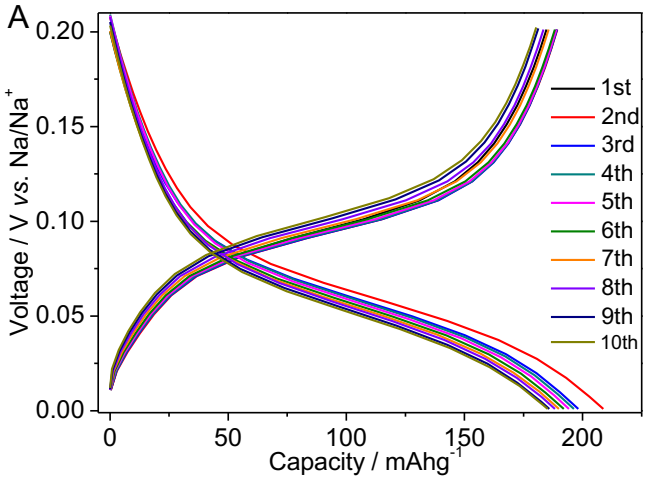
Electrochem test:1 M $NaClO_4$ in EC:DEC 1:1

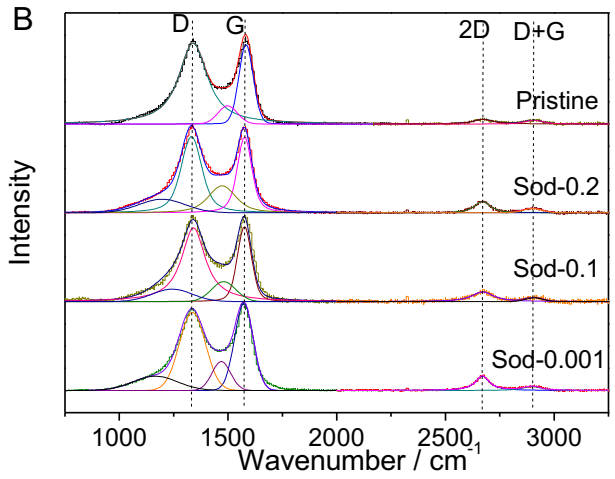
- **Single redox peak pair: direct phase change between Se and Na_2Se without the formation of soluble sodium polyselenide Na_2Se_n (n≥4).**
- **Se-CCN half-cell cycling capacity is quite stable over 500 cycles (88% retention), the shuttle effect is minimized. Theoretical capacity = 678 mAh g^{-1} based on Se.**

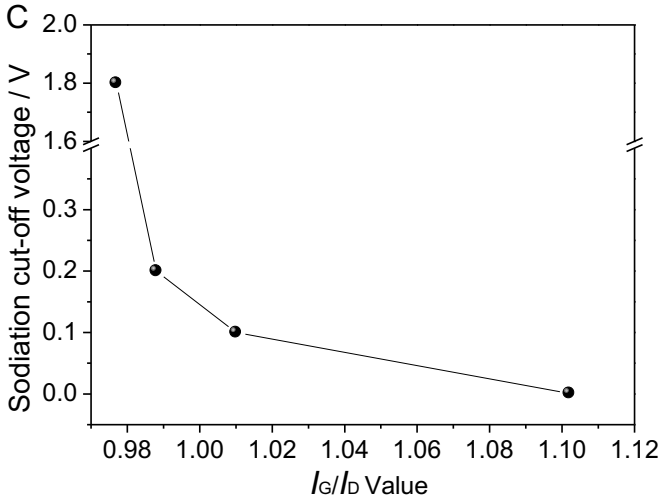
Pseudographitic Carbon Anode

- PGC is composed of partially ordered domains of graphene, with an interlayer spacing substantially larger than that of graphite.
- The dilated intergraphene layer spacing allows for reversible Na intercalation/deintercation.
- During intercalation, the PGC reversibly orders, i.e. it undergoes a partial staging reaction.

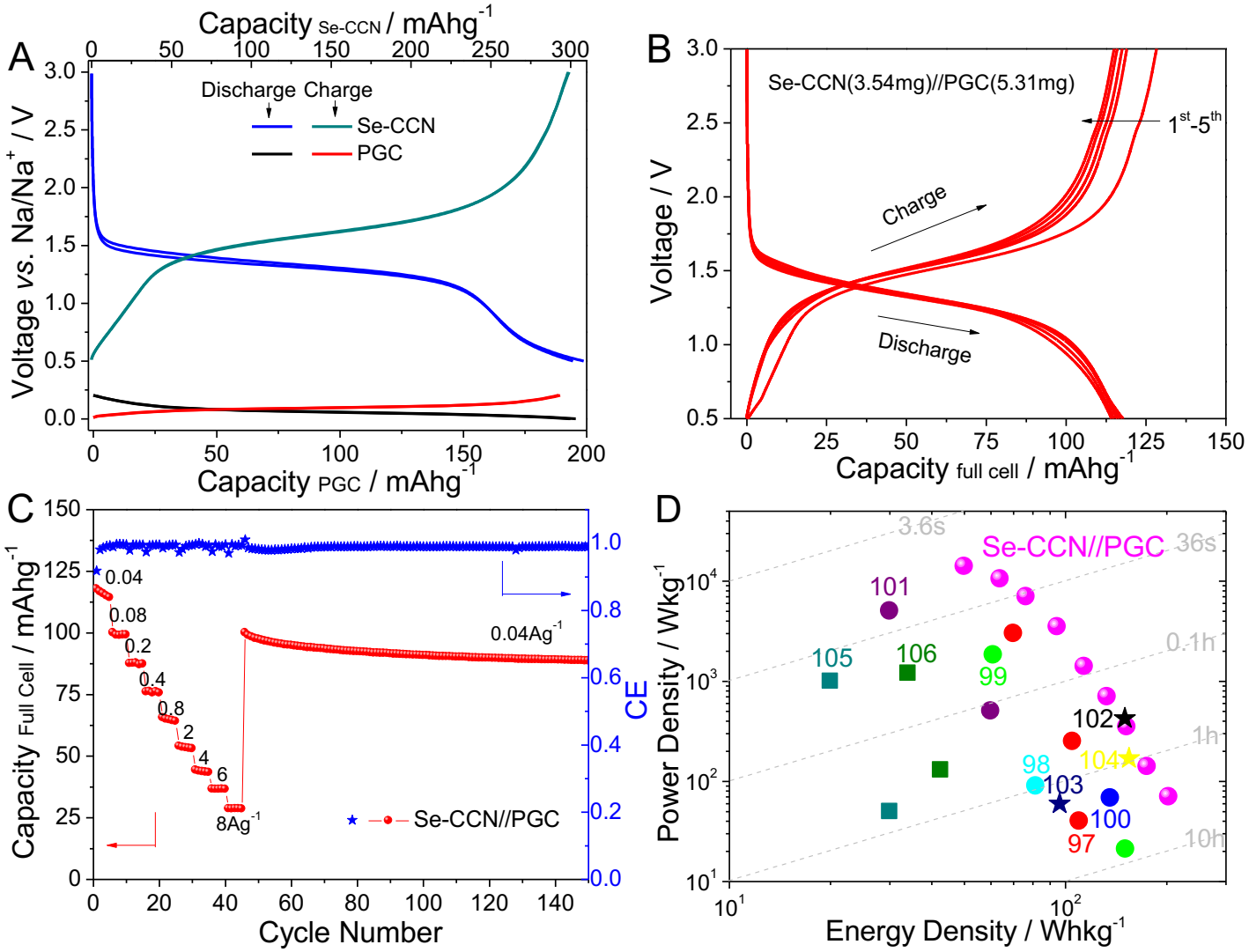








Full Cell: Pre-Sodiated Se-CCN Cathode vs. PGC Anode



- During battery charging Na^+ intercalates into the pseudographitic domains (i.e. $Na_xC \rightarrow xNa + C$) in the anode, Na_2Se transforms to Se.
- On the cathode side, Se-CCN displays 300 $mAhg^{-1}$ of capacity between 0.5-3 V vs. Na/Na^+ when normalized by the total mass of the material.

Selenium impregnated monolithic carbons as cathodes for high volumetric energy lithium and sodium metal batteries

David Mitlin[1], Jia Ding[2]

[1] *Clarkson University, Chemical & Biomolecular Engineering and Mechanical Engineering, 8 Clarkson Avenue, Potsdam NY 13699*

[2] *Materials Science and Engineering, State University of New York, Binghamton, New York, 13902, USA*

Adv. Energy Mater. 2017, 1701918

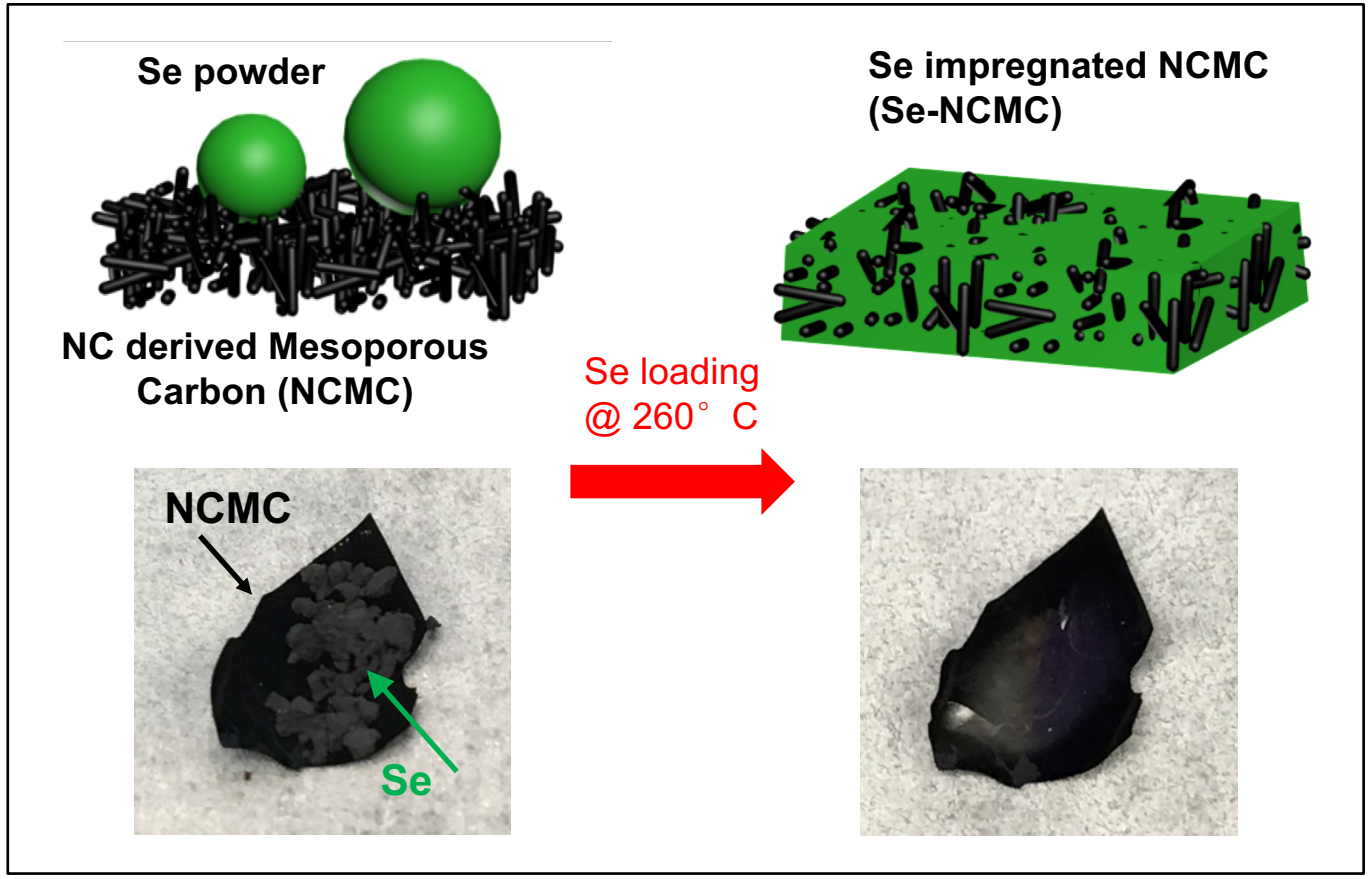
Acknowledgement
Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-SC0018074.

Experimental: Se impregnated monolithic carbons

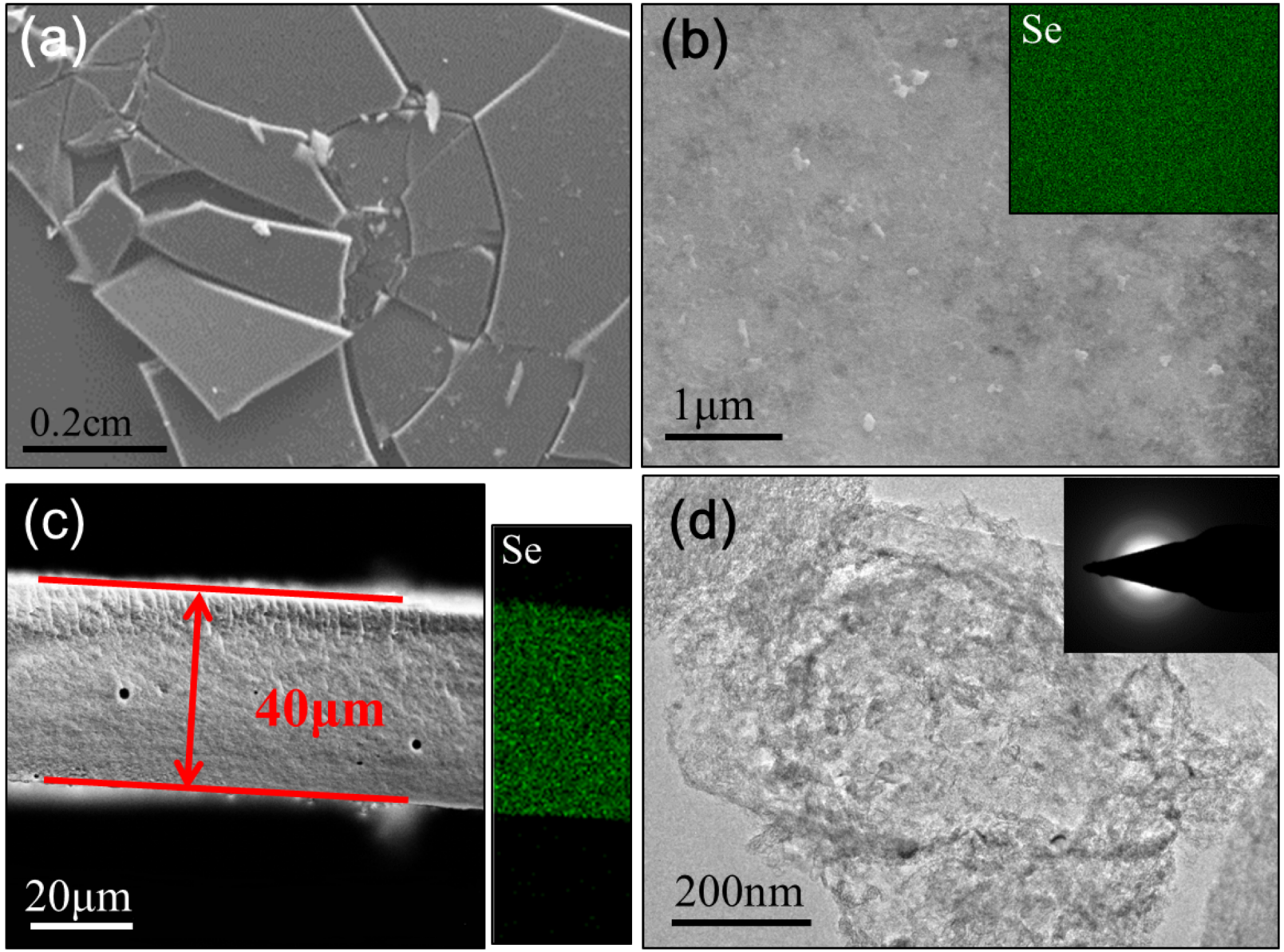
- NanoCellulose (NC) derived Mesoporous Carbon film (NCMC) was prepared by a sacrificial-template method, followed by carbonization.

- Start with a colloid of TEOS and NC, pyrolysis at 1000°C to get SiO_2/carbon, HF Etching to remove SiO_2, 260°C melt infiltration of Se

> 70wt.% loading Se

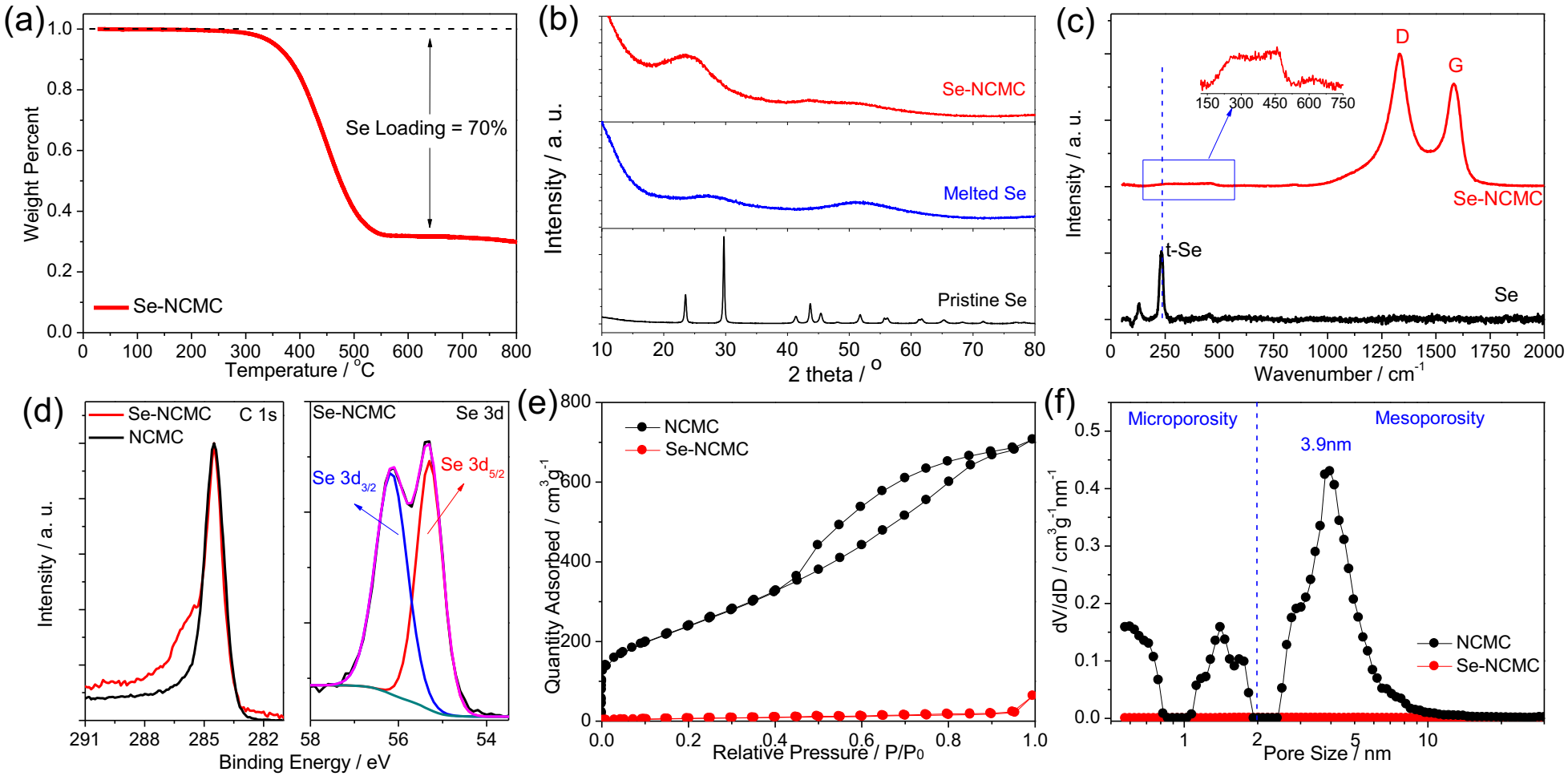


Structure: Se impregnated monolithic carbons



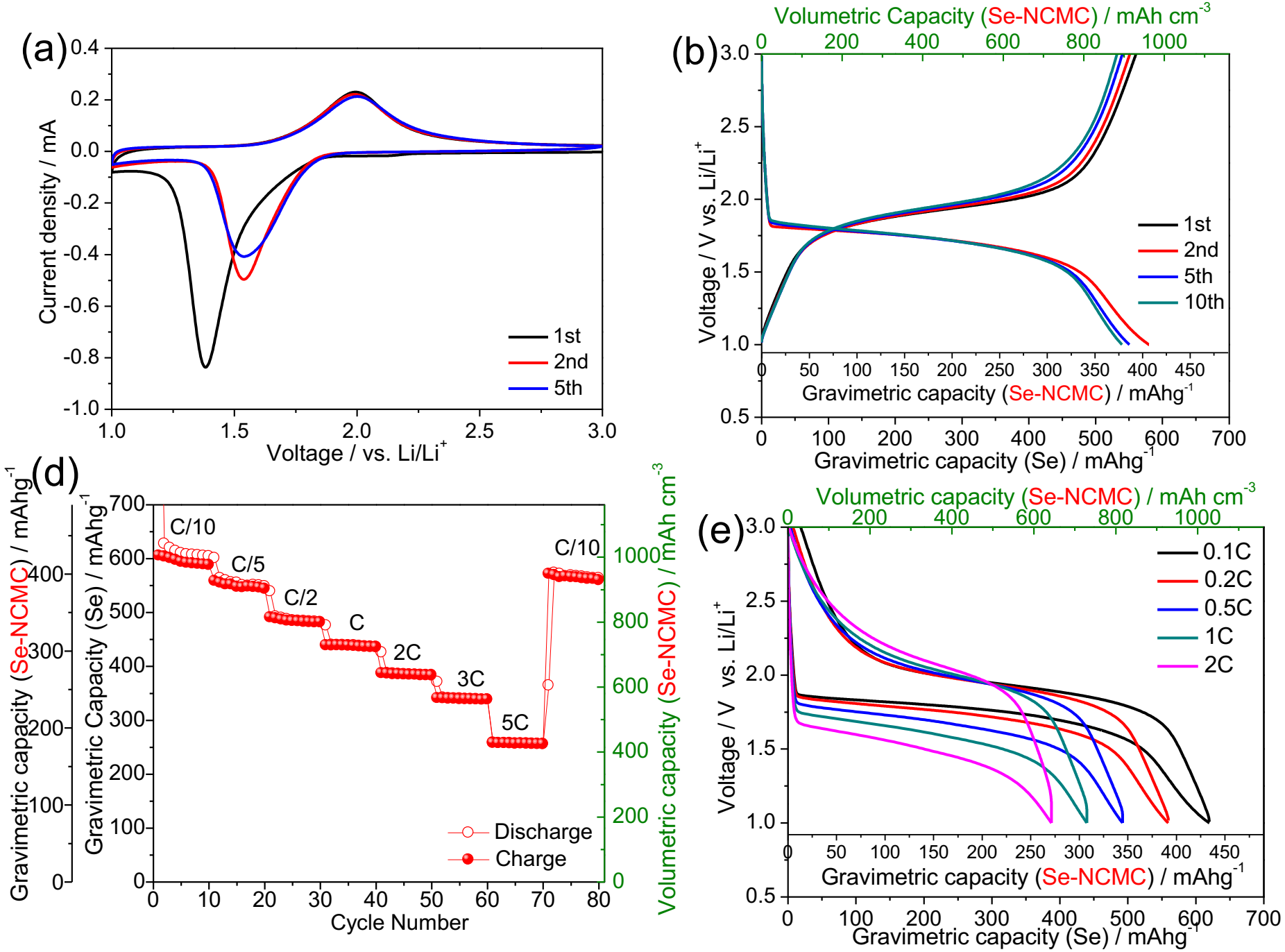
In Principle 2X in Energy compared to Powders

Structure: Se impregnated monolithic carbons

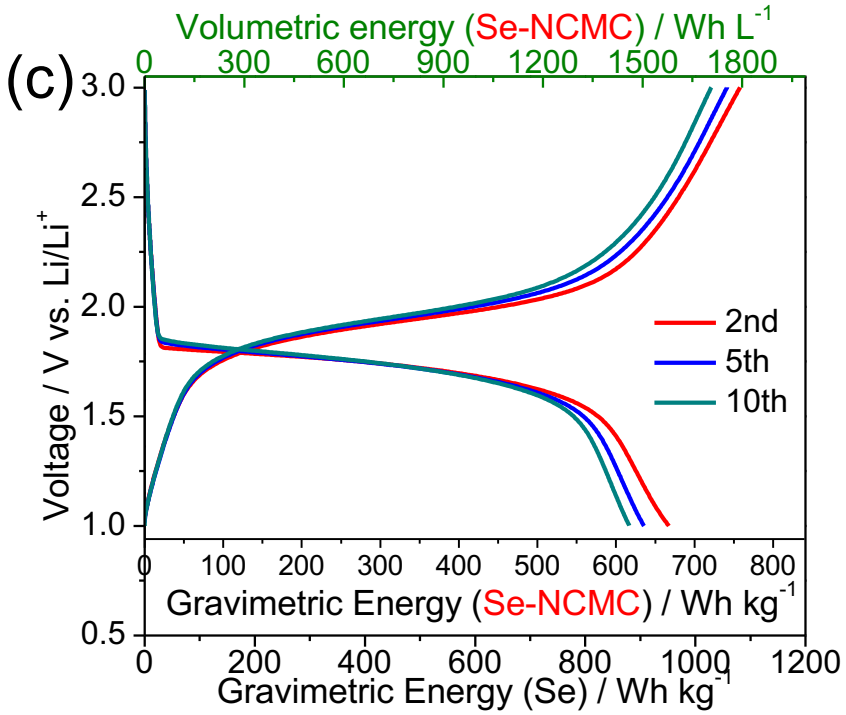


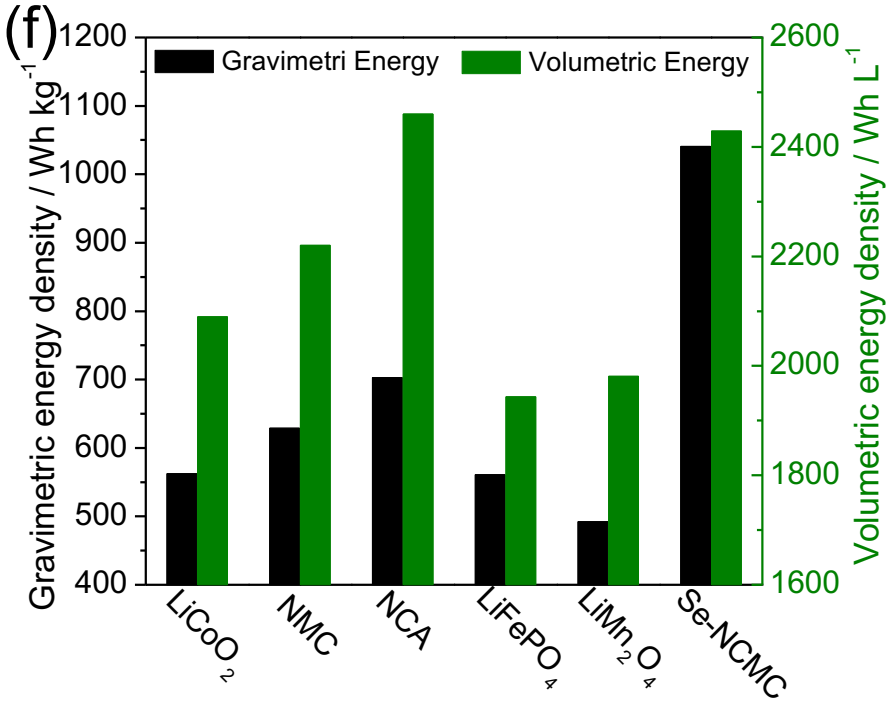
Selenium fills up the mespores and micropores, forming a dense self-standing monolith

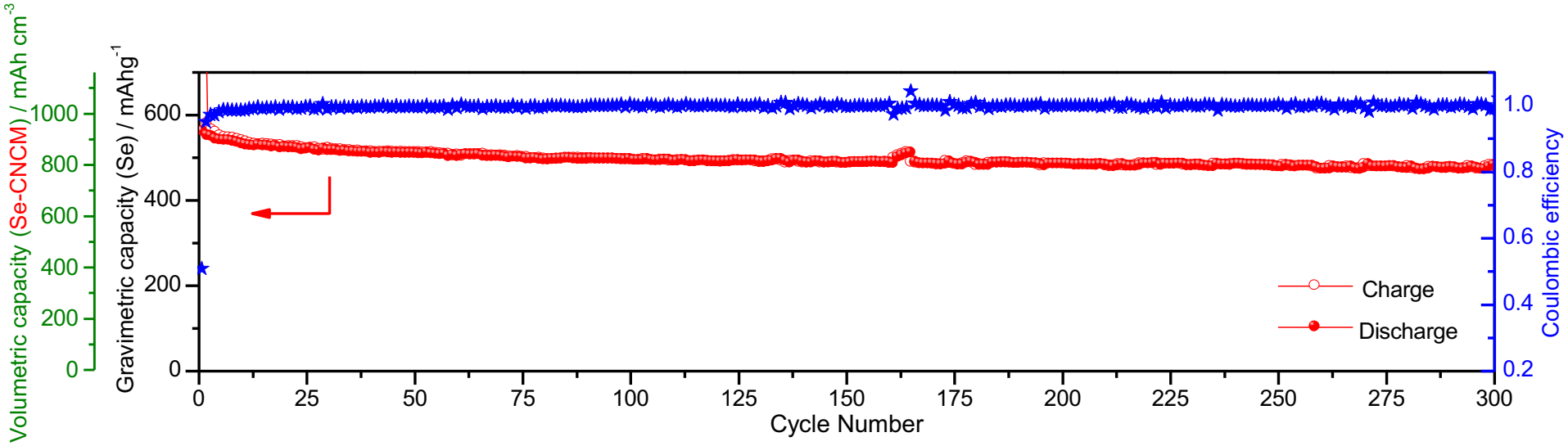
Performance vs. Lithium



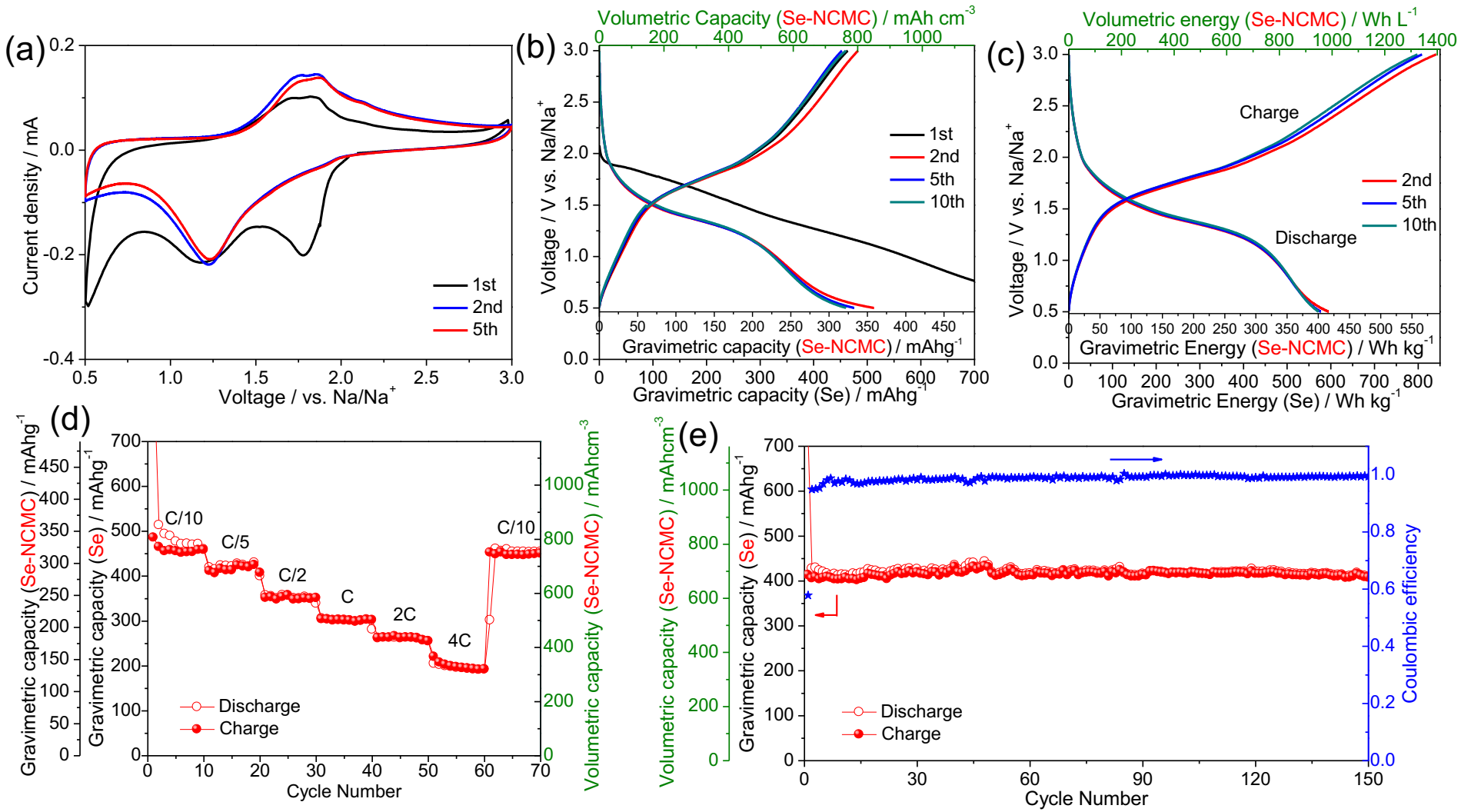
Performance vs. Lithium





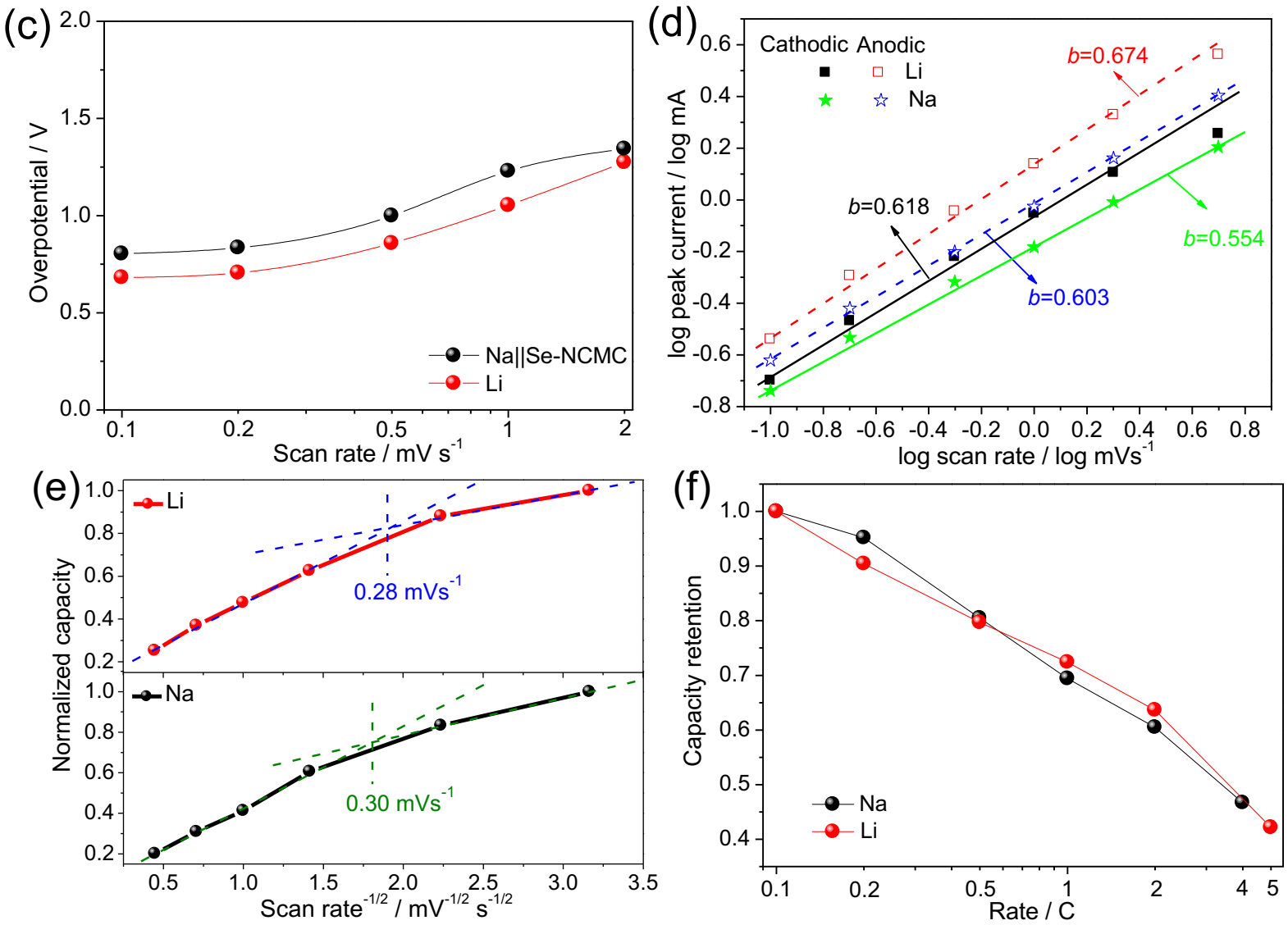


Performance vs. Sodium



Sodium Gives Lower Capacity and Energy and a Two Stage Plateau (hcp Na_2Se_2 intermediate)

Although Capacity with Na is Lower (less Se utilization), the Kinetics Seem Almost Identical



Overpotentials and Transition from Activation to Diffusion

Thank you for your attention!

Cover. *Energy & Environmental Science*, 2017, 10, 153-165.

Clarkson UNIVERSITY
defy convention