# Potassium Ion Batteries: A New Approach to Theoretical Computations of Anode Materials Liz Stippell **PI: Professor Oleg Prezhdo**

### Outline

**Potassium-ion batteries:** A potential alternative to Lithium-ion batteries

The new anode material: Generating structures from experimental data

Addressing density functional theory's shortcomings: Using ensemble DFT for more accurate results

Viability of the proposed anode: Calculations and comparisons

## Potassium-Ion Batteries

A potential alternative to Lithium-ion batteries

### Introduction to batteries



Flow of electrons and ions during the discharge stage



**Electrolyte** XPF<sub>6</sub> in EC:DEC (a mixture of ethylene carbonate and diethyl carbonate)

### The problem with lithium

Lithium 0.002% Earth abundance Uneven global distribution Expensive

ACS Applied Energy Materials 2020, 3 (10), 9478-9492.

Source: United States Geological Survey

	Min	<b>Reserves</b> <sup>6</sup>	
	<u>2021</u>	2022 <sup>e</sup>	
United States	W	W	1,000,000
Argentina	5,970	6,200	2,700,000
Australia	55,300	61,000	76,200,000
Brazil	e1,700	2,200	250,000
Canada	<u> </u>	500	930,000
Chile	28,300	39,000	9,300,000
China	e14,000	19,000	2,000,000
Portugal	e900	600	60,000
Zimbabwe	e710	800	310,000
Other countries <sup>8</sup>			3,300,000
World total (rounded)	<sup>9</sup> 107,000	<sup>9</sup> 130,000	26,000,000

🗯 GOV.UK

<u>Home</u> > <u>Transport</u> > <u>Maritime and shipping</u> > <u>Maritime and the environment</u>

News story

Government takes historic step towards net-zero with end of sale of new petrol and diesel cars by 2030 ∨ Menu

Q

### What makes an ideal ion?



### What makes an ideal ion?



## The New Anode Material

**Generating Structures from Experimental Data** 

### The need for new anode materials

#### Problem

The Potassium ion is 1.8x larger than the Lithium ion. It is also more reactive with graphite, a commonly used anode material in Lithium-Ion Batteries



Pristine Graphene Anode with Potassium lons			
Volume Expansion	58%		
Cycling Stability	75.5 mAh/g (100 cycles @ 0.05 A/g)		

### The need for new anode materials

#### Solution

#### Use nitrogen doping to create more stable and efficient anodes

Creates defects in the graphene structure that provide space for the larger potassium ion

The addition of pyridinic (6-member ring) and pyrrolic (5-member ring) nitrogen removes carbon atoms to create holes Creates accessible active sites in the graphene structure

Doping creates lone pair electrons on the nitrogen atoms that helps facilitate potassium adsorption

# Nitrogen-doped carbon nano necklace (N-CNN)



### Structural Data

Carbon	Nitrogen	Oxygen	Nitrogen Composition		
			Pyridinic N	Pyrrolic N	Graphitic N
85.63%	6.68%	7.69%	42.44%	55.70%	1.86%





STEM image elemental mapping



### Generating the molecular structure



### The importance of large-scale system analysis



14

# Addressing Density Functional Theory's Shortcomings

**Employing ensemble DFT for more accurate results** 

### Overview of density functional theory (DFT)

The energy is described by known terms of **independent** electrons, with a term introduced that accounts for the "unknown" (exchangecorrelation energy)



$$E = V_{ext}(\vec{r}) - \frac{1}{2} \sum_{i=1}^{N} \vec{\Delta_i^2} + \sum_{i>j}^{N} \frac{1}{r_{ij}} + E_{XC}$$
  
External Kinetic Hartree Exchange-  
potential energy energy correlation  
energy

$$\rho(\vec{r}) = \sum_{i} |\phi_{i}(\vec{r})|^{2}$$

### Where DFT breaks down: electron correlation

#### **Electron Correlation**

If there is a strong electron correlation, the electrons cannot be assumed to act independently of one another, and therefore a non-interacting approach for energy is inaccurate



#### $E_{corr} = \langle \Phi_{HF} | H - E_{HF} | \Psi \rangle$

The correlation energy is the difference between the exact Hamiltonian (H) and the HF energy

#### $P(\overrightarrow{r_1}, \overrightarrow{r_2}) \neq P(\overrightarrow{r_1})P(\overrightarrow{r_2})$

The correlated motion of (2) electrons cannot be taken as the product of the independent motions of said electrons

WIREs Computational Molecular Science 2015, 5 (1), 146-167.

### Electron correlation in the N-CNN



### Ensemble DFT (eDFT): spin-**R**estricted Ensemble-referenced Kohn-Sham (REKS)-DFT

The total energy of electrons in their ground state is a functional of the electron density. The electron density is described by a single Slater Determinant, which may be mapped onto a reference system The electron density is now

Advanced Review

 $\rho_s(\vec{r}) = \sum_{L=1}^{M} \lambda_L \rho_L(\vec{r}) \qquad \qquad E[\rho_s] = \sum_{L=1}^{M} \lambda_L E[\rho_L]$ 

Spin-restricted ensemble-referenced Kohn–Sham method: basic principles and application to strongly correlated ground and excited states of molecules Michael Filatov\*

The electron density is now described by a **weighted sum of Slater Determinants**, which can be mapped onto a reference system. A reference potential will always exist in eDFT

### REKS-DFT: expanding the energy term

$$E[\rho_{S}] = \sum_{L=1}^{M} \lambda_{L} E[\rho_{L}]$$

$$\lambda_{1} = \frac{n_{a}}{2}$$

$$\lambda_{2} = \frac{n_{b}}{2}$$

$$\lambda_{3} = -\lambda_{4} = \lambda_{5} = -\lambda_{6} = \frac{1}{2} f(n_{a}, n_{b}) = \frac{1}{2} (n_{a}n_{b})^{1 - \frac{1}{2} (n_{a}n_{b} + \delta)}$$

$$E[\rho_{S}]$$

$$= \frac{n_{a}}{2} E[\dots \phi_{a} \overline{\phi_{a}}] + \frac{n_{b}}{2} E[\dots \phi_{b} \overline{\phi_{b}}] + f(n_{a}, n_{b}) \left(\frac{1}{2} E[\dots \phi_{a} \phi_{b}] - \frac{1}{2} E[\dots \phi_{a} \overline{\phi_{b}}] + \frac{1}{2} E[\dots \overline{\phi_{a}} \phi_{b}] - \frac{1}{2} E[\dots \overline{\phi_{a}} \phi_{b}]\right)$$

\* Indicates singular Slater Determinant: allows for use of XC functionals

$$n_a$$
,  $n_b$  are two electrons in the  
degenerate state  
(due to fractionally occupied  
orbitals)  
 $n_a + n_b = 2$ 

WIREs Computational Molecular Science 2015, 5 (1), 146-167.

Damping Factor  $\delta = 0.4$ Allows for smooth convergence when the ensemble determinant collapses into the standard KS determinant.

### **REKS-DFT: Collapsing into KS-DFT**

**Interpolation Function:** b  $f(n_a, n_b) = (n_a * n_b)^{1 - \frac{n_a * n_b + \delta}{2(1 + \delta)}}$ b а а Fractional Occupation **Interpolation Function Numbers**  $f(n_a, n_b) = (n_a * n_b)^{1 - \frac{1.4}{2(1+0.4)}}$  $= (n_a * n_b)^{\frac{1}{2}}$  $n_a \sim n_b \sim 1$ **REKS-DFT KS-DFT**  $f(n_a, n_b) = (n_a * n_b)^{1 - \frac{0.4}{2(1+0.4)}}$  $n_a \sim 2$  $n_b \sim 0$  $\approx (n_a * n_b)^1$ 

### Summary of REKS-DFT: methods comparison

### eDFT (REKS)

- Applies to any system
- Energy described by sum of weighted Slater Determinants
- Collapses into KS-DFT at weak correlations

### DFT (KS)

- Does not apply to every system
- Energy described by single Slater Determinant
- Does not account for interactions between electrons

## Viability of the Proposed Anode

**Calculations and Comparisions** 

# Experimentally described properties of the N-CNN and relevant benchmarks

Property	N-CNN	Graphite
Cycling Stability	174 mAh/g (1,000 cycles @ 1 A/g)	75.5 mAh/g (100 cycles @ 0.05 A/g)
Interlayer Volume Expansion	11%	58%



### **REKS-DFT: computational process in GAMESS**

#### GAMESS: General Atomic and Molecular Electronic Structure System Journal of Computational Chemistry 1993, 14 (11), 1347-1363. Run a Restricted Hatree-Fock (RHF) calculation SCFTYP=RHF Needed to compute the eigenvalues. GAMESS can make an initial guess of the eigenvalues for REKS, but it is a poor guess DFTTYP=PBE Take eigenvalues from RHF Coordinates: XYZ format calculation for use in REKS SCFTYP=REKS calculation

### Adsorption Energy

**Adsorption:** The attachment of an ion to the surface of a solid

**Adsorption Energy:** The energy decrease that occurs when an atom/ion undergoes adsorption on a surface

**Experimental.** Initial spacing 4 Å, after discharging the spacing ranges from 4.2 Å to 4.7 Å (average spacing of 4.45 Å after discharging)

#### Why negative adsorption energies?

The more negative the adsorption energy, the higher stability of the adsorbed structure. Values lower than -0.87 eV are ideal.

physica status solidi (a) **2020**, 217 (21), 2000433. Adsorption Energy vs. Interlayer Distance, pristine graphene





Increasing Nitrogen doping at active sites increases magnitude of adsorption energy

### Adsorption Energy



Journal of Molecular Modeling **2023**, 29 (5), 139.



### **Open-Circuit Voltage**



Volume change ( $\Delta V$ ) and entropy change ( $\Delta S$ ) are negligible and can therefore be ignored:

 $CNN + xK^+ + xe^- \leftrightarrow K_xCNN$ 

$$OCV = -\frac{E_{ads}}{\Delta n * Z * F}$$

### Maximum Theoretical Capacity

$$C = \frac{xF}{M}$$

x = Maximum concentration of K+ ions
Determined by adsorption concentration test
F = Faraday constant (26.8 Ah/mol)
M = Molar mass of anode material = 5758.643 g/mol

For competitive theoretical capacity: Specific Capacity Li-graphite system = 372 mAh/g

$$372\frac{mAh}{g} = 0.372\frac{Ah}{g} = \frac{xF}{M} = \frac{x \times 26.8\frac{Ah}{mol}}{5758.643 g/mol}$$

 $x = 79.5 \approx 80 a toms = 17.2\% w.r.t.structure$ 



### Maximum Theoretical Capacity



 $C = \frac{xF}{M}$ 

# Summary: competency as compared to other potential K+ anode materials

Material	Cycling Performance
N-CNN	174 mAh/g (1,000 cycles, 1 A/g)
N/S codoped carbon nanocapsule	150 mAh/g (2,000 cycles, 2 A/g)
Carbon microspheres knitted by Carbon nanotubes	155 mAh/g (1,000 cycles, 0.279 A/g)
N-doped Carbon nanosheets	151 mAh/g (1,000 cycles, 1 A/g)
P-doped glucose combined with multiwalled Carbon nanotubes	148.1 mAh/g (950 cycles, 0.2 A/g)

## **Conclusions and Future Work**

### Conclusions

✓ There is a need to produce new batteries with other ions such as Potassium to combat issues regarding Lithium

✓ Random structural generation methods can be used to generate structures based on experimental XPS data

✓ The REKS DFT method provides an opportunity for higher accuracy calculations for systems DFT may struggle with

✓ The anode material described in this work has competitive characteristics as compared to other anode materials

### Future Work

- Large-scale study comparing various doping concentrations to see if there is an optimal doping composition
- Apply the doping/defect generation method to other types of doping such as boron and silicon
- Address discrepancies in literature: adsorption energies of nitrogendoped active sites, importance of doping and type of doping
- Apply REKS DFT to other systems, such as those involving metal complexes, crystal structures

# Extra Slides

### Synthesis of N-CNN

- Homogenous mixture of the precursors (ZIF-67, PAN) are electrospun to create a fiber membrane
- 2. Annealing treatment in  $H_2/Ar$  at 700° C
  - 1. Pyrolysis of organic ligands (heating in absence of oxygen)
  - 2. Carbonization of the structure (Transforming material into a carbonbased material, in the absence of oxygen)
  - 3. During this simultaneous process, the structure becomes doped with Nitrogen.
  - 4. The Cobalt is then etched away using sulfuric acid.

*ZIF: Zeolitic Imidazolate Framework PAN: PolyAcryloNitrile* 



### Generating the Molecular Structure



### Generating the Molecular Structure

$$A_{2} = A_{0} - \frac{N_{pyridine-final}}{3} - N_{pyrrole-final} + Ox$$
  
$$C_{remove} = \frac{N_{pyridine-final}}{3} + N_{pyrrole-final}$$

$$\begin{split} N_{pyridine} &= 6.68 * 0.4244 = 2.83\% \\ N_{pyrrole} &= 6.68 * 0.557 = 3.72\% \\ N_g &= 6.68 * 0.0189 = 0.13\% \\ Ox &= 0.0769 = 7.69\% \end{split}$$

$$\begin{split} N_{pyridine-final} &= 0.0283 * A_2 \\ N_{pyrrole-final} &= 0.0372 * A_2 \\ N_{g-final} &= 0.0013 * A_2 \\ Ox_{final} &= 0.0769 * A_2 \end{split}$$

Carl	bon	Nitroge	n Oxygen	Nitrogen Composition		sition
				Pyridinic N	Pyrrolic N	Graphitic N
85.6	53%	6.68%	7.69%	42.44%	55.70%	1.86%
	Inputs					
	$A_0$ = Starting number of carbons					
	N <sub>pyridine</sub> = Percent of pyridine as compared to the entire structure					
	N <sub>pyrrole</sub> = Percent of pyrrole as compared to the entire structure					
	N <sub>g</sub> = Percent graphitic nitrogen as compared to the entire structure					
	Ox <sub>final.</sub> = Percent oxygen of the final structure					

### Generating the Molecular Structure

Oxygen Nitrogen



### Generating the Structure: Improving Oxygen Doping

- Bonds mentioned in experimental XPS:
  - 1. C=O
  - 2. C-OH
  - 3. C-O-C
  - 4. COOH
- C-O-C, C-OH: out of plane, no replacement of Carbon (will have to change Z coordinates)
- C=O, COOH: appears to only be present on edges



### Generating the Structure: Creating Pyrrolic Nitrogens

• Carbon pyrrole angles: 107.18 degrees (iqmol minimization)



### Generating the Structure: Creating Pyrrolic Nitrogens

- Determining how much to move the points by
  - Take origin as point to revolve angle around
  - Know that point to be moved lies ~120° from origin
  - Know that length of bond = 1.51 Å\* = r

• New points will be (theta represents change in angle):  $x' = xcos(\theta) - ysin(\theta)$ 

• Points G, H in new geometry:

$$new = original_x + x_{change}$$
  
$$new = original_y + y_{change}$$

 $x = rcos(\theta)$  $y = rsin(\theta)$ 

 $y' = ycos(\theta) + xsin(\theta)$ 

 $\begin{aligned} x_{change} &= x' - x \\ y_{change} &= y' - y \end{aligned}$ 

\*In pi-conjugated system, this value ~1.48



### **REKS-DFT: Fractionally Occupied Orbitals**

Fractionally occupied orbitals appear from ensemble KS densities



### **REKS-DFT: Expanding the Energy Term**



 $n_a$ ,  $n_b$  are two electrons in the degenerate state  $n_a + n_b = 2$ 

\* Indicates singular Slater Determinant

### Why REKS-DFT?







#### Key Finding:

As system length increases, singular determinant DFT methods produced unreasonable energy values

# Experimentally Described Properties of the N-CNN

Property	N-CNN	Graphite
Cycling Stability	174 mAh/g (1,000 cycles @ 1 A/g)	75.5 mAh/g (100 cycles @ 0.05 A/g)
Interlayer Volume Expansion	11%	58%

### Calculations and Benchmarks



#### Discrepancies in Adsorption Energies Í ΔEa= -3.128 eV ΔEa= -3.195 eV 0.312 eV 0.145 eV difference difference a b 0 $\Delta E_a = -3.05 \text{ eV}$ $\Delta E_a = -3.44 \text{ eV}$

# Coulombic Efficiencies & the Solid Electrolyte Interface (SEI)

- SEI formed through interactions between potassium ions and functional group remnants from PAN starter
- SEI greatly decreases the efficiency and capacity of the anode material

Cycle	Capacity (mAh/g)		
1st	1378		
2nd	1012		
50th	313		
100th	288		



### Conclusions

- ✓ There is a need to produce new batteries with other ions such as Potassium to combat issues regarding Lithium
- ✓ Random structural generation methods can be used to generate structures based on experimental XPS data
- ✓ The REKS DFT method provides an opportunity for higher accuracy calculations for systems DFT may struggle with
- ✓ The anode material described in this work has competitive characteristics as compared to other anode materials