s-Tetrazines as Active Materials for Na-ion Battery

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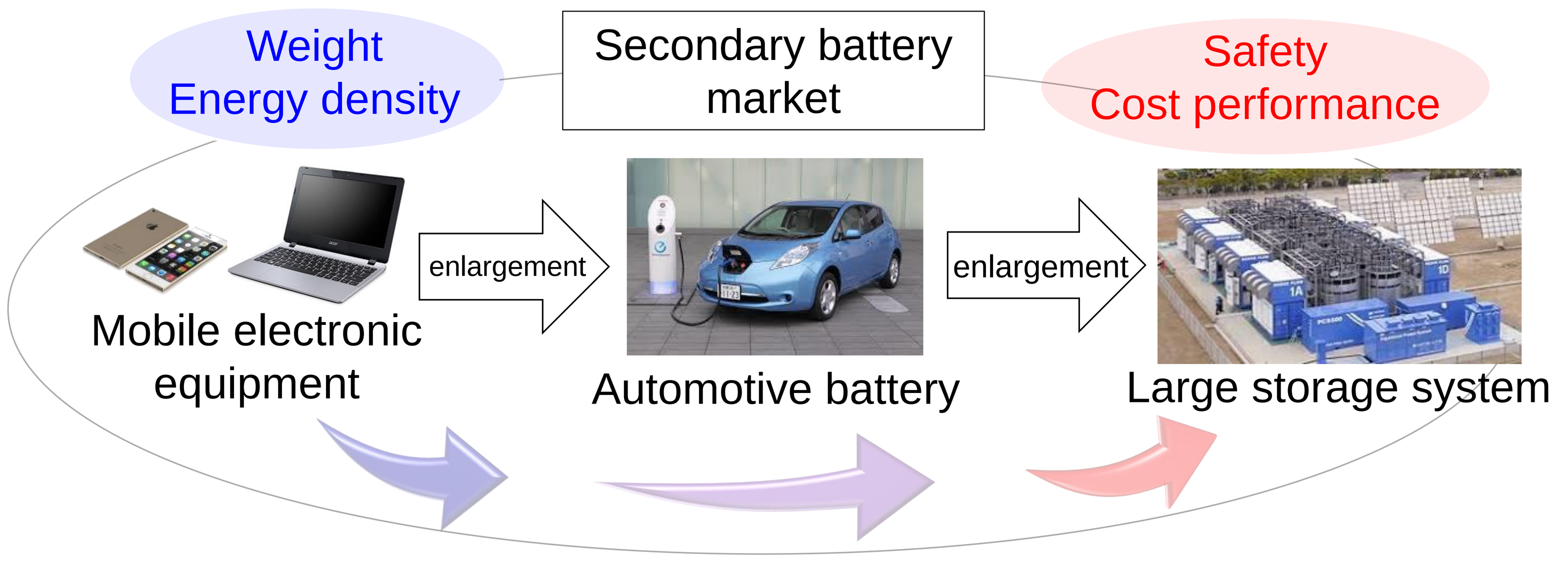
Introduction

■Change of society needs against secondary battery



■Comparison of Na and Li

	Clarke number	Cost (carbonate)	Theoretical capacity	Ion volume	Standard electrode potential (V vs.SHE)
Na	2.63	150 $/t	1166 mAh/g	6.54 Å³	-2.714 V
Li	0.006	5000 $/t	3861 mAh/g	3.05 Å³	-3.045 V

Disadvantage
- ◆Low energy density
- ◆Large ion-volume

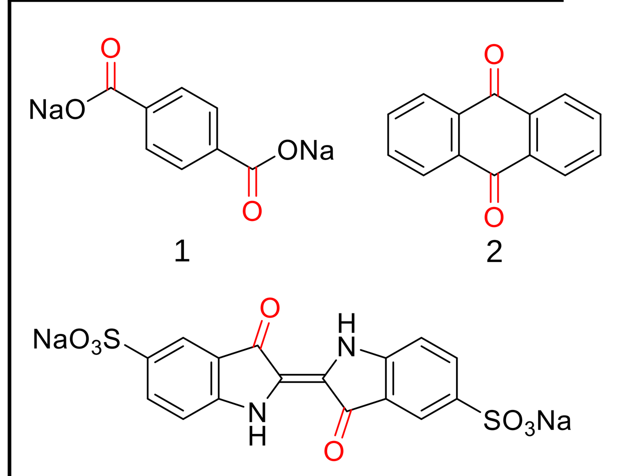
Organic Electrode

Advantage
- ◆Multi-electron redox reaction
- ◆Systematic control of host structure

■Examples of organic electrode materials for Na ion batteries

Structure	Teoretical capacity (mAh/g)	Potential (V) Discharge / Charge	Diacharge capasity 1st / 2nd	Ref.
1	255	0.18 / 0.5	225 / 105	C. Wang, *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 3124.
2	257	1.57, 1.89 / 1.92. 2.18	214 / 207	C. Guo, *et al.*, *Chem. Commun.* **2015**, *51*, 10244.
3	115	1.8 / 2.0	105 / 89	M. Yao, *et al.*, *Sci. Rep.* **2014**, *4*, 3650.
4	170	1.2 / 1.4	220 / 170	C. Luo, *et al.*, *Angew. Chem. Int. Ed.* **2018**, *57*, 2879.
5	586	0.7 / 2.2	567 / 520	H. Zhao, *et al.*, *Angew. Chem.* **2017**, *129*, 15536.
6	221	1.8 / 2.0	222 / -	J. Hong, *et al.*, *Nat. Commun.* **2014**, *5*, 5335.

Conventional type (C=O)



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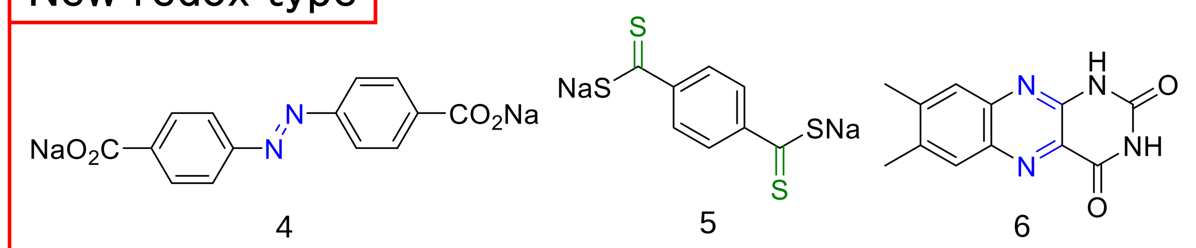
New redox type



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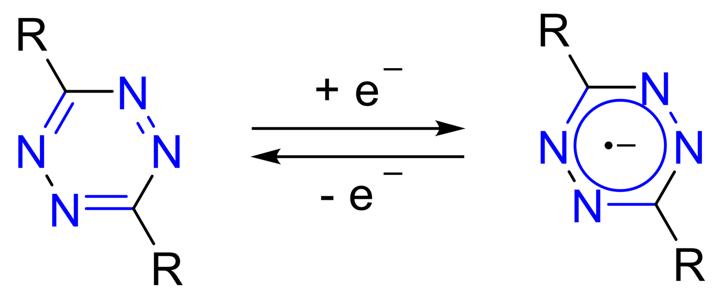
➢Redox-active organic compounds will lead to **the creation of new organic secondary batteries** and **provide important guidelines for molecular design as useful electrode materials**.

This Work

■Tetrazines

Cyclic π-electron compound stable at r.t.

High electron affinity



s-tetrazins

Form stable anion radicals (at the reducing end)

Easy to synthesize with inexpensive raw materials

■Previous research (Li-ion：D.J. Min *et al.*, *ChemSusChem.* **2019**, *503*, 12.)

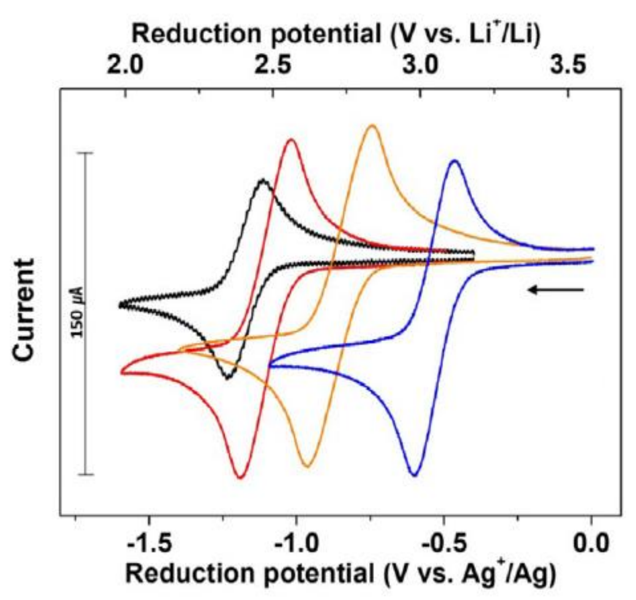
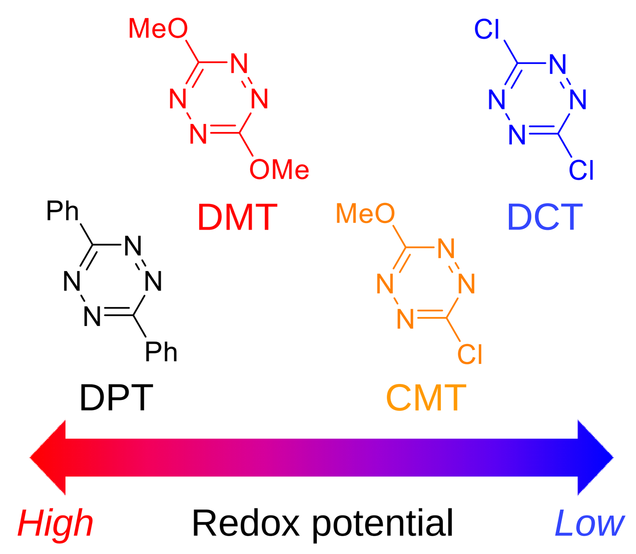


Fig. Cyclic voltammetry of *s*-tetrazines



➡ Chemical stability (DPT is promising)

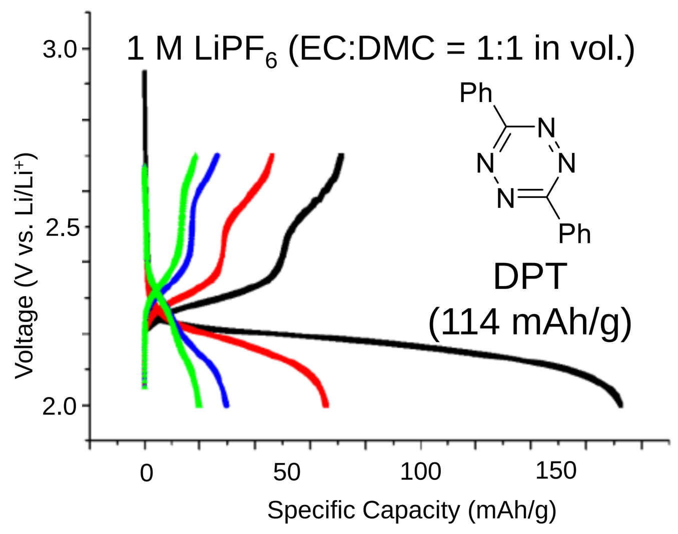
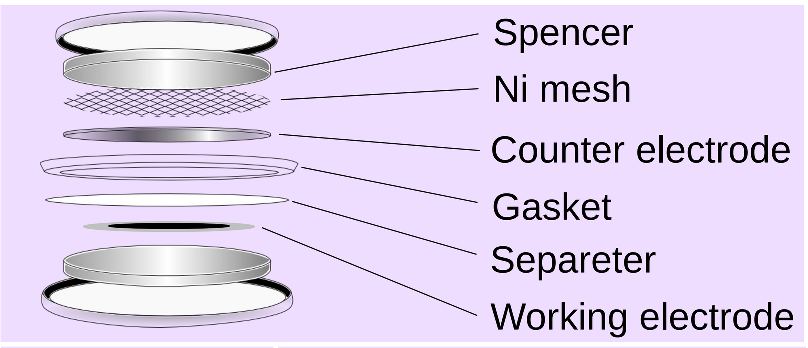
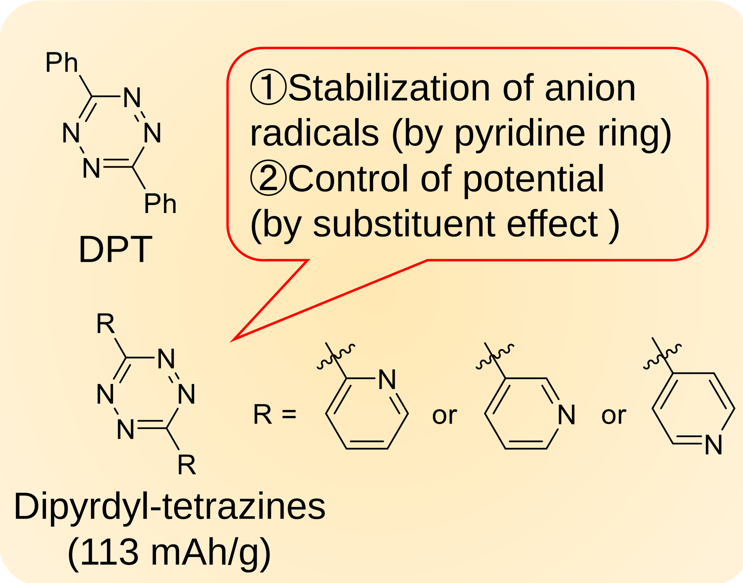


Fig. Charge/discharge profile of DPT

■Cell fabrication

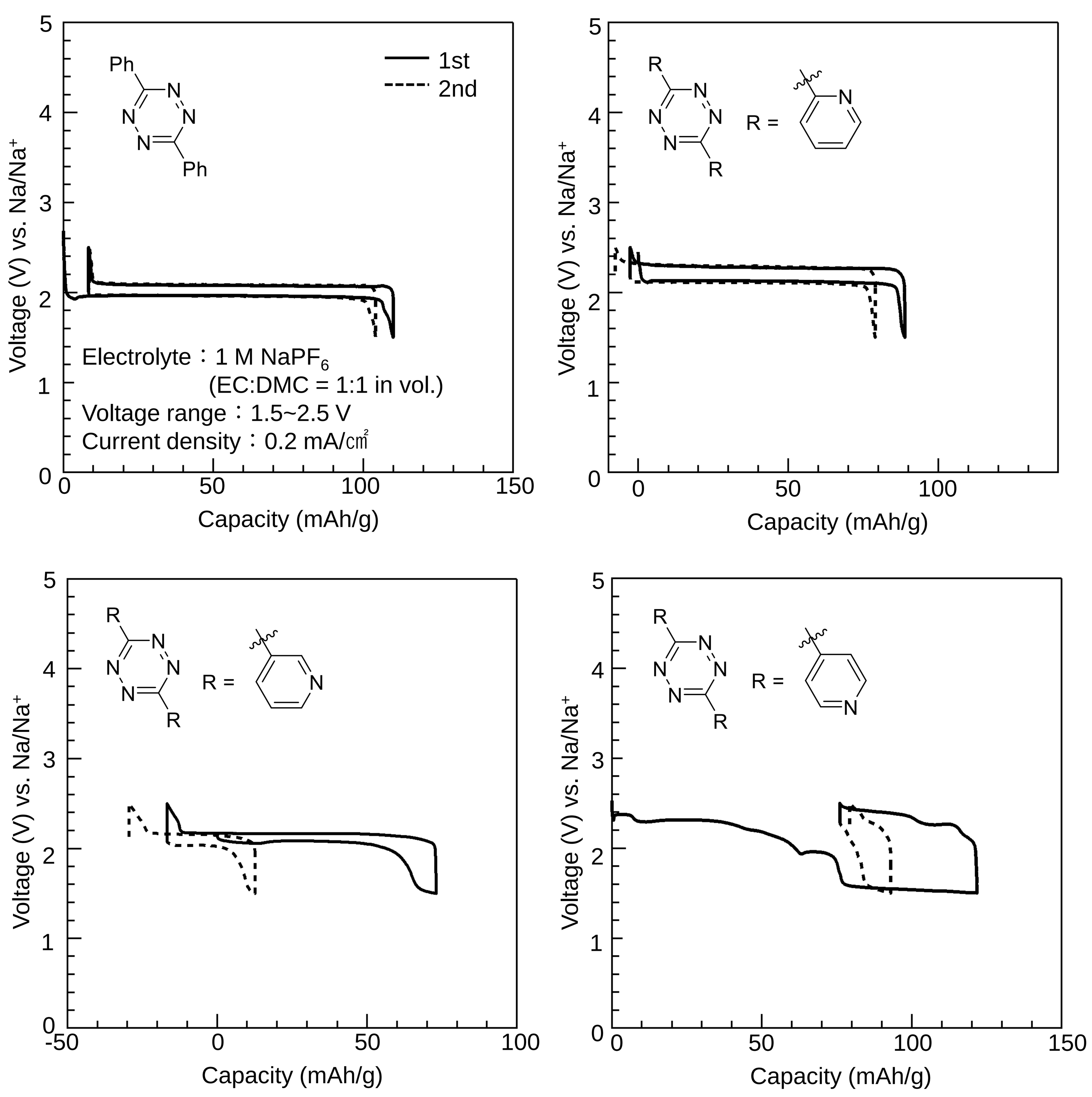


Conductive material	Acetylene black (AB)
Binder	Polytetrafluoroethylene (PTFE)
Working electrode	**s-tetrazines**：AB：PTFE ＝70：25：5
Counter electrode	Na metal



Results and Discussion

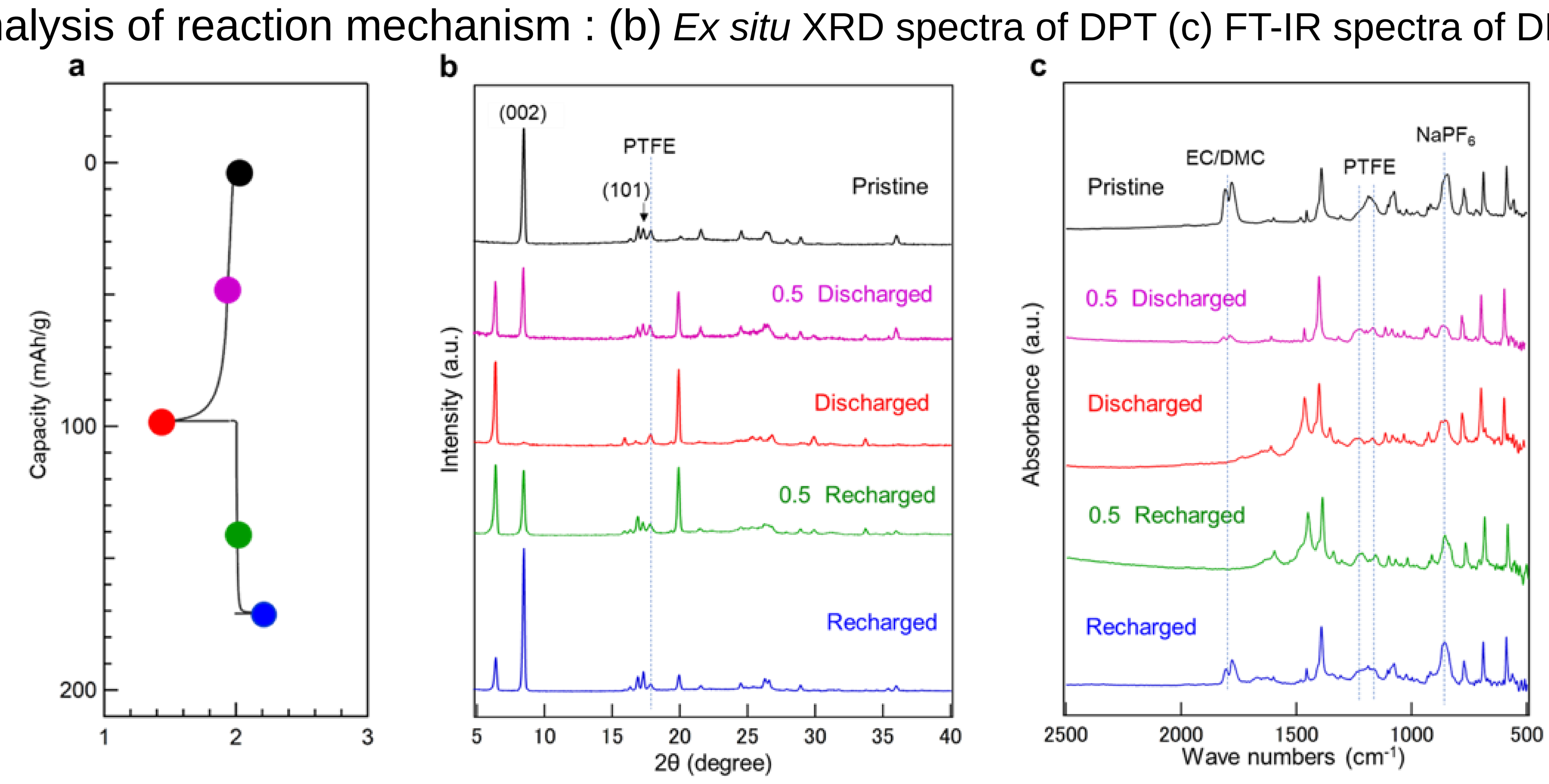
■Charge/discharge characteristics of *s*-tetrazines



The discharge voltage increases by about 0.1 to 0.2 V with the pyridyl groups (compared to DPT)

➢ It is suggested that the voltage can be tuned by introducing a substituent (electron-withdrawing/-donating) by molecular design.

■Analysis of reaction mechanism : (b) *Ex situ* XRD spectra of DPT (c) FT-IR spectra of DPT



➢ The 002 diffraction peak observed at 8.8° has decreased upon discharging and perfectly disappeared at the end of the discharge cycle and the 002 peak recovered after charging the cell that is indicating the reversibility.

➢The new peaks at 1466 cm⁻¹ and 1599 cm⁻¹ appeared assigned to discharge but decreased after charging, indicating that the reaction was reversible.

Conclusion

Investigation of the properties of *s*-tetrazines as electrode materials for Na-ion batteries

➢ DPT was operated as electrode materials for Na-ion batteries, and the initial discharge capacity was about 110 mAh/g (theoretical capacity: 114 mAh/g).The cycle characteristics were not satisfactory, mainly due to leaching into the electrolyte.

➢ The potential can be changed by the effect of substituents such as pyridyl groups.

➢ *s*-tetrazines have a flat charge-discharge curve around 2 V (vs. Na), which is attributed to a two-phase equilibrium reaction, as revealed by X-ray diffraction.

Acknowledgemant

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