DURATION: *2 years*

RESEARCH OBJECTIVES

- Development of a four-volt-sodium-ion-battery
- Use of NVPP to overcome the disadvantages of NVP
- Investigation of the effects of different carbon materials and morphology adjustments on the sodium storage mechanism and theoretical capacity of NVP materials
- Development of a presodiation strategy

BRIEF SUMMARY

The high Na-ion diffusion ability of the well-known cathode material $Na_3V_2(PO_4)_3$(NVP) for sodium ion batteries (SIB) is hindered by the large bulk structure and poor electronic conductivity, which leads to poor electrochemical performance in terms of rate capability and cycling stability and thus impedes its practical application. In the literature, it was discovered that the sodium storage mechanism and theoretical capacitance of NVP materials are influenced by different preparation methods, including carbon material modification and morphology of NVP materials.

In the literature, a vanadium-based ortho-diphosphate, $Na_7V_4(P_2O_7)_4PO_4$(NVPP), was reported, which addresses these limitations of the NVP cathodes. By engaging the V^{3+}/V^{4+} redox couple, NVPP exhibits single well-defined potential plateaus at 3.88 V vs. Na/Na^+, which is optimal for stable operations within an electrochemical stability window. Combined with the robust host frameworks, NVPP exhibits unprecedented cycle life, maintaining substantial capacity retention over 1000 cycles. In particular, the observed single plateau and stable cycling performance are due to the existence of a very shallow intermediate phase along the battery's reaction from the initial to deintercalated phase, a concept that can be used to understand existing electrochemical properties or for future developments.

The crystal structure of NVPP, as resolved by analyzing the complementary X-ray diffraction (XRD) pattern, exhibits the tetragonal P-421c space group with lattice parameters a = 14.225(3) Å and c = 6.364(17) Å. Despite the difference in structure compared to NVP material, the main tendency of the step-by-step Na ion intercalation mechanism remains. In the current work, we demonstrate how the intercalation mechanism of NVPP can change due to the appearance of an intermediate intercalation phase using synchrotron operando diffraction techniques. After obtaining stable cycling with the nearly achieved theoretical capacity 98.2 mAh/g in the NVPP half-cell, the full cell was constructed with investigated earlier bio-waste derived hard carbon as a negative electrode [4]. The cyclability of the full cell without presodiation additive has fast decay. The becoming famous presodiation strategy implies mixing cathode active material with easily degradable material at the specific potential value. The $Na_2C_4O_4$ additive shows improved cycling stability and higher specific capacity for the positive electrode. This presodiation additive electrochemically decomposes at 3.8V, providing the additional Na^+ ions, which can compensate for sodium ions deficiency in the full cell because of the formation of solid electrolyte interphase on the hard carbon surface.

Fig 1: Schematic drawing of the full cell setup

Fuse the Waste

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LAUFZEIT: *2 Jahre*

FORSCHUNGSZIELE

- Einsatz von Kohlenstoff/Schwefel Kompositen zur Unterdrückung des Shuttle Effekts.
- Vergleich der elektrochemischen Leistungsfähigkeit zwischen flüssigen Elektrolyten und Gel-Polymer-Elektrolyten

Raumtemperatur-Natrium-Schwefel (RT Na–S) Batterien haben in den vergangenen Jahren großes Interesse als Energiespeicher der nächsten Generation geweckt. Die Technologie verspricht geringe Kosten, eine hohe Verfügbarkeit von Natrium und eine hohe theoretische Kapazität von Schwefel (1675 mAh/g). Der unerwünschte Shuttle-Effekt, welcher durch die Auflösung intermediärer Polysulfide während des Lade- und Entladezyklus entsteht, beeinträchtigt jedoch die langfristige Leistung von Na–S-Batterien.

In früheren Untersuchungen wurde gezeigt, dass polymerbasierte Kohlenstoff-Schwefel-Komposite einen shuttle-freien Effekt für RT Na–S-Batterien erreichen können, indem diese eine Kombi-

nation aus physischer Eingrenzung und kovalenter Bindung in einem einzigen Material nutzen. Diese Verbundstoffe weisen eine hervorragende elektrochemische Leistung mit vernachlässigbarere Kapazitätsabnahme und eine höhere coulombische Effizienz auf.

Nach unserem Wissen wurden Faktis-artige Materialien aus elementarem Schwefel, Altfrittieröl (WCO) und Eierschalen (EGS) gewonnen werden können bisher nicht erfolgreich als Kathodenmaterialien für RT Na-S-Batterien untersucht.

Um den Einfluss von Polymermaterialien auf die Leistung von elementarem Schwefel in Na-S-Batterien zu analysieren, wurden erste elektrochemische Messungen durchgeführt. Ein Kugelmühlenverfahren wurde zur Herstellung des CNF-S Kathodenkomposits (Schwefel (35%) und multiwandige Kohlenstoffnanoröhren (35%)) eingesetzt. Nach der Aktivierung durch Kugelmühlen wurde leitfähiger Kohlenstoff (C65, 20%) und der Binder Polyacrylsäure (PAA, 10%) für die Slurry-Zubereitung hinzugefügt.

Die elektrochemische Leistung des Komposits wurde mit flüssigen Elektrolyten (1M NaCF3SO3 in Tetraglyme) sowie einem Gel-Polymer-Elektrolyten (PEO-PVDF-HFP-ZIF8) getestet, welcher mit demselben flüssigen Elektrolyten durchsetzt ist. Das Polymer besteht aus 50% PEO (Polyethylenoxid) und 50% PVDF-HFP (Poly(vinylidenfluorid-co-hexafluorpropylen)). Der unterschiedliche Mechanismus der Polysulfidbildung ist in Zyklovoltametriemessugen sichtbar (Abb. 1).

Der poröse Komposit-Gel-Polymer-Elektrolyt kann flüssige Elektrolyte absorbieren sowie die Diffusion von Natriumpolysulfid unterdrücken. Gleichzeitig besitzen die einheitlichen ZIF-8 (zeolitic imidazolate framework) Schichten eine hohe chemische Affinität zu Polysulfiden und eine hohe Leitfähigkeit, welche den "Shuttle-Effekt" chemisch unterdrücken können.

Abb 1: Zyklovoltametrie Messungen von CNF-S Komposite in flüssig und Gel-Polymer

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DURATION: 2 Jahre

RESEARCH OBJECTIVES

- Use of carbon/sulfur composites to suppress the shuttle effect.
- Comparison of electrochemical performance between liquid electrolytes and gel polymer electrolytes.

BRIEF SUMMARY

Room-temperature sodium–sulfur (RT Na–S) batteries have recently gained attention as next-generation energy storage devices owing to their low cost, the abundance of sodium, and the high theoretical capacity of sulfur (1675 mAh/g). However, the notorious shuttle effect, caused by the dissolution of intermediate polysulfides during cycling, limits the long-term performance of Na–S batteries. As was previously investigated [1], the polymer-based carbon–sulfur composites can possess shuttle-free effect for RT Na–S batteries by utilizing the combination of physical confinement and covalent bonding in a single material. The composites demonstrate excellent electrochemical performance, including a negligible capacity fading and a high coulombic efficiency.

However, to the best of our knowledge, factice-like materials derived from elemental sulfur, waste-cooking oil (WCO) and eggshell (EGS) have not been explored successfully yet as cathode materials for RT Na-S batteries.

To investigate impact of polymer material to the elemental sulfur performance in Na-S battery, the preliminary electrochemical measurements have been done. The ball-milling procedure [2] was applied for the preparing CNF-S cathode composite (sulfur (35%) and multi-walled carbon nanotubes (35%)); after ball-milling activation, conductive carbon (20%) C65 and binder Polyacrylic acid (PAA, 10%) was added for slurry preparation. The electrochemical performance of the composite was tested in the liquid electrolyte 1M NaCF3SO3 in tetraglyme (Fig. 1) and with gel polymer electrolyte PEO-PVDF-HFP-ZIF8, which is swilled with same composition of liquid electrolyte, with polymer proportion 50% PEO (Poly-