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ARTICLE TYPE

Small things make big difference:

Binder effects on the performance of Li and Na batteries

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Li and Na batteries are very important as energy storage devices for electric vehicles and smart grid. It is well known that, when an electrode is analysed in detail, each of the components (the active material, the conductive carbon, the current collector and the binder) makes a portion of contribution to the battery performance in terms of specific capacity, rate capability, and cycle life, etc. However, there has not yet been a review on binder, though there are already many review papers on the active materials. Binders make up only a small part of the electrode composition, but in some cases, they play an important role in affecting the cycling stability and rate capability for Li-ion and Na-ion batteries. poly(vinylidene difluoride) (PVDF) has been a main-stream binder, but there have been discoveries that aqueous binders sometimes can make the battery perform better, not to mention they are cheaper, greener, and easier to use for electrode fabrication. In this review, we focus on several kinds of promising electrode materials, to show how their battery performance can be affected significantly by binder materials: anode materials such as on Si, Sn and transitional metal oxides; cathode materials such as

LiFePO₄, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, LiCoO₂ and sulphur.

1. Introduction

Electrochemical energy storage and conversion systems play a crucial role in our daily life and are also of great interest for our future because they offer solutions to our environmental issues and energy crisis. The development of greener, cheaper, and safer rechargeable batteries is considered today as a goal of strategic importance for energy storage technology.¹⁻⁴ One of the most important types of rechargeable batteries in daily life would be the Li-ion batteries (LIBs), which provide high energy density, long cycle life, and relatively good power capability.^{5,6} The schematic drawing in Figure 1 shows current and future promising energy storage systems plotted using cost vs. energy. The current Li-ion battery is suitable for portable devices. The cost and safety issues are the major obstacles for Li-ion batteries to be used in electrical vehicles and smart grids.⁷⁻⁹ The Li-ion supercapacitor with high rate capability and relatively high energy density would be a good candidate to replace the currently used lead acid batteries for power tools and car starter batteries.¹⁰ The newly developed high energy density systems such as Li-sulphur and Li-air batteries would be more suitable for electric vehicles. However, the safety issue will still be a major concern for such systems due to the involvement of pure Li metal.¹¹ The sodium ion battery as one of the lowest cost systems would be a good candidate for the storage of renewable energy. Further development is required as the current state-of-the-art sodium ion batteries show poor rate capability, short cycle life, and low energy density.^{12,13} As most of the previous reviews have been intensively focused on the active materials for both anode and

cathode materials¹⁻¹³ with little attention to binders, here, we will only focus on the effect of various binders on the performance of electrode materials in Li-ion batteries and Na-ion batteries.

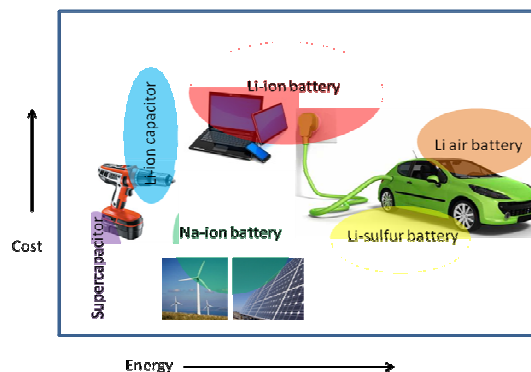


Figure 1. Cost vs. Energy plot for different energy storage system.

Batteries can rationally be divided into two types: the primary battery and the rechargeable battery. The only difference between these two types of batteries is the rechargeability. Therefore, the cycle life is a very important factor for rechargeable batteries. As demonstrated in Figure 2, both Li and Na ion batteries are composed of anode and cathode electrodes which are soaked in electrolyte and separated by a separator. Both electrodes are consisted of the active materials, a conductive agent, the current

collector and a binder. The active materials are to determine the energy of the electrode. The conductive agent can improve the rate capability of the electrode owing to the enhanced transportation of electrons. The binder is used to glue the active materials and conductive agent together with the current collector. Therefore, the electrons can flow from/to the outside circuit through the active materials-conductive agent-current collector chain. Although binders only occupy 2-5% of the mass in the commercial electrode configuration, the binder material is one of the most crucial electrode components for improved cell performance, especially for the cycle life. Without the binder, the active materials will lose contact with the current collector, resulting in capacity loss.

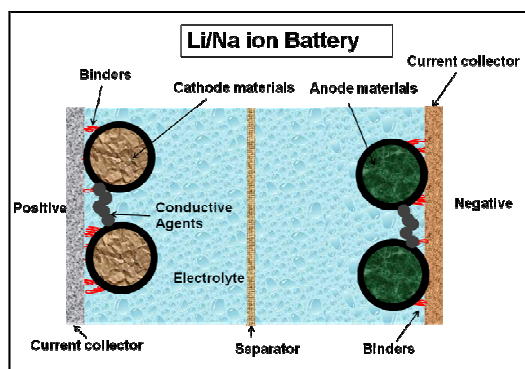


Figure 2. Schematic drawing of Li/Na ion battery

Typical binders used in the Li/Na ion battery are summarized in Table 1. Poly(vinylidene difluoride) (PVDF) binder is the most widely used binder for Li-ion cells. This is due to its good electrochemical stability and binding capability, as well as its ability to absorb electrolyte for facile transport of Li to the active material surface.¹⁴⁻¹⁹ However, PVDF requires the usage of toxic and expensive organic solvents. On the other hand, the other three types of binder are naturally abundant and can be dissolved in water, which will make the electrode preparation process cheap and environmentally friendly. Recently, aqueous binders have been gradually replacing PVDF binder for the anode.^{20,21} The advantages of aqueous binders are as follows: (1) low cost, (2) no pollution problem, (3) enhancement of the active material ratio in a cell owing to the reduction of binder content, (4) no requirement for strict control of the processing humidity and (5) fast drying speed in electrode fabrication. SBR/CMC composite agent is generally used in the aqueous binder; styrene-butadiene rubber (SBR) is the primary binder and sodium carboxymethyl cellulose (CMC) is the thickening/setting agent. Since the binders' function is different in different materials and systems, we will review the recent findings in details based on the major active materials for both battery systems.

2. Binder for Lithium ion battery

2.1 Anode materials

2.1.1 Carbon based materials

Graphite based materials have been the most common commercially used anode materials for Li-ion batteries for more than 20 years. Lee first reported the usage of CMC as binder for graphite.²² CMC can lead to improved adhesion strength, giving the as-fabricated cell an attractive cycle life with more than 90% of the initial discharge capacity retained after 200 cycles. During the electrode preparation, the important step is to make the uniform slurry and coated onto the current collector. Although the slurry can be homogeneous, after drying, it will be hard to maintain the uniform distributions of the binder and active materials. Wang et al. proposed that the acetylene black and CMC binder may become concentrated near the contact points between two adjacent graphite spheres because of the capillary effect of the binder solution.²³ The conductive bridge (acetylene black/binder) between graphite spheres is very effective for improving the electrical contact between graphite spheres during long cycling. Organic-based electrode sheet shows more non-uniform distributions of the binder and the graphite. According to the migration-controlled drying kinetics, the migration of the binder to the top surface of an electrode sheet is primarily caused by the flow of solvent during drying. Because of the lower evaporation rate of N-methyl pyrrolidone (NMP) and the longer drying time for the organic-based slurry, the uniformity of PVDF in the dried electrode sheet was found to be much poorer than for the water-based SBR/CMC.²⁴ Therefore, the performance in terms of adhesion, resistance, and charge-discharge efficiency was much poorer than that of the water-based electrode.

Chong et al.²⁵ reported that lithium poly(acrylic acid) (PAALi) and sodium poly(acrylic acid) (PAANa) offered better cell performance for spherical natural graphite in terms of capacity and initial coulombic efficiency (Figure 3) than PVDF, which is attributed to a more favourable polymer conformation in the composite. The initial coulombic efficiency of the cells with PAALi and PVDF is 92.6% and 85%, respectively. For PVDF, 70% of the solid electrolyte interphase (SEI) is formed in the first cycle,²⁶ and several subsequent cycles to form a stable interface.²⁷ A more effective and stable SEI layer appeared to form in fewer cycles with the PAAX binders, where X = Li, Na, or K.²⁷ For the PAAX, the Li, Na, or K dissociates, leaving negative charges on the polymer chains that suppress the aggregation of the polymer through electrostatic repulsion.²⁸ With less polymer aggregation, a more homogeneous coating may be obtained. The PAA based binders resulted in brittle electrodes that showed macroscale cracks upon drying; however, the cracks can be suppressed if small amounts of SBR (0.5-3%) are added to the electrode. Unfortunately, the conductivity decreased monotonically with the addition of SBR. Therefore, the rate capability of the electrode would be limited.

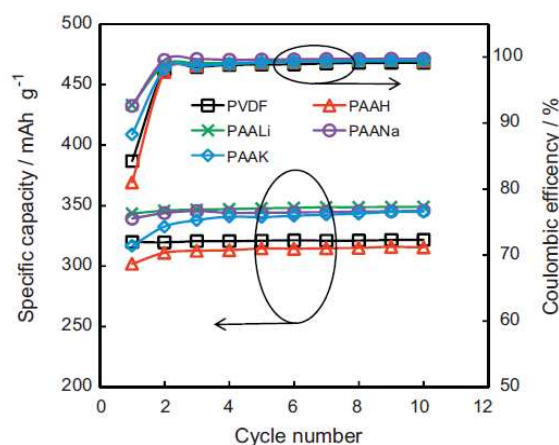


Figure 3. The cycle performance of spherical natural graphite anode with different binders.

2.1.2 Silicon-based materials

Silicon is one of the most promising anode materials for Li-ion batteries because it has highest theoretical capacity (3579 mAh g^{-1} , $\text{Li}_{3.75}\text{Si}$) and the raw materials are abundant in nature. However, the cycling stability is the major problem for Si-based materials due to the large volume expansion up to 270% after lithiation.^{29,30} In this regard, the elastomer is an attractive binder because it permits a high active material ratio and high flexibility compared to conventional PVDF binder. Buqa et al. first reported that nano-Si electrode containing 1% sodium carboxymethyl cellulose (CMC) as binder shows the same cycling stability as an identical electrode containing 10% conventional PVDF binder.³¹

Li et al. proposed that the CMC binder may act as a surface modifier promoting the formation of a stable SEI passive layer.³² Lestriez et al. claimed that the extended conformation of CMC in solution facilitates an efficient networking process between the conductive agent and the Si particles.³³ Hochgatterer et al. reported that the chemical bonding between CMC binder and Si particles contributes to the enhanced capacity retention of Si/C composite electrodes.³⁴ They suggested that the cohesive strength between the binder and active particles is an important factor.

This hypothesis was supported by a previous report that replacing the PVDF binder with a modified acrylic adhesive increased the capacity retention of a Si/C electrode from 67% to 90% (over 50 cycles). The peel strength of the acrylic adhesive (7 N) was much higher than that of PVDF (0.4 N).³⁵ Choi et al. reported that the use of a high-strength polyamide-imide (PAI) binder can increase the initial coulombic efficiency of a Si-based electrode from 29% to 75%.³⁶ Garsuch et al. reported that when a lithium-exchanged Nafion was used to as binder for crystalline silicon and carbon composite, it showed reversible specific capacities ranging from 800 to nearly 1000 mAh g^{-1} between 0.9 and 0.17 V.³⁷ These results indicate that the choice of binder system has a critical impact on the performance of alloy anodes.

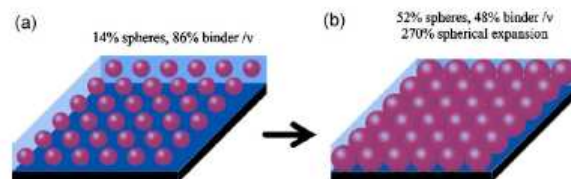


Figure 4. Simple model to calculate the Si concentration in electrodes.

A simple model was proposed by Beattie et al. to explain the excellent cycling results for low-Si-concentration electrodes.³⁸ They used geometrical considerations to design an electrode that can accommodate large changes in volume due to particle lithiation and delithiation during cycling (Figure 4). The largest Si loading was calculated to be 20 vol % based on the theoretical expansion of Si (270%). Since the electrode porosity was not considered in the model, an electrode with 33 wt % Si (100 nm) + 33 wt % CMC + 33 wt % carbon was also shown to cycle well and with high capacity of 1200 mAh g^{-1} . Our group reported a simply mixed nano-sized Si and graphene composite using CMC as binder that could achieve a capacity of 1168 mAh g^{-1} based on the total composite weight and a capacity of more than 2000 mAh g^{-1} based on the contribution of Si up to 30 cycles.³⁹

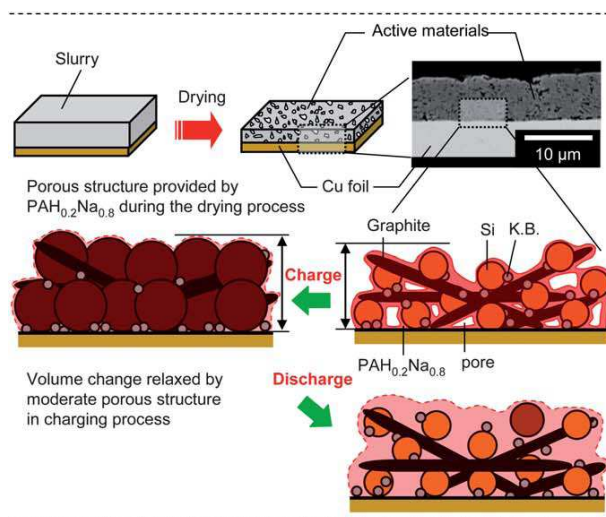


Figure 5. Schematic illustrations of the improved mechanism for the Si-graphite composite electrodes with PAH_{0.2}Na_{0.8}.

Han et al. investigated the impact of the degree of neutralization of poly(acrylic acid) on electrode performance for Si-graphite composite electrodes.⁴⁰ Excellent capacity retention for a 100 cycle test with a high reversible capacity of approximately 1000 mAh g^{-1} is achieved with 80% neutralized (PAH_{0.2}Na_{0.8}) PAA as a binder for Si-based composite electrodes. It was found that 80% neutralized PAA provides a moderately porous structure inside the composite electrode with 10 wt% binder content because of its unique rheological properties during the drying process after the slurry is coated onto the current collector. The self-formed

porous structure arising from the partially neutralized PAA is beneficial for buffering the volume expansion caused by lithiation of Si, as shown in Figure 5.

5 So far, the highest performance that an aqueous binder can achieve for Si materials was reported by Magasinski et al. Alginate, a high-modulus natural polysaccharide extracted from brown algae, yields a remarkably stable Si-based anode.⁴¹ Unlike many polysaccharides commonly found in terrestrial plants,
10 alginate, a major constituent of brown algae and many aquatic microorganisms, contains carboxylic groups in each of the polymer's monomeric units. An alginate binder allowed for a stable capacity of $\sim 1800 \text{ mAh g}^{-1}$ for up to 100 cycles which was far better than for Si anodes using PVDF and Na-CMC as binders
15 (Fig. 6). Such electrodes also show excellent high rate capability. At a current density of 4200 mA g^{-1} , the reversible Li extraction specific capacity of an alginate-based Si anode is in the range of 1700 to 2000 mAh g^{-1} (Fig. 6). The surface bonding between the binder and the Si can be observed.

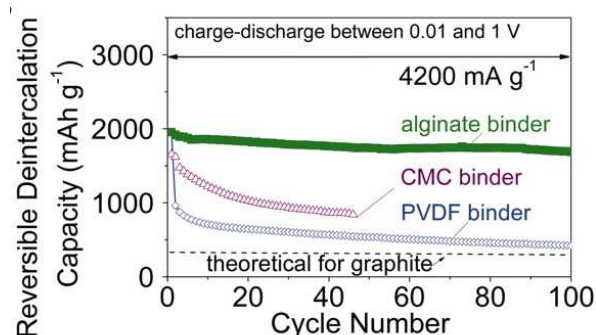


Figure 6 Reversible Li-extraction capacity of nano-Si electrodes with alginate, CMC, and PVDF binders vs. cycle number.

25 The high concentration of functional (carboxylic) groups in PAA and CMC is probably a major cause of its superior performance. A certain fraction of the COOH groups in PAA form strong hydrogen bonds with OH groups on the Si (or C) surface. The remaining carboxy groups form ionically conductive COOLi
30 groups and, together with the solid electrolyte interphase (SEI) formed during the first Li insertion, protect the Si-C interface and thus the anode electrical connectivity from degradation upon solvent intercalation. To see the influence on mechanical properties of the binder, atomic force microscopy (AFM) was used to measure the mechanical properties of the binder and silicon surface. Magasinski et al. reported that the moduli of PAA and Na-CMC do not change when exposed to diethyl carbonate (DEC). In contrast, the stiffness of PVDF was significantly
35 decreased by contact with DEC as shown in Figure 7.⁴²

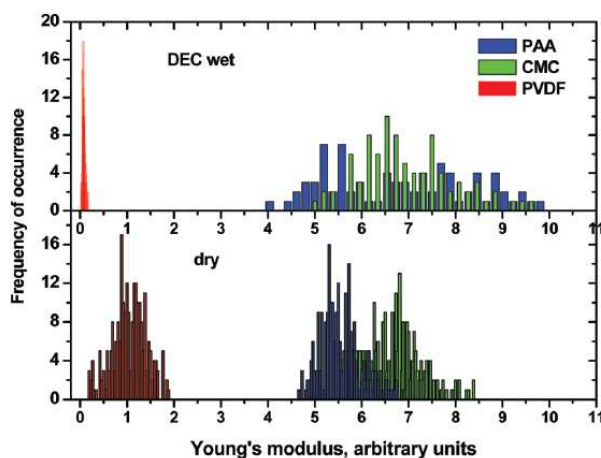


Figure 7. Results of AFM stiffness measurements for films made from PAA, CMC, and PVDF.

45 Through a combination of experimental and theoretical simulations, Liu et al.⁴³ developed a new conductive binder poly(9,9-dioctylfluorene-co-suorenone-co-methylbenzoic acid) (PFFOMB) as shown in Figure 8 for Si electrode showing high capacity of 2100 mAh g^{-1} for Si (1400 mAh g^{-1} for the electrode)
50 and long cycle life up to 650 cycles. The molecular structures of PFFOMB are based on polyfluorene (PF)-type polymers. Carbonyl C = O was introduced to tailor the lowest unoccupied molecular orbital (LUMO) electronic states so that the electrons could cathodically dope the polymer to achieve adequate
55 electronic conductivity during lithiation and delithiation in the potential range of 0.01 V–1 V (Li/Li⁺). Methylbenzoic ester - PhCOOCH₃ (MB) was added to improve the polymer adhesion. The developed polymer features much improved electric conductivity and a robust mechanical binding force, which
60 maintains electrical connectivity and accommodates the Si volume change simultaneously. However, the toxicity nature of the binder and the low initial coulombic efficiency are still disadvantages.

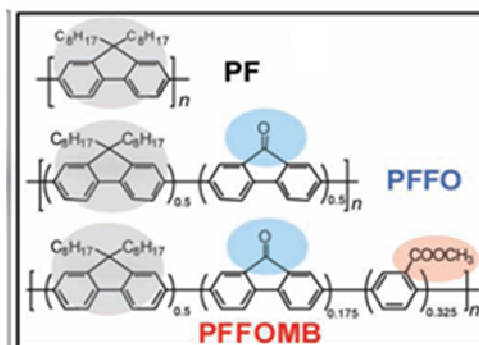


Figure 8. Molecular structure of the PF-type conductive polymers, with two key functional groups in PFFOMB, carbonyl and methylbenzoic ester.

70 Koo et al.⁴⁴ reported that nano-sized silicon powder in a three-

dimensionally interconnected network of poly(acrylic acid) and sodium carboxymethyl cellulose as binder exhibits a high reversible capacity of over 2000 mAh g⁻¹ after 100 cycles at 30 °C and maintains a superior capacity of 1500 mAh g⁻¹ for the high current density of 30 A g⁻¹ at 60 °C. The use of cross-linked polymers binder better accommodated the expansional strain of silicon in the fully lithiated state compared to PVDF binder (Figure 9) because the polymer chains are linked in three dimensions.

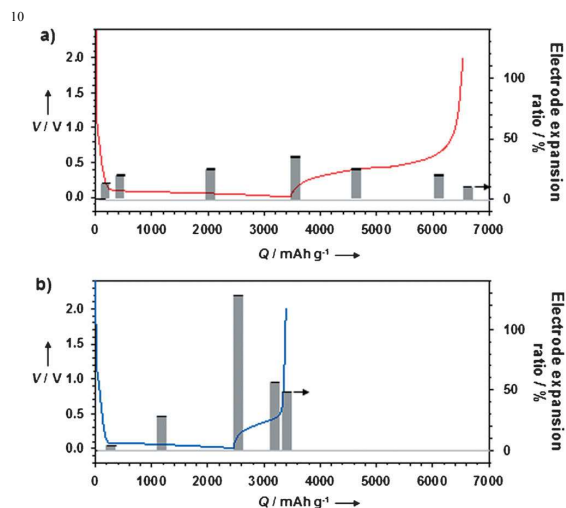


Figure 9. Charge–discharge profiles of a) cross-linked PAA-CMC binder (red line) and b) PVDF binder (blue line) at the current density of 175 mA g⁻¹ at 30 °C in the potential range of 0.005 to 2.0 V versus Li/Li⁺. The black lines represent the electrode volume changes during Li insertion and extraction processes.

Ryou et al.⁴⁵ demonstrated that cross-linked alginate (Alg) and catechol, which is a mussel-inspired adhesive materials (Figure 10) exhibit superior cycling performance compared to Si-PVDF, indicating that binding based on catecholic adhesion and hydrogen bonding is more effective for cycling performance than simple van der Waals interactions. After 400 cycles, both Si-Alg-C and Si-Alg fully retain their initial capacities of around 2000 mAh g⁻¹. The binders can be directly observed at the peeling interface between the detached electrode film and the Cu foils. At this interface, Si-Alg-C shows much more elongated bridges than those observed for Si-Alg and Si-PVDF, indicating the much better film adhesion resulting from Alg-C.

Further studies to improve the performance would be devoted to exploring new binder materials and different types of carbons to introduce artificial porosity and limit electrolyte decomposition. The initial coulombic efficiency is also a crucial factor if the Si materials are to be used commercially in a full cell. The large amount of binder used in the electrode may reduce the volumetric density of the electrode and bring in more side reaction to further lower the coulombic efficiency.

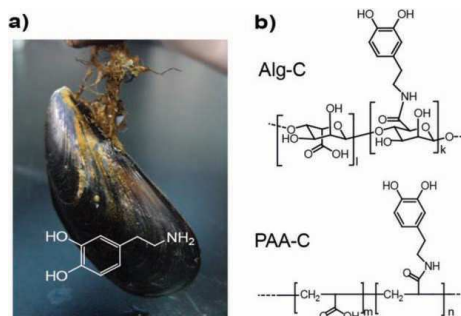


Figure 10. a) Mussel; the inset shows the chemical structure of dopamine inspired by mussel foot proteins. b) Structural formula of Alg-C and PAA-C conjugated polymer binders

2.1.3 Sn and other alloy based

CMC was also used as a binder to investigate its effects on the electrochemical performance of Sn-based materials. Our group reported that using CMC as binder for commercial SnO₂ nanoparticles showed much better performance than that of the carbon-coated commercial SnO₂ nanoparticles using PVDF as binder in terms of cycling stability.⁴⁶ The highest specific capacity reported was 502 mAh g⁻¹ up to 50 cycles at a current density of 100 mA g⁻¹.

Dahn et al.⁴⁷ reported that a lithium polyacrylate (Li-PAA) binder performed even better than the CMC binder. An amorphous SnCoC electrode using Li-PAA binder showed excellent capacity retention of 450 mAh g⁻¹ for at least 100 cycles as compared to less than 20 cycles when using the PVDF or CMC binders. The results indicated that the choice of binder system has a critical impact on the performance of Sn-based alloy anodes.

Our group demonstrated that nano-Sn/polypyrrole composite using CMC as binder had both enhanced capacity retention and good rate capability. Scanning electron microscope (SEM) images showed that both CMC and polypyrrole (PPy) can work as composite binders and prevent the formation of cracks in electrodes during the charge–discharge process, leading to good cycling stability, as shown in Fig. 11, despite the big volume changes.⁴⁸

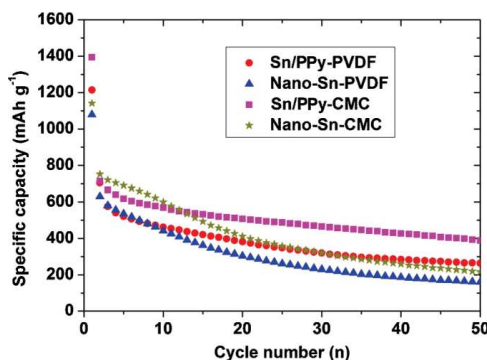


Figure 11. Cycle life of nano-Sn and nano-Sn/PPy composite electrodes using CMC and PVDF as the binder, respectively.

2.1.4 Transition metal oxide

Li et al. reported that Fe_2O_3 electrodes using CMC binder and two other new binders show better cycling performance (about 800mAhg^{-1} for 100 cycles) compared to electrodes made from conventional PVDF binder.⁴⁹ By combining CMC binder and carbon composite, our group demonstrated that Fe_2O_3 can deliver a high specific capacity (1210mAh g^{-1} at a current density of 0.1 C), enhanced rate capability and excellent cycling stability (720mAh g^{-1} at a current density of 2 C up to 220 cycles).⁵⁰ Other transition metal oxides, such as NiO and CuO, were also investigated using CMC as binder and showed much enhanced cycling stability compared with PVDF as binder.^{51,52} The active materials using PVDF as binder detach themselves from the substrate very easily after cycling, while the electrode using CMC as binder shows good adhesion. The gap between the electrode materials and binder can be clearly observed in Figure 12.⁵¹

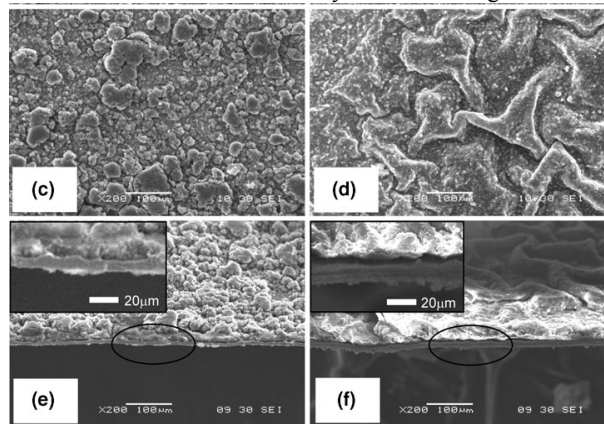


Figure 12. SEM images of NiO electrodes with CMC binder (left) and PVDF binder (right): (c, d) after cycling; (e, f) cross-sections of electrodes after cycling. Insets in (e) and (f) show enlargements of the indicated areas.

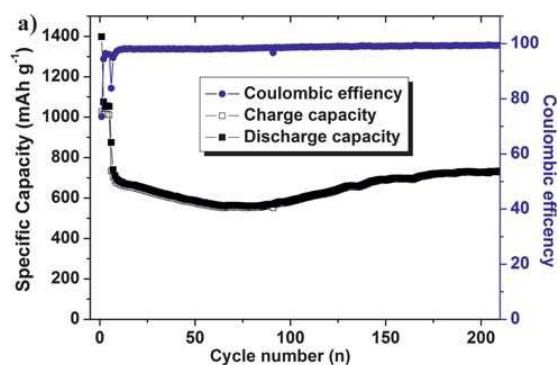


Figure 13. Typical cycling performance of Fe_2O_3 materials vs. Li.

Capacity increase during cycling has been commonly observed in many reports on the transition metal oxides. One typical example was shown in Figure 13. This is probably due to the

decomposition of electrolyte during cycling and also related to the formation of new SEI layers. This phenomenon is one of the deadly drawbacks for transition metal oxide to be used for commercial battery as anode because the electrolyte is very limited amount in the commercial cell. The continuous decomposition of electrolyte will lead to the battery die after certain cycles. Other disadvantages include big charge and discharge potential separation, low initial coulombic efficiency, and large volume expansion.

2.1.5 $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Spinel lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), has attracted great interest as a safe anode material for rechargeable Li-ion batteries because of its high and flat Li insertion voltage at $\sim 1.55\text{V}$ versus Li/Li^+ , which prevents the growth of lithium dendrites and the decomposition of electrolyte as well as providing long cycle life and high rate capability.⁵³ The binder for high-capacity anode materials, such as silicon, tin, and transition metal oxides, as we mentioned before, should have high adhesive capability to endure large volume changes during the lithium intercalation and de-intercalation processes. The adhesion strength of the polymer is one of the most important factors that should be considered when choosing the binder for high-capacity anode materials. LTO experiences no volume changes during cycling, indicating that the focus of using new binder would be different. Our group reported that the high rate capability of LTO electrodes using CMC as binder is much better than that for those using PVDF as binder.⁵⁴ The LTO electrodes using CMC as binder showed the highest specific capacity of 62mAh g^{-1} at a current density of 40C, whereas those using PVDF as binder showed a capacity of only 25mAh g^{-1} . The charge curves of electrodes using PVDF as binder start to show sloping curves from 20 C, whereas those using CMC as binder still show a flat plateau, even at 40 C as shown in Fig. 14. This indicates the kinetic difference between the two different binders. Further electrochemical impedance studies showed that the electrodes with CMC and PVDF as binder had the same lithium diffusion coefficient, but the electrode with CMC as binder had a much lower charge transfer resistance, a lower apparent activation energy, and a lower apparent diffusion activation energy than the electrode with PVDF as binder.

Lee et al.⁵⁵ reported an investigation of the influence of molecular weight and degree of substitution of CMC when used as the binder for LTO anodes. The results showed that the LTO electrode that contained relatively low molecular weight and high degree of substitution CMC showed high specific capacity and good rate capability owing to its low charge transfer resistance, high ionic conductivity, and good wettability with the electrolyte. Recently, Tran et al.⁵⁶ reported the fabrication of $200\text{ }\mu\text{m}$ thick LTO electrodes using a novel poly(PEGMA-co-MMA-co-IBVE) copolymer binder, containing methyl ether methacrylate (PEGMA), methyl methacrylate (MMA), and isobutyl vinyl ether (IBVE), and with active material loadings up to 28mg cm^{-2} , which can deliver an area specific capacity of 4.2mAh cm^{-2} at the C/2-rate.

The major challenge for the use of LTO in large-scale application is destructive gas generation with associated swelling during the charge and discharge.^{57,58} The generated gases mainly contain H_2 , CO_2 and CO , which originate from interfacial reactions between

LTO and the surrounding alkyl carbonate solvents. The reactions occur at the very thin outermost surface of the LTO (111) plane, which result in transformation from the (111) to the (222) plane and formation of the (101) plane of anatase. He et al.⁵⁹ reported that a carbon coating and the SEI film formed around the coating worked effectively in synergy to separate LTO from the surrounding electrolyte solution and prevent the interfacial gassing reactions. A future direction is to design a new binder to coat the LTO surface to both allow high ionic conductivity and separate the LTO from the electrolyte.

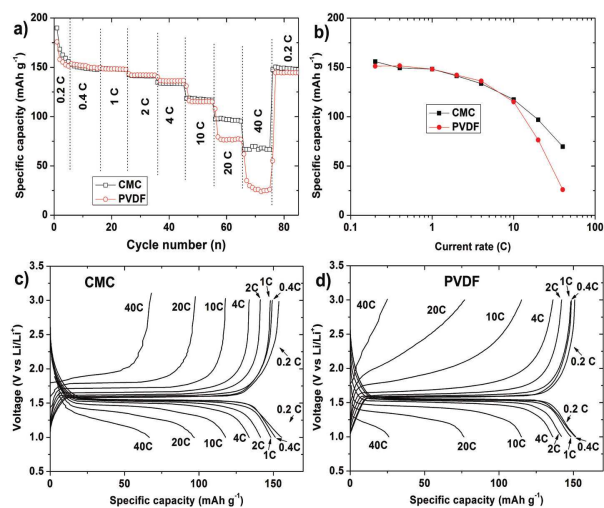


Figure 14. (a) Cycle life of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microsphere electrodes at different current densities from 0.2 to 40 C using CMC (squares) and PVDF (circles) as binders. (b) Rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microsphere electrodes at different current densities using CMC (squares) and PVDF (circles) as binders. (c, d) Charge and discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microsphere electrodes at different current densities from 0.2 to 40 C using CMC (c) and PVDF (d) as binders.

2.2 Cathode materials

Since the successful for the aqueous binder used for anode materials,^{60,61} a new trend is now being developed to replace the PVDF binder in the cathode. Many reasons have been brought up: the safety aspects of the battery, the high cost of cathode materials, and a growing interest in high capacity and high energy. Fluorine is one of the degradation products in the battery leading to the production of stable LiF. Depending on the liquid electrolyte, the formation reaction of LiF and other harmful products is accelerated.^{62–64} Furthermore, self-heating thermal runaway can be induced. With respect to safety and environmental concerns, it is better to find an alternative to PVDF. Thus, the switch from non-aqueous to aqueous systems is imperative. The research effort has started with the preparation of the cathode slurry,⁶⁵ however, the transition from the non-aqueous to the aqueous coating process appears to have encountered some unexpected difficulties related to instability of cathode in water, slurry formulation, viscosity control, and film

processing, which must be overcome for successful implementation in Li-ion batteries.

2.2.1 LiCoO_2

LiCoO_2 is still the most important cathode materials since the first commercial Li-ion battery.^{66–68} Although the use of water-based binder is a new process expected to have high potential, aqueous binders are rarely used in the lithium-ion battery industry especially for the cathode, which may be due to the significant dissolution problems of LiCoO_2 in water⁶⁹ and the difficulty in controlling the dispersion properties of oxides.⁷⁰ Li et al.⁷¹ reported the effects of the pH of a water-based slurry on the dispersion homogeneity and cell performance of LiCoO_2 cathodes. The binder content increased with the distance from the bottom to the top of the dried electrode sheet for LiCoO_2 system when CMC was used as binder.⁷² Thick electrode cathode films with active mass loadings over 30 mg cm^{-2} were reported by Tran et al.⁷³ using polyethylene glycol (PEG)-based binders. High coulombic efficiency of 98.7% can be achieved, indicating that the aqueous binder could be used for LiCoO_2 cathode.

2.2.2 LiFePO_4

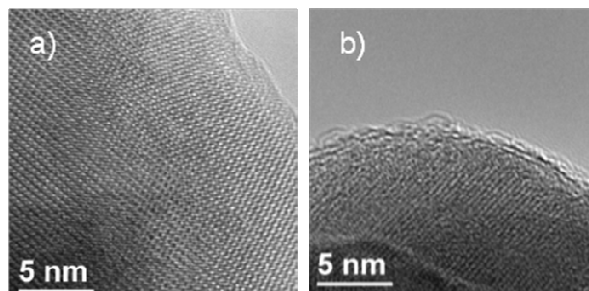


Figure 15. HRTEM images of LiFePO_4 powders: (a) initial and (b) after immersion for 24 h in water.

So far, only several groups have reported on using CMC as a slurry thickener or as a binder for LiFePO_4 cathodes.^{74–79} Guerfi et al.⁷⁴ reported the usage of water-soluble binder with an elastomer on saturated organic compounds and a thickener of CMC for LiFePO_4 cathode materials. The electrochemical performance shows that lower irreversible capacity losses were obtained with cathodes using the water-soluble binder. Porcher et al.^{75–77} investigated the usage of CMC as binder for LiFePO_4 . Their study revealed that LiFePO_4 slightly changes upon aging when it is brought into contact with water. A Li_3PO_4 layer of a few nanometers grows at the grain surface (see high resolution transmission electron microscope (HRTEM) image in Fig. 15), and at the same time the Fe(III) percentage in the active material increases.⁷⁵ The increase of Fe(III) content is less than 5% based on the Mössbauer results with a similar loss of capacity for LiFePO_4 by limiting the processing time within 24 h. Lee et al.⁷⁸ reported that the addition of PAA significantly decreased the viscosity of the LiFePO_4 and CMC slurry, leading to an increased solid concentration and improved discharge capacity in terms of

volumetric density. Lux et al.⁷⁹ reported that the high rate capability can be enhanced by using CMC as binder via shortening the processing time to 30 min and using a higher drying temperature (170 °C) for the electrode, as shown in Figure 16. The initial capacity (140 mAh g⁻¹) of the electrode using CMC as binder is lower than that for the one using PVDF as binder (155 mAh g⁻¹), but the capacity retention has been significantly enhanced to 105 mAh g⁻¹ after 1000 cycles. The results reported showed that LiFePO₄ can be processed in aqueous slurries and that CMC could be used as an alternative binder for LiFePO₄ cathode, as a water-soluble binder for Li-ion batteries. However, there is still no safety effects reported that are related to the aqueous binder.

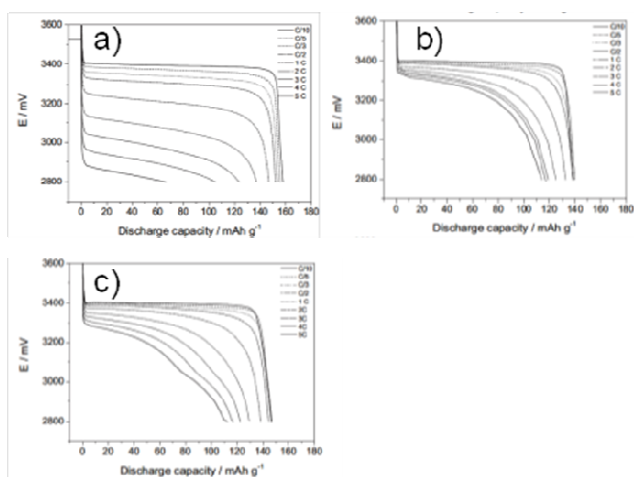


Figure 16. Rate performance and the discharge voltage profiles of LiFePO₄ electrodes using (a) PVDF binder and CMC binder dried at (b) 120°C and (c) 170°C.

2.2.3 Other cathode materials

Li et al.⁸⁰ found that CMC can be used as the binder for the high voltage (up to 4.8 V) cathode material Li₂MnO₃-LiMO₂ (M = Ni, Mn, or Co) and giving it improved cycling stability and a very promising rate capability compared to PVDF binder. Wang et al. reported CMC as a binder in high voltage (5 V) LiNi_{0.4}Mn_{1.6}O₄ cathode with close to the theoretical capacity (146 mAh g⁻¹) and low self-discharge (~10%).⁸¹ LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC) is one of the most promising large-scale commercial cathodes for lithium ion batteries, with the overwhelming advantages of high operating voltage, high specific capacity, cyclic stability, and structural stability.⁸²⁻⁸⁶ Our group reported that LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ electrode using CMC as a binder showed lower initial capacity but improved high rate capability in comparison with the current commercial PVDF binder (Fig. 17).⁸⁷ The possible reason is that the lower activation energy of the electrode using CMC as binder facilitates the transport of lithium ions compared with alginate and PVDF. Partial loss of lithium lost could be found in the both LiNi_{0.4}Mn_{1.6}O₄⁸¹ and NMC⁸⁷ samples when mixed with CMC binder in the water. This is probably due to the exchange between Li⁺ in the cathode

material and the protons in the water, as confirmed by synchrotron X-ray diffraction refined results. It is worth point out that many cathode materials such as LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, LiMn₂O₄, and LiFePO₄ have been investigated as cathode materials in aqueous electrolyte with excellent cycling stability.⁸⁸⁻⁹¹ This again confirmed that the cathode materials could be stable when contact with water. More work has to be done on cathode materials to evaluate the possibilities for commercial application of aqueous binders for lithium ion battery from safety aspects.

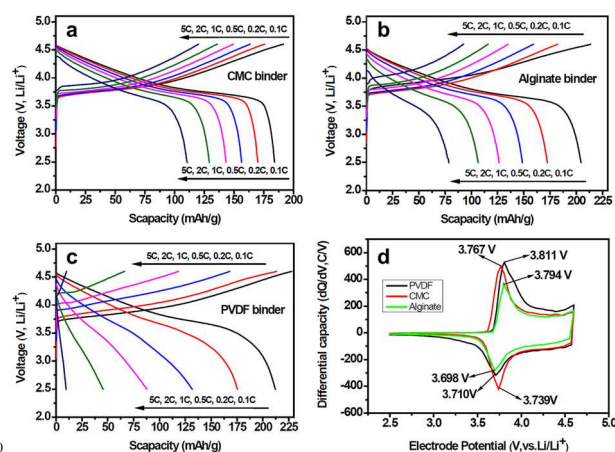


Figure 17. Initial charge-discharge curves of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ at various current densities in the voltage range of 2.5-4.6 V using different binders: (a) CMC, (b) alginate, and (c) PVDF; (d) dQ/dV curves for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ with CMC, PVDF, and alginate binders.

3. Lithium Sulphur battery

Lithium sulphur (Li-S) batteries utilize sulphur as the cathode and lithium metal foil as the anode. Although the main attention has been given to the cathode materials, there are some interesting research papers on the binder. In our view, the choice of binder relates to the cathode composition and the electrolyte. As a whole, the binder, the cathode materials, the electrolyte and even the cell assembling technique decide the performance of the cell. In other words, the function of the binder cannot be judged only by the binder, it should be put in the whole system of a cell and related to other components of the cell. Bearing this in mind, we now might get some inspiration from the following examples. The binder materials for Li-S batteries have been dominated by two kinds of polymers: polyethylene oxide (PEO) and PVDF. In the earlier stage of research on Li-S batteries, PEO was widely used as the binder. Cheon et al.⁹² compared the sulphur cathode with different amounts (8%, 13% and 18%) of PEO as the binder, and found that with the binder taking up a larger percentage in the cathode, the cycling performance improved correspondingly. However, researchers paid their effort to find a better binder than PEO, and two successful cases were Gelatin⁹³⁻⁹⁵ and poly(acrylamide-co-diallyldimethylammonium chloride) (AMAC)⁹⁶. Regarding a composite binder carboxy methyl

cellulose (CMC) and styrene butadiene rubber (SBR), there have been two papers reporting opposite results with Rao et al⁹⁷ claimed that CMC + SBR is better than PEO, while Lacey et al⁹⁸ reported that PEO is better than CMC + SBR. Concerning these two inverse results, the factors that contribute might be the difference in varied aspects: sulphur materials (CNF-S composite vs pure sulphur), current collectors (carbon coated Al foil vs uncoated Al foil), electrolytes (1 M kg⁻¹ lithium bis(trifluoromethylsulfonyl)imide in N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide / poly(ethylene glycol) dimethyl ether vs 1M LiTFSI and 0.25 M LiNO₃ in 1, 2-dimethoxyethane/1,3-dioxolane) and electrode preparing methods (unknown vs ball milling for 2 h).

Later, PVDF became the main-stream binder for Li-S batteries. However, when PVDF is applied as the binder, the toxic dispersant NMP and longer heating time for electrodes are two disadvantages. Therefore, researchers have been searching for environmentally friendly water soluble binders which can contribute a better cell performance. Varied materials have been proved to be better choices than PVDF, and they are CMC + SBR^{97, 99}, polyacrylic acid (PAA)¹⁰⁰, Na-Alginate¹⁰¹ and poly(vinylpyrrolidone) (PVP)¹⁰². A recent work¹⁰³ also showed excellent performance of Li-S batteries with PAA as the binder. Through ball milling with polydopamine (PD), sulphur and carboxylic acid functionalized multiwall carbon nanotube (MWCNT-COOH), covalent bonds formed through the crosslinking between PD/PAA and PD/MWCNT-COOH demonstrated a strong binding effect with sulphur and good cycling performance for Li-S batteries was achieved.

Schneider et al¹⁰⁴ applied three kinds of water soluble binders (i.e. nafion, Teflon, polyacrylonitrile-CMC) in Li-S batteries, and demonstrated them as promising environment friendly binders. Carbonyl β -cyclodextrin (C- β -CD)¹⁰⁵, which was prepared through treatment of β -cyclodextrin (β -CD) with H₂O₂, can be a better binder in Li-S batteries, compared with PVDF, polytetrafluoroethylene (PTFE) and β -CD (Figure 18).

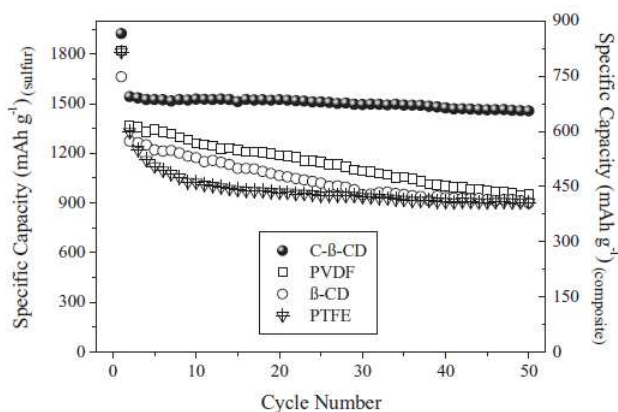


Figure 18. Cycle performance of PAN-S composite cathode with PTFE, β -CD, PVDF and C- β -CD (carbonyl β -CD prepared through treatment of β -CD with H₂O₂) at 0.2 C.

4. Sodium-ion battery

Sodium-ion batteries (SIBs) are similar in some ways to lithium-ion batteries. In both types of battery, ions are shuttled between the battery's positive and negative electrodes during charging and discharging, with the electrolyte serving as the medium for moving those ions. Taking into account recent concerns about a possible lithium shortage with the spread of electric vehicles, it is urgent to search for alternative energy storage systems that could complement the existing Li-ion technology. For this purpose, Na-ion technology can be a suitable choice in terms of battery cost, safety, and raw material abundance. Due to the increased size and heavier weight of the Na atom compared to the Li atom, the volumetric energy density and specific energy density obtainable for the sodium-ion battery would be significantly less than those obtainable with the lithium-ion battery. However, recent computational studies by Ceder et al. on voltage, stability, and diffusion barriers to Na-ion and Li-ion materials indicate that Na-ion systems can be competitive with Li-ion systems.⁶ In any case, Na-ion batteries would be interesting for very low cost systems for grid storage, which could make renewable energy a primary source of energy rather than just a supplemental one. The foundations of Na-ion technology must be deeply explored, however, in order to be ready to introduce new alternative energy storage systems onto the market. The search to develop commercially available Na-ion batteries requires finding and optimizing new electrode materials and electrolytes, in order to obtain batteries that are more economical, safer, and have longer life.^{12,13}

The binder effect was only investigated for anode of sodium materials by several groups.¹⁰²⁻¹⁰⁶ There are three major kinds of anode materials, including carbon materials, alloy-based materials such as those containing Sn, Sb, and P, and insertion type sodium metal oxide materials as reviewed in the latest review paper.¹⁰⁷ The theoretical capacities and the volume expansion ratios are shown in Fig. 19. It can be found that the expansion ratio for sodium based anode materials is more serious than for lithium based anode materials due to the bigger size of Na⁺ ions leading to poor cycle life. Therefore, what we have learned about the binder effect on lithium anode materials could be useful for sodium anode materials. A good binder must ideally maintain adhesion of the electrode to the current collector, maintain ionic contact, and facilitate the formation of a stable interface with the electrolyte. Komaba et al.¹⁰² reported that Sn electrodes with high capacity (500 mAh g⁻¹) for more than 20 cycles were achieved by choosing an appropriate binder and electrolyte additives. Qian et al.¹⁰³ reported that a Sb/C nanocomposite with CMC as binder can deliver a reversible capacity of 610 mA h g⁻¹, high rate capability at a very high current of 2000 mA g⁻¹ and long-term cycling stability with 94% capacity retention over 100 cycles. Darwiche et al.¹⁰⁴ found that commercial microsize Sb showed good cycling performance with Na, with a capacity of 600 mAh g⁻¹ (theoretical capacity 610 mAh g⁻¹) up to 160 cycles and with a coulombic efficiency of 98% when using carboxymethyl cellulose (CMC) as binder and fluoroethylene carbonate (FEC) as an additive. Qian et al.¹⁰⁵ and Kim et al.¹ reported independently that an amorphous phosphorus composite with carbon could deliver a high capacity of 1764 mAh g⁻¹ at the current density of 250 mA g⁻¹ using CMC as

binders and 1890 mAh g⁻¹ at the current density of 143 mA g⁻¹ using PAA as binder, respectively. Although there is no data comparison with PVDF, the binders play an important role in long-term cycling stability. Great efforts need to be made to further develop appropriate low-cost active materials for SIBs. More work should be carried out to further improve the lower initial coulombic efficiency.

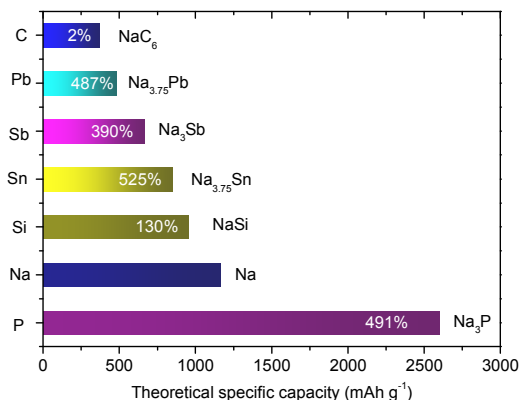


Figure 19. Theoretical specific capacity and volume expansion ratio of different anode materials for sodium battery.

5. Conclusions and outlooks

Small things do make a big difference. The binders only makes up a small part of the electrode composition, but it plays an important role in the cycling stability and rate capability for the Li-ion battery and the Na ion battery. The additional advantages of changing over from PVDF to aqueous binders are that the aqueous binders are cheap, green, and easy to process for electrode fabrication.

For big volume expansion anode materials in LIBs, carefully designed elastomer binder with strong cohesive strength in the interfaces of substrate|binder|active particles will be the most promising next generation binders. Further research should also focus on improving the initial coulombic efficiency for anode materials and investigating the safety aspects. Since the battery industry only can allow the volume expansion less than 6% to keep the full battery functional, the expansion of anode materials should also be reduced to lower than 10%.

For cathode materials in LIBs, aqueous binders could be used in water stable cathode like LiFePO₄ to reduce the cost and improve the cycle life and rate capability. However, the processing time should be short to restrict the structural change in water. For some other lithium transition metal oxide cathodes, there is still a big problem with the stability of such materials in water, which would lower the specific capacity. The safety aspects of binders are also worth to be investigation.

The sodium ion battery is only in its early stage of development. The binder effect on SIBs would be an interesting topic for research.

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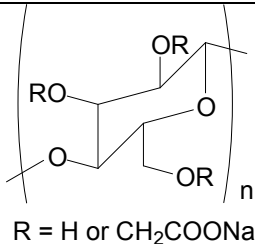
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Table 1. Typical binders, their molecular structures and the corresponding electrode materials and references

| Names | Molecular Structures | Electrode materials | References | | |
|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|----------|--------------------|
| Polyvinylidene fluoride (PVDF) | $\left(\begin{array}{cc} \text{H} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{F} \end{array} \right)_n$ | Graphite | 25, 26, 27 | | |
| | | Si | 31, 35, 45 | | |
| | | SnO ₂ | 46 | | |
| | | SnCoC | 47 | | |
| | | Sn | 48 | | |
| | | Fe ₂ O ₃ | 49 | | |
| | | NiO | 51 | | |
| | | CuO | 52 | | |
| | | Li ₄ Ti ₅ O ₁₂ | 54 | | |
| | | Sulphur | 97, 99-102, 105 | | |
| | | Carboxymethyl cellulose (CMC) |  <p>R = H or CH₂COONa</p> | Graphite | 22, 23 |
| | | | | Si | 31, 32, 33, 34, 39 |
| SnO ₂ | 46 | | | | |
| SnCoC | 47 | | | | |
| Sn | 48 | | | | |
| Fe ₂ O ₃ | 49, 50 | | | | |
| NiO | 51 | | | | |
| CuO | 52 | | | | |
| Li ₄ Ti ₅ O ₁₂ | 54, 55 | | | | |
| LiCoO ₂ | 72 | | | | |
| LiFePO ₄ | 74-79 | | | | |
| Li ₂ MnO ₃ -LiMO ₂ (M = Ni, Mn, or Co) | 80 | | | | |
| LiNi _{0.4} Mn _{1.6} O ₄ | 81 | | | | |
| LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂ | 87 | | | | |
| Sb | 107, 108 | | | | |
| Sulphur | 104 | | | | |
| Amorphous Phosphorus | 109 | | | | |
| Polyacrylic acid (PAA) | $\left(\begin{array}{c} \text{HOOC} \\ \\ -\text{CH}_2 - \text{CH}- \end{array} \right)_n$ | Graphite | 25, 27, 28 | | |
| | | Si-graphite | 40 | | |
| | | SnCoC | 47 | | |
| | | Sulphur | 100, 103 | | |
| | | Amorphous phosphorus | 109 | | |
| Polyethylene glycol (PEG) | $\text{HO} \left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ \text{H} & \text{H} \end{array} \right)_n$ | LiCoO ₂ | 73 | | |
| | | Sulphur | 92-98 | | |