REVIEW

Check for updates

Alternative binders for sustainable electrochemical energy storage – the transition to aqueous electrode processing and bio-derived polymers

Dominic Bresser, [iD] [ab] Daniel Buchholz, [ab] Arianna Moretti, [iD] [ab] Alberto Varzi [iD] [ab] and Stefano Passerini [iD] *[ab]

In this review, we discuss the most recent developments in the field of green binders for batteries and supercapacitors and explain how they could decrease cost and environmental impact, and yet improve the performance of electrochemical energy devices. The different classes of green binders reported to date in the literature are firstly classified according to their processability (the solvent required for electrode manufacturing), chemical composition (F-free), and natural availability (synthetic or bio-derived). The benefits originating from their employment are analysed for different devices. The most popular lithium-ion batteries are thoroughly discussed both from the anode and the cathode side. While high capacity Si-based anodes benefit from enhanced cyclability due to the interaction between the active particles' surface and the functional groups of, *e.g.*, polysaccharides such as carboxymethyl cellulose and alginate, the transition to water-processable cathodes is certainly more challenging. In particular, strategies to suppress the aluminium corrosion affecting most lithiated transition metal oxides are discussed. Despite the much more limited literature available, the role of the binder is increasingly recognized in the emerging field of lithium–sulphur and sodium-ion batteries, and electrochemical double layer capacitors and, therefore, here discussed as well.

[a] Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, D-89081 Ulm, Germany
[b] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany. E-mail: stefano.passerini@kit.edu, dominic.bresser@kit.edu, daniel.buchholz@kit.edu, arianna.moretti@kit.edu, alberto.varzi@kit.edu

Dominic Bresser is presently establishing a young investigator research group at the Helmholtz Institute Ulm (HIU), affiliated with the Karlsruhe Institute of Technology (KIT), Germany, focusing on the development of alternative anode materials for lithium-ion batteries. Prior to this, he held a postdoctoral position at CEA in Grenoble, France, where he was studying new macromolecular electrolytes. Beforehand, he completed his PhD at Muenster University, Germany, on nanostructured lithium-ion active materials. He is co-author of >50 peer-reviewed publications (h-index: 24; Scopus), 3 book chapters, and 16 patents and patent applications.

Dominic Bresser

Daniel Buchholz studied chemistry at the University of Muenster and completed his PhD studies at MEET battery research centre – University of Muenster with the focus on the synthesis, optimization and characterization of new and existing cathode materials for lithium- and sodium-ion batteries. He is co-author of 41 publications in peer reviewed international scientific journal (h-index: 21; Scopus).

Daniel Buchholz

3096 | *Energy Environ. Sci.,* 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

Broader context

Compared to other technologies, electrochemical storage offers the most energy efficient way to store electricity produced from renewable sources. This is leading to a continuously growing market of devices such as batteries and electrochemical double layer capacitors. However, it also raises concerns about the impact that their production and disposal could have on the environment. Interestingly, although simply considered as an inert component, the polymeric binder, indispensable for electrode production, is one of the factors defining the cost, environmental friendliness, and recycling/disposal of such devices. In fact, the state-of-the-art fluoropolymers, *e.g.*, poly(vinylidene difluoride) (PVdF), are not only expensive, but require a toxic solvent (*i.e.*, *N*-methyl-2-pyrrolidone, NMP) for electrode manufacturing. Greener alternatives are represented by water-processable F-free polymers, which may additionally allow for a cost reduction by a factor of 2–3 for the polymer and by a factor of about 100 for the processing solvent (NMP *vs.* water).

1. Introduction and outline

Our society is presently facing the great challenge to switch from depleting energy sources like oil, coal, or gas, to renewables such as solar and wind. With regard to their inherent intermittency and commonly decentralized generation, however, efficient and sustainable energy storage is of utmost importance. Beside large-scale solutions like hydropower or compressed air, electrochemical energy 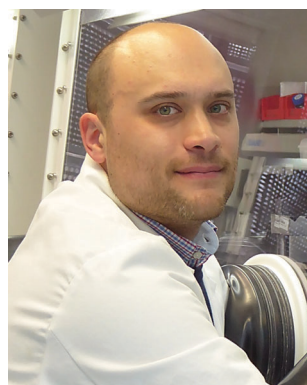storage, including secondary batteries and electro-chemical double-layer capacitors (EDLCs), is currently considered to be the most suitable technology, particularly for relatively smaller applications like transportation or short- to mid-term stationary energy storage.[1–4] As a matter of fact, the number of electric vehicle (EV) sales has steadily increased within the past years and the same trend is observed for the implementation of secondary batteries and EDLCs for buffering the intermittent energy supply by solar and wind.[1–4] Consequently, batteries and EDLCs play a vital role for moving towards a more sustainable "energy future". However, some concerns arise from the making of these devices. With respect to lithium-ion batteries, the cathode processing is based on the use of fluorine-containing polymers, in particular poly(vinylidene difluoride) (PVdF), as binders for the electrode preparation, and teratogen and toxic *N*-methyl-2-pyrrolidone (NMP)[5–9] as a solvent/dispersant. Switching to aqueous electrode processing routes and non-toxic binders, as already achieved, *e.g.*, for graphite-based lithium-ion anodes, would provide a great leap forward towards the realization of ideally fully sustainable and environmentally friendly electrochemical energy storage devices.

Herein, we will initially present a summary of the general advantages for aqueous electrode processing technologies compared to those based on NMP, followed by a brief classification of the presently investigated aqueous binders with regard to their processability and biocompatibility. After this introductory part, the focus will be set on the recent developments and achievements concerning the implementation of aqueous

Arianna Moretti is senior scientist at the Karlsruhe Institute of Technology, Helmholtz Institute Ulm (Ulm, Germany) since April 2014. She completed her PhD at University of Camerino (Italy) on synthesis, electrochemical and structural characterization of cathodes materials for lithium ion batteries and afterward spent one year as a postdoc at the MEET battery research center at the University of Muenster (Germany). Her research activities are currently focused on vanadium oxides materials and ionic liquids based electrolytes for lithium, sodium and magnesium batteries.

Arianna Moretti

Alberto Varzi studied Chemistry of Materials at University of Bologna (Italy) and graduated in 2008. He continued his education in Germany and received a PhD in 2013 from the Ulm University and ZSW. After a postdoctoral period at WWU Münster/MEET, he is now a senior scientist at the Helmholtz-Institute Ulm for Electrochemical Energy Storage of the Karlsruhe Institute for Technology. Currently his research interests are focused on materials for lithiumion, lithium–sulfur batteries and supercapacitors.

Alberto Varzi

Stefano Passerini is Professor at the Karlsruhe Institute of Technology (KIT), Helmholtz Institute Ulm (HIU, Germany) since January 1, 2014. Formerly Professor at the University of Muenster (Germany), he co-founded the MEET battery research centre (Muenster, Germany). His research activities are focused on electrochemical energy storage in batteries and supercapacitors. He is co-author of more than 400 scientific papers (h-index: 70; Scopus), a few book chapters and several international patents. In 2012, he has been awarded the Research Award of the Electrochemical Society Battery Division.

Stefano Passerini

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | **3097**

binders for lithium-ion battery (LIB) electrodes, *i.e.*, anodes and cathodes, and sodium-ion batteries as a promising alternative, in particular, for stationary applications, before eventually reviewing the research efforts conducted towards water-processed EDLCs as a high-power complement for efficient and effective energy storage.

1.1 General advantages of aqueous electrode processing

The major advantage of implementing large scale water-based processing is certainly related to the reduction of the environmental impact of LIB production. A comparative life cycle assessment (LCA), studying the impact of the transition from NMP to water, showed substantially reduced emissions of CO_2 equivalents for the latter.[5–8,10] Most importantly, NMP is an hazardous, teratogenic and irritating compound, while PVdF is mutagenic and teratogenic.[8]

As a consequence, several countries like the USA[11] or the European Union (EU)[12] started to limit the use of NMP to a minimum. In fact, Annex XVII to REACH (Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; EU) states that after May 9th 2020 *"NMP shall not be used as a substance on its own or in mixtures in a concentration equal to or greater than 0.3% unless manufacturers and downstream users take the appropriate risk management measures and provide the appropriate operational conditions to ensure exposure of workers is below the Derived No-Effect Levels (DNELs) of 14.4 mg m^{-3} for exposure by inhalation and 4.8 mg kg^{-1} per day for dermal exposure"*. Moreover, it has very recently, *i.e.*, in April 2018, been included in the list of substances of very high concern that may

have serious and often irreversible effects on human health and the environment by the EU, following a proposition of the Netherlands. Not least considering the battery manufacturing in these countries, this raises concerns about the whole electrode processing chain, from mixing of the slurry to the final solvent recovery (Fig. 1). The exposure of humans to these chemicals, as well as their release in the working environment, has therefore to be controlled carefully or ideally fully prevented.

Besides, the implementation of aqueous processing has also an impact on production costs and, in turn, on the overall battery price. Recent projections foresee a price of 100 \$ kW h^{-1} for LIBs to be reached in 2030.[13] A processing cost breakdown study indicates the reduction of costs associated with the use, drying and recovery of the organic solvent to be a key point to reach this ambitious target.[14] A simple comparison of binder and solvent costs already indicates the convenience of water-based electrode processing. NMP is rather expensive (1–3 \$ kg^{-1}; compared to about 0.015 \$ L^{-1} for water) and so is PVdF with a price of 8–10 \$ kg^{-1}. The most commonly used aqueous binders like carboxymethyl cellulose (CMC) are significantly cheaper at 2–5 \$ kg^{-1} and even the rather costly alginate is only about 8 \$ kg^{-1}, *i.e.*, still at the lower end of the cost range for PVdF.[15,16] Even though such an analysis will eventually have to be carried out by industry, these numbers already indicate the potential cost reduction by transitioning to water-based electrode processing from the materials' point of view.

The impact of the solvent on the electrode drying process is poorly investigated in the scientific literature so far – especially when it comes to a comparison of different binders. Generally,

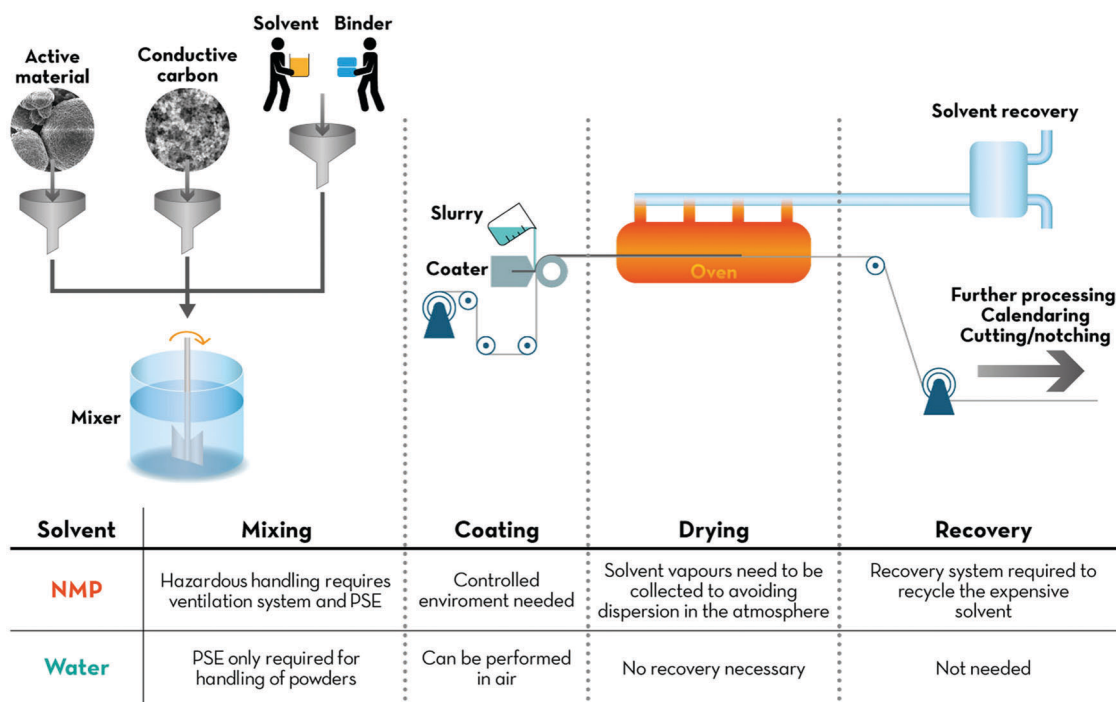| Solvent	Mixing	Coating	Drying	Recovery
NMP	Hazardous handling requires ventilation system and PSE	Controlled enviroment needed	Solvent vapours need to be collected to avoiding dispersion in the atmosphere	Recovery system required to recycle the expensive solvent
Water	PSE only required for handling of powders	Can be performed in air	No recovery necessary	Not needed

Fig. 1 Simplified schematic description of a generic battery/EDLC electrode manufacturing process. From left to right, the main advantages of water over NMP are highlighted for each step, from the initial mixing of the slurry, its coating on the current collector, the drying of the electrode layer and, finally, the solvent recovery.

3098 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

aqueous processed electrodes are reported to be more hydrophilic, but a drying temperature of 100 to 120 °C appears to be sufficient to reduce the residual water content to an acceptable level, *i.e.*, below 50 ppm.[17,18] In fact, when preparing aqueous processed electrodes on the lab-scale, one easily recognizes that the electrode drying is much faster compared to NMP-processed ones. This finding was recently confirmed by Susarla *et al.*,[19] reporting that the equilibrium vapour pressure of water is 35-times higher compared to NMP (in line with the substantially lower boiling point of 100 °C *vs.* 203 °C), even though the latent heat of evaporation of water, *i.e.*, the energy that is required to induce the liquid-to-gas phase transition, is 4-times higher than the one for NMP. This potentially results in relatively faster evaporation of water, leading to shorter drying times. A recent simulation of the corresponding cost revealed that the cost per kW h is presumably comparable for both systems, when evaluating the drying step only.[17] The key for saving energy, *i.e.* cost, and reducing the required investment in the case of aqueous electrode processing, however, is the dispensability of recovering the NMP solvent *via* condensation and/or distillation to prevent release into the environment.[14,17] In fact, according to the aforementioned calculation, this cost reduction may account for almost half of the current electrode processing and associated plant capital costs.[17]

1.2 Classification of aqueous binders

The term "green" is widely used to express the environmental friendliness of materials and processes. However, its meaning can significantly vary depending on the context of use. When talking about polymeric binders, green alternatives could be identified according to (i) processability, (ii) chemical composition and (iii) natural availability (see Fig. 2). According to the first criterion, binders soluble or dispersible in environmentally benign solvents, such as water or ethanol, could be classified as green alternatives. Poly(tetrafluoroethylene) (PTFE), also known as Teflon® (Dupont), is highly hydrophobic with strong C–C and C–F bonds providing high chemical and mechanical stability, rendering it very suitable for highly resistant coatings and membranes.[20] It can be dispersed in water and stabilized by wetting agents, thus making electrode processing feasible. These wetting agents, however, are frequently environmentally and/or biologically hazardous chemicals (*e.g.*, fluorine-containing carboxylic acids and/or ammonium lauryl sulphate). Hence, the potential aqueous processing alone does not make this binder a very green one. Recently, another water-processable binder, denoted as TRD202A (a fluorinated acrylate polymer latex), has been commercialized by JSR Corporation (Japan).[21,22] This fluorinated acrylate polymer promises enhanced adhesion to the current collector, low resistance, and long cycling life. Although their water processability would reduce the environmental impact of the electrode manufacturing, fluoropolymers are, however, more difficult to dispose of at the end of the life of the battery. In fact, they are not soluble in the majority of solvents besides a few expensive, flammable, and/or toxic ones (*e.g.*, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAC), NMP and dimethyl sulfoxide (DMSO)).[23] Consequently, the fluorinated binding agents cannot be easily separated from the electrode active materials and would require thermal treatments
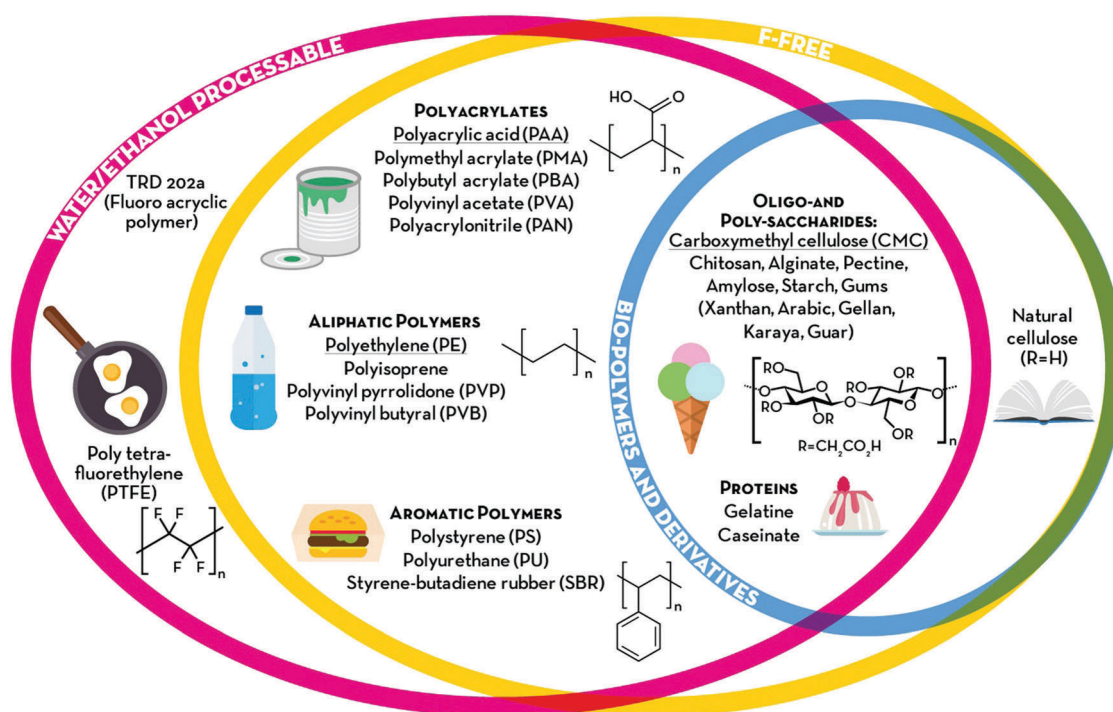

Fig. 2 Overview of the different classes of binders discussed in the present review. The polymers are divided into three main categories according to their processability (water and/or ethanol processable), chemical composition (F-free) and natural availability (bio-polymers and derivatives).

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | **3099**

for their elimination. This raises further environmental concerns, as most of the decomposition products of fluoropolymers in N_2 (e.g., cycloperfluorobutane, hexafluoropropene, perfluoroisobutene, fluorophosgene, and other fluorocarbons) are extremely toxic[24] and known to affect the ozone layer. Thus, F-free compounds would represent a real step towards greener energy storage devices. To date, a variety of synthetic polymers have been proposed as alternative binders for both batteries and supercapacitors. Polyacrylates are certainly the most common, with PAA being the most popular choice, often used in its neutralized water-soluble form (either with Li or Na). Other aliphatic and aromatic synthetic polymers, such as polyethylene (PE) and polystyrene (PS), have also been proposed as F-free electrode binders. Owing to their generally low glass transition temperature (T_g), these soft and rubbery materials are easy to process and provide good mechanical stability to the electrodes, which is expected to enhance cycling life. All these synthetic plastics are industrially produced in large volumes (several millions of tonnes per year) and already employed in a variety of fields, ranging from adsorbents to paint components, and food packaging. However, although such established industrial production could guarantee a smooth transition from PVdF-based electrodes; the electrode manufacturing would still rely on non-renewable materials. For this reason, bio-polymers and their derivatives would represent a more sustainable choice. Polysaccharides, for example, are naturally occurring polymers that can be extracted from a variety of non-edible sources. These generally share the same glucose monomer as the building block, while different glycosidic bonds and substituents on the pyranose ring define the peculiar properties of each polymer (e.g., cellulose, alginate, starch, etc.). As previously mentioned, CMC is the most famous bio-derived compound used in the current state-of-the-art production of LIB negative electrodes together with styrene–butadiene rubber. Although its primary role in LIB electrode processing is as a thickener, i.e., to stabilize the slurry and adjust its viscosity, its contribution to the electrode binding is now ascertained. Such a linear polysaccharide is a cellulose derivative, made water-soluble by replacing some –OH groups with carboxymethyl moieties (–CH_2COOH), and is extensively used as a thickener in the food industry. In Table 1, we provide an overview of the herein reviewed and discussed binding agents, summarizing the earlier mentioned classification parameters ('F-free', 'Processability', 'Synthesis', 'Sustainability', and 'Ease of disposal') in order to allow for a general ranking concerning the environmental friendliness of these binders. In addition, Table 1 provides an overview of the cited references, in which the electrolyte swelling and mechanical properties of the resulting electrodes (e.g., the coating adhesion, elastic behaviour, and tensile strength) are reported. Particularly the latter two columns and the number of given references, indeed, also serve as a rough indication for the stage of development of the different binders and may serve as a guideline for future studies.

2. Lithium-ion batteries

For many years, the binder has been considered to be of minor importance for battery electrodes. Indeed, PVdF was performing fairly well, and the scale of LIB production was not as high as

today, rendering processing issues secondary. However, the continuously rising demand for high-performance LIBs has led to a reconsideration of these aspects. In fact – beside the advantageous introduction of aqueous electrode processing technologies, as discussed in Section 1.1 – it was found that the binder plays a decisive role in the electrode performance, despite its rather low content of a few percent only (up to 5 wt%, but usually 2 wt%) with respect to the total electrode composition (i.e., active material, binder, and conductive additives), and its chemical and electrochemical inactivity. Nonetheless, the selection of a suitable binding agent commonly follows the following general criteria: (i) ensuring suitable cohesion between the active material particles and the additional electrode components as, e.g., the conductive agent; (ii) guaranteeing strong adhesion of the electrode coating to the current collector; (iii) facile electrode processing; (iv) insolubility in the electrolyte and low electrolyte swelling; (v) high chemical, thermal, and electrochemical stability, while not detrimentally affecting the electron and ion transport in the electrode composite; and (vi) providing low additional cost, ideally being also environmentally-friendly.

In light of these general considerations, we will review in the following the past and recent development and achievements in the field of lithium-ion batteries, starting from the anode side, for which aqueous electrode processing is already fairly well established and continuing with the cathode side, for which still several challenges remain to be overcome.

2.1 Anodes – active materials with limited volume variation upon lithiation

(a) **Graphite as state of the art.** The manufacturing of graphite anodes via an aqueous process is, nowadays, a state-of-the-art method. Early efforts to switch from organic solvent-based preparation to water-based can be dated back to the early 2000s and focused mainly on the use of sodium carboxymethyl cellulose (Na-CMC)[25] and styrene butadiene rubber (SBR).[26] Cellulose derivatives are used in many industrial applications, i.e., cosmetics, food, drugs, textiles, and construction. Pure cellulose is not soluble in water, but some of its esters or ethers derivatives, like CMC, are. Therefore, they are commonly employed as stabilisers, emulsifiers, and thickening and binding agents in aqueous solutions. The physical–chemical properties of cellulose-based polymers are dependent on the molecular weight, particle size, nature of substituents and degree of substitution (DS).[27] Na-CMC is a linear polymer constituted of glucose units bound via glycosidic β-(1 → 4) linkages. The carboxymethylation of the cellulose backbone is achieved by reacting it with an alkali solution (generally NaOH) and chloroacetic acid or its sodium salt. The DS value in commercial products varies between 0.4 and 1.5.[28] A condition for efficient tape casting, resulting in uniform and densely packed electrodes, is to achieve a homogeneous and stable dispersion of the components. However, due to the hydrophobic nature of the particles, water suspensions of natural graphite (still the most common anode material) are not stable. Interestingly though, when Na-CMC is added to the dispersion, hydrophobic

3100 | Energy Environ. Sci., 2018, 11, 3096–3127

This journal is © The Royal Society of Chemistry 2018

Table 1 Summarizing overview of the herein reviewed binding agents, including a general ranking concerning their environmental friendliness according to such parameters as 'F-free', 'Processability', 'Synthesis', 'Sustainability', and 'Ease of disposal'. Furthermore, an overview of those references reporting studies on the electrolyte swelling and the mechanical properties of the resulting electrodes (e.g., the coating adhesion, elastic behaviour, and tensile strength) is provided

Name of Binder (incl. the corresponding derivatives)	F-free	Processability	Synthesis	Sustainability	Ease of disposal	"Green score"	Binder properties Swelling with electrolyte	Mechanical (adhesion, elastic behaviour, tensile strength, …)
State of the art								
CMC	+	+	+	+	+	+5	40, 138, 158	12, 44, 81, 119[a], 134, 136, 158, 304, 200, 201
PTFE	−	+	−	−	−	−3	n.a.	n.a.
PVdF	−	−	−	−	−	−5	40, 158, 165	12, 134, 136, 158, 166, 300, 303, 306
Alternatives								n.a.
Agar-agar	+	+	+	+	+	+5	n.a.	n.a.
Alginate	+	+	+	+	+	+5	84, 138, 165	46, 86, 91, 97, 300
Amylose	+	+	+	+	+	+5	n.a.	95
Arabic gum	+	+	+	+	+	+5	n.a.	n.a.
Carrageenan	+	+	+	+	+	+5	n.a.	n.a.
Caseine	+	+	+	+	+	+5	n.a.	304
Chitosan	+	+	+	+	+	+5	n.a.	136, 137, 166
Cyclodextrines (carbonyl-beta)	+	+	+	−	+	+5	n.a.	90
Ethylene propylene diene monomer (EPDM) rubber	+	0	0	+	0	+1	n.a.	n.a.
Gelatine	+	+	+	+	+	+5	n.a.	46
Gellan gum	+	+	+	+	+	+5	n.a.	n.a.
Guar gum	+	+	+	+	+	+5	56	56, 57
Karaya gum	+	+	+	+	+	+5	n.a.	94
Cellulose (natural)	+	+	+	+	0	+4	n.a.	n.a.
Pectine	+	+	+	+	+	+5	n.a.	57, 95
PEDOT-PSS	+	+	+	+	+	+4	n.a.	100, 136
Polyacrilic acid (PAA)	+	+	0	−	0	+1	40, 78, 69, 138, 158	12, 36, 44, 69, 81, 133, 158, 300
Poly(methyl acrylate) (PMA)	+	+	+	−	0	+2	n.a.	n.a.
Poly(vinyl alcohol) (PVA)	+	0	0	−	0	+1	n.a.	78
Poly(vinyl acetate) (PVAc)	+	+	+	−	0	+2	n.a.	n.a.
Polyacrylonitrile (PAN)	+	+	0	−	0	+2	n.a.	n.a.
Polyisoprene (PIpr)	+	0	0	+	0	+3	n.a.	n.a.
Polyaniline (PANi)	+	+	+	−	0	+2	n.a.	n.a.
Polyethylene (PE)	+	0	0	−	0	+1	n.a.	n.a.
Polyimide (PI)	+	0	0	−	0	+1	n.a.	n.a.
Polystyrene (PS)	+	0	0	−	0	+1	n.a.	n.a.
Polyurethane (PU)	+	0	0	−	+	+2	n.a.	n.a.
Polyvinyl butyral (PVB)	+	0	0	−	0	+1	n.a.	308
Polyvinyl pyrrolidone (PVP)	+	+	+	−	+	+3	n.a.	306, 307
Starch	+	+	+	+	+	+5	n.a.	n.a.
Styrene butadiene rubber (SBR)[b]	+	0	0	−	0	+1	40	44, 133, 200, 201
Tara gum	+	+	+	+	+	+5	56	56
Tragacanth gum	+	+	+	+	+	+5	n.a.	46
TRD202A	−	+	n.a.	n.a.	−	n.a.	n.a.	n.a.
Xanthan gum	+	+	+	+	+	+5	n.a.	91, 134, 139

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, 11, 3096–3127 | 3101

Table 1 (continued)

Green score legend	+	0	–
F-free	yes		no
Processability	Water/ethanol-based slurry		Organic solvent-based slurry (e.g., NMP)
Synthesis	No chemistry involved (natural binder) or aqueous chemistry	Non-aqueous chemistry	Non-aqueous chemistry involving fluorinated chemicals
Sustainability	Obtainable from renewable sources		Derived from non-renewable sources (e.g., petroleum)
Ease of disposal	Recyclable by water treatment (simple washing)	Suitable for hydrometallurgical with no F emissions	Hydrometallurgical or pyrometallurgical methods required and F emissions

^{a} CMC in combination with a not specified water-soluble elastomer. ^{b} Commonly used in combination with other binders as, for instance, CMC.

interactions between the graphite particles and the CMC backbones are established. The carboxylic groups of Na-CMC adsorbed on the graphite surface dissociate and stabilize the suspension.[26] Hence, Na-CMC acts as a thickening agent and surfactant, avoiding graphite sedimentation. On the other hand, the formation of a stable graphite suspension does not occur when only SBR is used. However, the combination of CMC and SBR was found to retard the graphite sedimentation and to form denser, but less brittle electrodes.[26] The properties of CMC depend strongly on the DS, which influences the conformation and charge density of the polymeric chains in water, e.g., a lower DS results in higher hydrophobicity and, thus, stronger interaction with graphite.[29]

Electrodes made with CMC and CMC–SBR mixtures displayed lower 1st cycle irreversible capacity loss (ICL) than PVdF-based electrodes,[26,30] which is attributed to faster SEI-formation induced by the interactions between carbon and Na-CMC.[30] It is recognized that the presence of hydroxyl and carboxyl functions is the key feature which is responsible for the improved electrochemical performance, as displayed by the electrodes featuring CMC and other synthetic and natural polyelectrolytes with respect to PVdF. For example, gelatine was found to act as a surface modifier providing nucleation centres for the formation of a thinner passivation film, hence, reducing the lithium consumption associated with the solid electrolyte interphase (SEI) build-up.[31–33] The reactivity of CMC with the electrolyte was studied in more detail by El Ouatani et al.[34] via XPS. The authors found that CMC readily reacts with the electrolyte upon simple soaking (prior to cycling), generating a protective surface layer composed of R–O–PF$_4$ and LiF. The efficacy of this "artificial SEI" is evidenced by the better cyclability (in sulfolane-based electrolytes) of graphite electrodes made with CMC and practical loading compared to their PVdF counterparts.[35]

However, the role of the functional groups of the binder is better illustrated in polyacrylates (e.g., PAA or poly(methyl acrylate) (PMA)), which contain a higher number of functional groups than CMC and, thus, adsorb more strongly on the graphite surface via hydrogen bonding.[36] Komaba et al.[37–39] proposed that Li$^+$ is coordinated by the polarized oxygen atoms along the polymeric chains of polyacrylates (like in poly(ethylene oxide); PEO) promoting its de-solvation from solvent molecules (ethylene carbonate (EC) or propylene carbonate (PC)). Although the amount of binder in the electrodes used for these studies was often quite high (5–15 wt%), it has been demonstrated that a homogenous coating of graphite particles with polyacrylates behaves like an "artificial SEI", as found for Na-CMC, enabling reversible cycling in non-SEI forming solvents such as PC[37] or in PC-rich electrolytes.[40] Moreover, the solvent up-take of polyelectrolytes is found to be lower than that of PVdF, reducing the risk of co-intercalation of other species (e.g., PC molecules) together with Li$^+$.[40] These findings are extremely interesting, as PC has a lower melting point than EC (−49 °C and +36 °C, respectively) and its use as the main solvent or co-solvent in the electrolyte formulation would enlarge the operational temperature range of LIBs. Nevertheless, the ability of functionalised binders to act as an "artificial SEI" decays when reducing the

3102 | Energy Environ. Sci., 2018, 11, 3096–3127

This journal is © The Royal Society of Chemistry 2018

binder amount to practical values (2–5 wt%) as a result of the incomplete particle coverage.[40] Generally, a more uniform graphite particle coverage is achieved when using Li-PAA and Na-PAA rather than for non-neutralized PAA. The more extended conformation in water of dissociated Li/Na-PAA, due to electrostatic repulsion between the carboxyl groups, was proposed as the reason for the higher slurry viscosity and the better uniformity of the particle coating.[38] Better first cycle coulombic efficiency, a smoother electrode surface after cycling, and prolonged cycle life when using neutralized Li-PAA and Na-PAA were also reported by Chong *et al.*[41] These authors highlighted the importance of carefully dosing the SBR amount (used to compensate for the brittleness of polyacrylates as for Na-CMC), since a monotonous decrease of the electronic conductivity was found upon increasing the quantity of the elastomer.

When moving from laboratory to pilot-line scale studies,[42] which implies practical loadings of graphite (>2 mA h cm^{-2}) and the used binder (<5 wt%) as well as different mixing and drying conditions, the Na-CMC–SBR mixture outperforms both Na-PAA and the Na-CMC/Na-PAA mixture in terms of rheological properties of the slurry, coating adhesion, and electrochemical performance. Furthermore, it is found that Na-PAA is more sensitive than Na-CMC/SBR to different mixing methods and drying conditions. The electrodes based on the Na-CMC/SBR formulation preserved their adhesion strength upon doubling the electrode loading, while both PVdF and Na-PAA showed a significant loss of their initial mechanical properties.

Interestingly, as mentioned in the introduction, the binder may affect also the battery safety. In fact, a DSC (differential scanning calorimetry) study on lithiated graphite revealed that less heat is generated upon SEI breakdown for electrodes made with CMC or polyacrylate compared to PVdF, confirming the protective nature of the SEI formed in the presence of the former binder layers.[43]

The binding ability of polyacrylate, arising from the high number of functional groups, has been exploited by cross-linking PAA with CMC to prepare thick graphite electrodes (13.8 mg cm^{-2}). The electrodes, which included also SBR in the formulation, displayed better adhesion and capacity retention and, at the same time, reduced resistance compared to those prepared with CMC/SBR.[44]

The extended work conducted on CMC and polyacrylate stimulated further investigation of other functionalised binders and, especially, of bio-derived polymers such alginate, chitosan, gums (*e.g.*, guar, xanthan, karaya, tragacanth, and arabic), agar–agar, pectine, and carrageenan.[45–48] All of them are stable (at least) up to 200 °C and, thus, compatible with the relatively high electrode drying temperatures. Additionally, they are electrochemically inert in the potential range from 0 to 3 V *vs.* Li/Li$^+$.[45] They are, therefore, potential alternatives to Na-CMC, providing the advantage of possessing functional groups, which, instead, have to be chemically introduced into cellulose. However, although the published studies are very encouraging, little is known about the processability, stability, and rheological properties of large-scale slurries made with such bio-polymers. Indeed, the viscosity of the binder solution will determine how

easily the solid content of the slurry can be dispersed and, thus, the mixing conditions. The final slurry must be stable over time and no sedimentation should occur to obtain a homogenous coating. For instance, a recent study reported higher stability and viscosity for Na-alginate slurries (of different compositions) compared to Na-CMC.[49] These properties are key factors to assess the feasibility of up-scaling innovative electrode formulations.

To summarize, polymers with hydroxyl and carboxyl functional groups such as CMC and PAA have been demonstrated to be suitable binders for graphite electrodes, with improved performance compared to PVdF and with "artificial SEI" formation ability.

(b) Titanium-based alternatives – TiO$_2$ and Li$_4$Ti$_5$O$_{12}$. The low working potential of graphite grants a quite high energy density with respect to its eventual application in Li-ion full-cells. Nonetheless, it can be a source of severe safety issues due to the risk of metallic lithium plating and, consequently, dendrite formation upon cell overcharge. This aspect stimulated the search for alternative anode materials and, among them, titanium-based compounds are emerging. TiO$_2$ polymorphs and Li$_4$Ti$_5$O$_{12}$ spinel (LTO) offer a working potential above 0.8 V, thus, excluding the risk of Li plating and bypassing the SEI formation requirement.[50] However, it should be mentioned that the LTO surface can react with carbonate-based electrolytes, generating gases, which also raises safety concerns, especially for pouch-cell-type lithium-ion cells. Although still under debate, the presence of water residues, for example, from aqueous electrode processing, seems to be a triggering factor.[51] Anatase is a cheap and environmentally friendly material with a theoretical capacity of 335 mA h g^{-1}, while Li$_4$Ti$_5$O$_{12}$ has a very stable structure, but a theoretical capacity of only 175 mA h g^{-1}. The insertion of 0.5 equivalents of Li in TiO$_2$ (which corresponds to a practical value of 165 mA h g^{-1} for a micrometric sized material) results in only 3% volume change.[52] Li$_4$Ti$_5$O$_{12}$ is considered a zero-strain material as the complete lithiation to the rock-salt structured Li$_7$Ti$_5$O$_{12}$ is accompanied by a volume increase of only 0.2%.[50,52] Both materials are suitable for applications requiring high power rather than high energy (*e.g.*, hybrid electric vehicles, HEV). Therefore, it was logical to extend the study of aqueous processing also to these interesting alternative anodes to pursue sustainable battery production. Kim *et al.*[53] introduced the use of CMC for the preparation of denser LTO electrodes for a greener and safer battery based on aqueous processed electrodes and an ionic liquid-based electrolyte. The investigation of the effect of CMC on the performance of LTO-based electrodes was extended by Chou *et al.*,[54] who found improved rate capability compared with PVdF-based electrodes. LTO electrodes made with CMC show lower charge transfer resistance and higher ionic conductivity that those made with PVdF,[54,55] as well as improved compactness and electrode wettability.[53] In a material with practically no volume change other characteristics rather than adhesion strength emerge as key factors to improve the performance. Indeed, although their adhesion strength was lower than CMC, tara gum, and in particular guar gum-based electrodes, show enhanced performance.[56,57] The effect is attributed to a more homogeneous coverage of LTO particles, and to the higher

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | 3103

electrolyte uptake of branched gum with respect to CMC resulting in a larger contact area between LTO and the electrolyte, reducing the charge-transfer resistance.[51] In fact, for active materials operating within the electrochemical stability window of the electrolyte, extended binder swelling, promoting electrode/electrolyte reactions at the interphase, is not detrimental. A recent study suggested that the binder influences the formation and composition of a passivation layer on LTO electrodes upon cycling. Interestingly, a thicker film is found for PVdF compared to CMC or PAA.[58] An important aspect to be considered is the alkaline nature of LTO water-based slurries, which triggers aluminium current collector corrosion upon coating (due to the high working potential there is no need to use heavy and expensive copper foil). This issue can be solved by including pH modifiers (e.g., mild acids) in the slurry formulation to buffer the pH to a value of about 6.5.[57] Higher compactness and better electrochemical performance of TiO_2 electrodes prepared with CMC and CMC–SBR with respect to PVdF were reported.[59–61]

2.2 Anodes – active materials with extensive volume variation upon de-/lithiation

(a) Silicon as anodes for next generation high energy LIBs. The interest in the development of Si-based anodes for LIBs increased markedly around 2010, registering a doubling of publications from 2009 to 2011. The electrochemistry of Si in its different forms, i.e., bulk crystalline or amorphous, nano and thin films, has been elegantly reviewed by Obrovac et al.[62] The lithiation of bulk crystalline silicon proceeds via a two-phase reaction (evidenced by a plateau at 0.17 V) and involves the formation of amorphous Li_xSi. The complete lithiation results in crystalline $Li_{15}Si_4$ with a corresponding capacity of 3579 mA h g^{-1}. Upon reversing the process, amorphous Li_2Si is formed via a two-phase reaction (with a plateau at 0.45 V), followed by complete delithiation (via a solid solution mechanism), leading to amorphous Si. This phase can be re-lithiated to reach, below 0.07 V, crystalline $Li_{15}Si_4$. Rhodes et al.[63] have experimentally shown that the potential region, where extensive fracturing of Si takes place, corresponds to the two-phase reaction of $Li_{15}Si_4$. Using nano-sized Si or Si alloys, the two-phase region and the formation of $Li_{15}Si_4$ are suppressed, thus improving the cycle life of the electrode.[64]
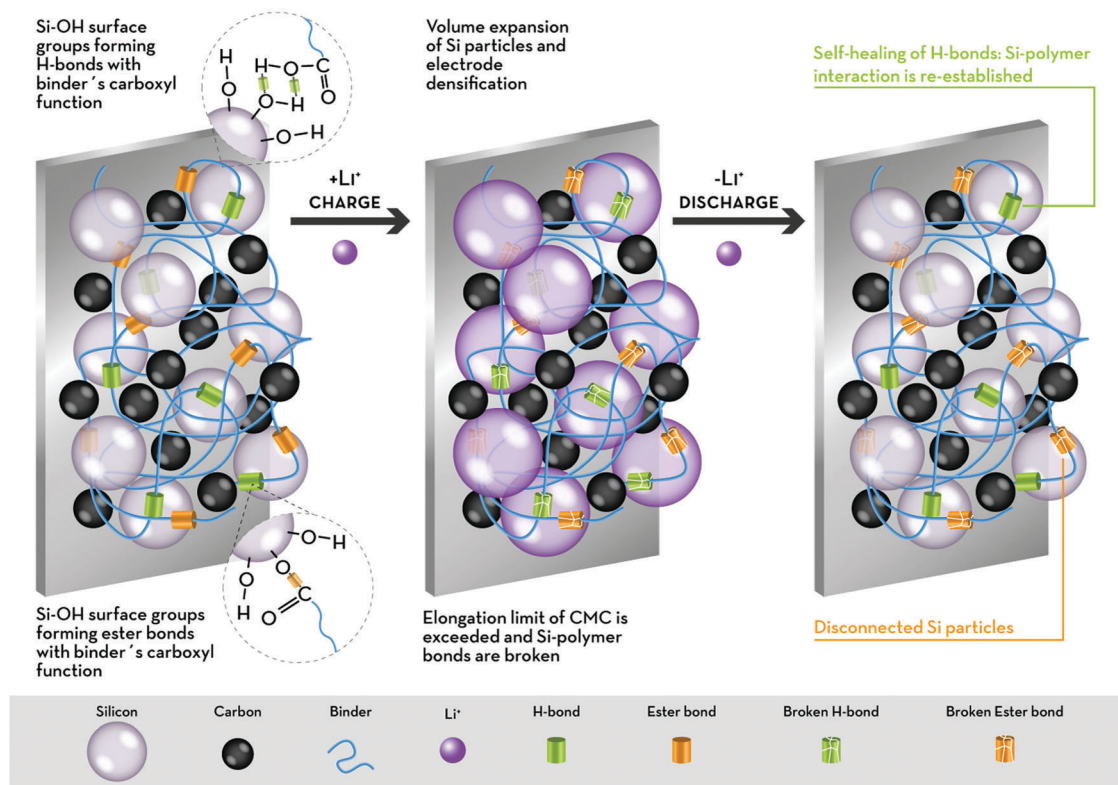
While the contact between the Si particles is easily retained upon lithiation (because the resulting volume expansion of lithiated Si, up to 280%, favours the contact between all particles in the composite electrode), the volume decrease upon delithiation can lead to electrode pulverization, a loss of mechanical properties and strong capacity fading. Therefore, a binder capable of chemically binding the Si particles while maintaining a certain flexibility and homogeneously coating their surface to avoid electrolyte decomposition, is expected to enable longer cycle life. In the search for an alternative binder to PVdF, it was quickly recognized that CMC could mitigate the negative effects associated with the large Si particle volume variation upon lithiation.[30,65–67] Surprisingly, however, the use of SBR together with CMC (a rather stiff and brittle polymer)

did not result in improved electrochemical performance, although improving the flexibility of the electrode.[65] Therefore it is the ability of CMC to chemically interact with the active materials particles (more precisely the characteristics of the formed bonds) to influence the electrochemical behaviour rather than the overall electrode flexibility.[68,69] Accordingly, further studies were conducted to clarify the nature of the potential interactions between Si and CMC, which are related to the Si surface characteristics during the aqueous processing. Upon exposure of Si to air or water, siloxane Si–O–Si and silanol Si–OH surface terminations are formed.[70] These are susceptible to forming both covalent and hydrogen bonds with the carboxyl groups present in the polymeric chains of many water-processable binders (e.g., CMC, alginate, pectine, gellan and xanthan gums, and carboxymethyl chitosan). Hochgatterer et al.[71] demonstrated the central role of the binder carboxyl groups by replacing them with hydroxyethyl and cyanoethyl groups. In fact, the Si-C-composite anodes prepared using such modified CMCs displayed poorer electrochemical performance than those employing the original CMC. Based on this evidence, a condensation reaction occurring between the carboxylic units and the silanol groups upon drying was proposed. The improved adhesion strength of covalently bonded Si and CMC with respect to the trapped Si particles in the CMC matrix was proven by atomic force microscopy (AFM).[72] Furthermore, a recent study evidenced that a thin layer of SiO_2 covering the Si particles is beneficial for the formation of ester bonds, thereby improving the electrode cyclability, although increasing the first cycle ICL.[73]

Using different polymers and modifying the Si surface, Bridel et al.[68] observed that when no Si–binder interaction can be established (i.e., when there are no accessible –OH groups on the Si surface) or if strong Si–binder covalent bonds are formed (e.g., peptide bonds between Si and the binder, e.g., chitin), the electrochemical performance of Si electrodes is rather poor. The volume change during the electrochemical process causes contact loss between carbon and Si in the first case, and the rupture of covalent bonds in the second scenario. Therefore, the authors suggest that the improved performance observed for Si–CMC electrodes must be ascribed to the formation of H-bonds, which are weak enough to break upon volume increase, but able to regenerate through the so-called ''self-healing'' mechanism, given the presence of residual water.[68] A schematic description is presented in Fig. 3.

Also the role of the slurry pH in the establishment of chemical bonds was investigated. In fact, adjusting the slurry pH to 3 should lead to the presence of SiOH and COOH, which are expected to promote the formation of covalent ester bonds upon electrode drying.[71,74,75] For example, Bridel et al.[75] compared the performance of electrodes made from slurries without adjusting the pH, to favour the formation of H-bonds in the dried electrode, and at pH = 3, to induce Si–binder ester bond formation upon drying. These authors observed that in this latter case, good long-term cyclability of the Si electrodes was achieved only by limiting the lithiation degree, i.e., when the volume expansion of the Si particles can be buffered by the electrode porosity. Indeed, lithiation degrees above 1.7 eq.

Fig. 3 Schematic illustration of the proposed interactions occurring between the carboxylic groups of CMC and Si particles. Both H-bonds and ester bonds are established with the silanol (Si–OH) groups on the Si particle surface. The volume expansion occurring upon lithiation causes the rupture of the bonds. During the de-alloying process, the Si particles shrink, but the ester bonds are not re-established. On the other hand, the self-healing property of the weaker H-bonds permits the contact between the binder and the Si particles to be retained.

of Li per Si result in exceeding the elongation limit of CMC (5–8%),[65] resulting in the rupture of the CMC–Si covalent bonds, which are not reformed. On the other hand, when the slurry pH is not controlled, the formation of the weak H-bonds is favoured leading to the full capacity retention of the electrodes for over 100 cycles, since these bonds can be regenerated spontaneously.[75]

However, it is important to note that at pH = 3 a better dispersion of the conductive carbon and Si is reported.[71] Additionally, a simulation study revealed that the CMC chains rearrange to increase the number of contact points between adjacent Si particles, giving rise to a "spring-like" conformation.[76] The CMC chain rearrangement is due to the tuning of inter- and intra-chain interactions, regulating the viscosity of the slurry.[74,76,77] The DS and the countercation (e.g., smaller cations lower the interactions due to the poor dissociation and less extended conformation in water) are also expected to affect inter- and intra-chain interactions.[68]

Further studies have proved that the cycling stability of Si anodes can be further improved by the use of polyacrylate binders.[69,78] In fact, polyacrylates possess more carboxyl groups than CMC, which can graft on the Si particle surface via H-bonds. It has been reported that during the electrode's drying step, linear PAA chains bridge and cross-link together via the formation of H-bonds and carboxylic anhydride groups, giving rise to a polymeric network with improved mechanical

properties and a more uniform particle coverage than linear chain polymers.[78] Different from PVdF, PAA does not significantly swell in the electrolyte, thus, retaining better adhesion and protecting the surface of Si from a direct reaction with the electrolyte, acting as an "artificial SEI".[78] Porcher et al.[79] carefully investigated the effect of PAA and Li-PAA on the coulombic efficiency obtained from Si electrodes with a practical loading of 2.5 mA h cm^{-2}. The study revealed that, compared to CMC, PAA and its neutralized form, Li-PAA (that has a more elongated chain conformation in solution), grant lower ICLs during the initial cycles, exploiting the "artificial SEI" behaviour due to the more uniform binder distribution. For PAA and Li-PAA with a low degree of neutralization (i.e., a low number of Li counter cations), the "spring-like" conformation mentioned for CMC was actually visualized by transmission electron microscopy (TEM).[80] Additionally, Erk et al. confirmed the optimised performance of PAA and Li-PAA as binders for Si electrodes with rather high areal capacity (5.1 mA h cm^{-2}).[80]

Recently, it has been shown that the mechanical strength and the cyclability of Si-based anodes can be further improved by including a "maturation" treatment in a humid atmosphere.[81,82] This study revealed that an essential parameter is the acidic pH of the slurry. Indeed, improved capacity retention and reduced first cycle coulombic efficiency can be obtained for both CMC- and PAA-based electrodes coated from acidic (pH = 3) slurries. The maturation in an acidic environment was reported to lead

to Cu corrosion, resulting in the formation of Cu–binder ester bonds and, thus, improving the adhesion of the coated electrode with the current collector. It was also observed that, during the maturation, the binder migrates from the surface and concentrates in the interstices between the Si particles and in the macropores generated by the carbon agglomerates, forming reinforcing bridges.[81,82]

The copolymerization reaction of PAA with other monomers or polymers allows tuning of the mechanical and chemical properties of the binder. Following this approach, Koo et al.[66] crosslinked PAA with CMC. The resulting Si composite electrodes outperformed those made with the single polymers. The achievement of an improved capacity retention and coulombic efficiency was attributed to the higher mechanical strength of the crosslinked PAA/CMC binder and to the reduction of the amount of free hydroxyl groups of crosslinked CMC, which can react with $LiPF_6$.[34,66] Instead, crosslinked PAA/PVA (poly(vinyl alcohol)) permits the Si anode cyclability to be improved due to the deformable properties introduced by PVA.[83]

Promising results have also been obtained using alginate, a natural polysaccharide.[84] Similarly to CMC and PAA, alginate does not show swelling or a change in stiffness when in contact with the electrolyte. Moreover, inspired by algae cells, the authors suggested Li^+ ion hopping to occur between neighbouring carboxylic groups, which could enhance the Li^+ ion conduction. Following this line, the more homogeneous distribution of functionalities in alginate with respect to CMC, appears to be responsible for the better performance observed. In addition, the high polarity of alginate results in a higher viscosity of the slurry, permitting the reduction of the total amount of binder in the electrode formulation.[31,84] Alginate was successfully employed to prepare electrodes with Si, which was obtained from the waste slurry of diamond-sliced solar grade crystalline Si-ingots.[85] The study showed that an appropriate surface treatment to obtain a thin SiO_x coating, coupled with a binder that can interact with the Si surface, enabled the reversible cycling of micro-plates (200 cycles at 0.2C in the voltage range 1.0 V to 0.01 V) without severe electrode pulverization. Recently, it has been reported that electrodes made with Al-alginate and Ba-alginate (caution, Ba salts are highly toxic) display enhanced adhesion compared to Na-alginate and higher Vickers hardness due to the crosslinked structure, induced by the multivalent cation.[86] The carboxylated form of chitosan (a highly abundant natural polysaccharide), offering $-NH_2$ groups for the interaction with the Si surface and cross-linking with other polymers, has also been successfully employed to prepare Si anodes.[87–89]

Similar to cross-linked polyacrylates, branched polysaccharides offer increased contact points for the binder/silicon interactions. Branched β-cyclodextrin, for example, shows higher adhesion strength than alginate and extended capacity retention due to the "self-healing" properties of the multiple H-bonds upon Si-anode delithiation.[90] Jeong et al.[91] observed stronger adhesion capability for native xanthan gum (and in general for charged polysaccharides rather than for neutral ones), which was attributed to the existence of ion–dipole interactions between $-COO^-$ and the Si surface, maximized by the double-helix superstructure of this polymer.

With regard to lithium conduction, a mechanism similar to that found in PEO (and polyacrylates, see graphite, Section 2.1(a)) has been proposed for guar gum (GG), another natural polysaccharide in which, however, only hydroxyl groups are present. Li^+ moves along the binder chain across complexations sites offered by the lone pairs of the oxygen heteroatoms assisted by the segmental motion of the polymer.[92] Another polymer from the family of natural gums, gellan, has been used to prepare Si-based anodes and the resulting electrodes showed better cyclability then CMC at both 20 and 60 °C.[93] The higher number of functional groups, leading to extended self-healing, non-covalent Si–binder interactions, and the more stable SEI formed, were identified as the sources of the observed improved performance. For karaya gum, a branched natural polysaccharide, the formation of both covalent and H-bonds was observed, as well as improved adhesion.[94]

Inspired by biological systems, Yoon et al.[95] investigated the influence of glycosidic linkages and side-chain substituents in polysaccharide binders. The α-glycosidic linkage, present in pectine and amylose, is more elastic than the β counterpart as in CMC, due to the chair-to-boat conformation transition taking place among pyranose rings upon elongation.[96] The elastic modulus determination confirmed their hypothesis, i.e., a lower resistance to elongation was found for pectin with respect to CMC. The measurement also revealed the role of side groups, as amylose (with only hydroxyl groups) presents an elastic modulus similar to the β-linked, more rigid CMC. The effect was attributed to the high level of inter-chain H-bonds possible for amylose. The elastic properties of pectine resulted in better mechanical characteristics and electrochemical performance compared to CMC.

Biological systems inspired also the work of Ryou et al.,[97] who introduced cathecol functionalities, responsible for the adhesion of mussels even on anti-adhesion materials,[98] in alginate and PAA polymers, thus increasing their adhesive properties on Si nanoparticles.

Wu et al.[99] followed a different approach, producing in situ a 3D electronically conductive binder. The reaction in water of Si nanoparticles, phytic acid, and aniline in the presence of a crosslinking agent, resulted in the formation of a viscous hydrogel, ready to be cast onto the current collector. Although the feasibility of the method to produce high loading electrodes for practical applications needs to be assessed, the in situ polymerized PANi–Si (PANi = polyaniline) showed improved cyclability and rate capability. The porous 3D matrix provides sufficient void space for Si expansion, while the in situ method grants uniform coating of the particles with the electronically conductive PANi binder. Recently poly(3,4-ethylenedioxy-thiophene): poly(styrene sulfonate) (PEDOT:PSS) conductive polymer cross-linked with polysaccharides has also been introduced as a water-soluble binder.[100–102] This approach has the advantage of reducing the conductive carbon additive in the electrode formulation, to exploit the ability of the polymer to sustain large volume changes (up to 400%[100]) and the derived electrode shows promising performance at relatively high Si loadings (1–2 mg cm^2).

3106 | Energy Environ. Sci., 2018, 11, 3096–3127

This journal is © The Royal Society of Chemistry 2018

In sum, a suitable binder for Si-based anodes should: (i) offer weak interaction with the electrolyte which implies no swelling, and no change in stiffness and mechanical properties; this allows direct contact with the renewed active material surface, which induces further electrolyte degradation, to be reduced/avoided; (ii) provide Li$^+$ conduction forming a uniform "artificial SEI" layer on Si particles; Li conduction can be assisted by segmental motion/coordination for neutral molecules (as in GG) or by hopping through carboxylic groups (as for PAA); (iii) include β-glycosidic bonds (as in branched polysaccharide-based binders) and functional groups that can induce ion–dipole interactions, providing more elongation and higher adhesion strength; (iv) possess self-healing properties to regenerate the interactions with the Si surface upon delithiation; and (v) allow for the formation of "bridges" between the particles and the current collector to improve the mechanical properties of the electrode.

The beneficial effect on the Si-based electrode performance originating from numerous sites for binder interactions with the active material and the current collector has been recently studied by Cao et al.,[103] using graft copolymers of glycol chitosan and Li-PAA. A systematic structure-to-property relationship study conducted by Kwon et al.[104] rationalized the importance of the above-mentioned characteristics. These authors synthesized different polymers, varying the ratio of the block units, each one accounting for a particular property, such as Meldrum's acid for crosslinking and covalent interactions, styrene for the backbone stiffness, methyl methacrylate for the flexibility, and hydrolysed Meldrum's acid neutralized with Li for the "self-healing" properties. The study revealed that the stiffness provides only minor improvements. Instead, to achieve better performance, the covalent interaction ability and polymer crosslinking play a major role with respect to the flexibility induced by the methyl methacrylate unit, confirming the initial studies.[65] Overall, however, the work of Kwon et al.[104] highlighted the self-healing ability of the polymer as the principal factor to achieve an enhanced cycle life of the Si-based anode.

(b) Other alloys and conversion materials. Several characteristics, i.e., the adhesive interactions, stiffness/flexibility of the backbone, spatial conformation and/or self-healing ability have to be balanced to obtain a binder that is compatible with materials which experience large volume variations upon de-/lithiation. Most of the materials which undergo alloying and/or conversion reactions with lithium fall into this group.[62,105,106] The conversion process involves a multi-electron reaction of a transition metal oxide (and also sulphide, nitrides, and phosphides) with lithium to form metallic nanoparticles embedded in a Li$_2$O matrix. Reversing the process results in the decomposition of the Li$_2$O matrix, enabled by the presence of the metallic nanoparticles. The high capacity associated with the conversion reaction, however, is commonly affected by rather rapid fading due to the structural re-arrangement and large volume changes. Only a few reports have been published on the impact of the binder for conversion-type anode materials. It is worth noting that the majority deal with Fe-based materials due to its abundance and environmental sustainability compared to,

for instance, the more expensive and toxic Co. Improved cycling stability has been reported for tin-based alloys when Li-PAA is used instead of CMC or PVdF – most likely due to the ability of this polyelectrolyte to modify the SEI layer and to induce enhanced ionic and electronic conductivity to the composite.[107] A more stable cycling behaviour has been reported for CoFe$_2$O$_4$ electrodes, prepared using alginate rather than PVdF, as a result of the formation of H-bonds as detected via FTIR (Fourier-transform infrared spectroscopy).[108] Similarly, Fe$_3$O$_4$ electrodes made with PAA[109] and NiFe$_2$O$_4$ anodes including arabic gum[110] or CMC[111] outperformed those prepared with PVdF. Aqueous based formulations with a CMC binder were also employed for carbon-coated ZnFe$_2$O$_4$ anodes, and investigated both in half-[112] and full lithium-ion cells with an LiFePO$_4$ cathode (also including CMC).[113] The latter was successfully cycled for 10 000 cycles without substantial capacity decay. A crosslinked CMC/PAA binder enabled enhancement of the cyclability of non carbon-coated Co$_3$O$_4$ by preserving the cohesion between the active material particles upon volume contraction/expansion.[114] Improved performance when using functionalized water processable binders has also been reported for flake-like SnS$_2$ nanoparticles[115] and hierarchically porous ZnMn$_2$O$_4$/bio-carbon anodes.[116]

2.3 Cathodes – water sensitivity issues vs. interface stabilization

(a) Getting started – LiFePO$_4$ as a 'model candidate' for water-processed LIB cathodes. Different from lithium-ion anodes, current LIB cathode processing on a commercial scale is still based on the use of PVdF as the binder and NMP as the corresponding solvent.[117] This has a rather simple reason – the reactivity of most commercially employed cathode materials with water. Nonetheless, the rapidly increasing importance of LIBs and the resulting need to further enhance their sustainability has recently led also to continuously increasing efforts targeting the replacement of NMP by water and the employment of fluorine-free binders. As a result of its relatively lower sensitivity towards water and moisture, most studies initially focused on the investigation of alternative binding agents for LiFePO$_4$ (LFP). This material, in fact, has several advantageous characteristics for application in LIBs such as, e.g., a rather high theoretical capacity of 170 mA h g^{-1}, high cycling stability due to its pronounced structural stability as a consequence of the strong Fe–P–O bonding, and good chemical and thermal stability.[118] Its energy density, however, is limited by the comparably low de-/lithiation potential of around 3.3 V. Nonetheless, the aforementioned relatively low sensitivity towards H$_2$O has rendered it the ideal candidate for the development of water-based electrode processing technologies for lithium-ion cathodes. To the best of our knowledge, the first study in this regard was published by Guerfi et al.[119] in 2007, reporting the use of a not defined water-soluble elastomer as the binder in combination with CMC as the thickener (a 1:1 mixture). The resulting electrodes revealed a high mechanical flexibility and good adhesion to the aluminium current collector. Moreover, the aqueous processed electrodes provided an increased reversible

capacity of 157 mA h g^{-1} for the first cycle (compared to 148 mA h g^{-1} for those comprising PVdF as the binder), comparable cycling stability, and less irreversible capacity at an elevated temperature (60 °C). Another interesting feature is certainly the higher electrode density of CMC-based electrodes (1.7 g cm^{-3} compared to 1.5 g cm^{-3} for PVdF), generally allowing for higher volumetric energy densities. Motivated by these results, Porcher et al.[120,121] investigated the stability of LFP in water, discovering that the material was not fully stable. In fact, the long-term exposure in water resulted in the formation of a few nanometres thin amorphous surface layer of Li_3PO_4 accompanied by the partial oxidation of Fe^{2+} to Fe^{3+}. This "lithium leaching" is also reflected by a slight increase of the slurry pH to about 9.[121] Nonetheless, their studies showed as well that this reaction with water leads to a loss of active material of only about 1% after 24 h immersion in water,[120] indicating that the corresponding capacity loss should remain negligible upon electrode preparation. This has been also confirmed by Lux et al.[122] later on, who detected solely divalent iron by means of Mössbauer spectroscopy for aqueous processed LFP electrodes. As a consequence, further studies focused in particular on the optimization of the electrode microstructure, i.e., the realization of a homogeneous dispersion of the comprised components, to enhance the electrochemical performance by ensuring a percolating network of the active material and conductive carbon. For this purpose, the proper dispersion of the (hydrophobic) carbon-coated LFP and conductive carbon particles is of utmost importance. One research strategy to achieve this is the addition of suitable surfactants. Such surfactants are commonly characterized by a (short) ionophobic part (e.g., a carbonaceous chain), which preferably interacts with the carbonaceous surface of the conductive additive as well as the carbon-coated LFP, and an ionophilic part, that allows for the homogenous dispersion in polar solvents such as, for instance, water. A schematic illustration of the underlying working principle is presented in Fig. 4, highlighting the proper dispersion of the hydrophobic electrode components in water, thus, allowing for the realization of a percolating electronically

conductive network of carbon black throughout the electrode coating layer. A comparative analysis, conducted by Porcher et al.,[123] of three different surfactants for which the ionophilic part was anionic (sodium dodecyl sulphate), non-ionic (iso-octylphenylether of polyoxyethylene; Triton X-100; Aldrich), or cationic (hexadecyltrimethyl ammonium bromide; CTAB), revealed that the therein investigated ionic surfactants are not suitable for large-scale electrode fabrication, as they induce corrosion of the aluminium current collector. The use of Triton X-100, however, resulted in better electronic wiring of the conductive carbon throughout the electrode, i.e., a more homogeneous electrode microstructure leading to enhanced rate capability. It appears noteworthy that the authors employed as a binder either a mixture of polyvinyl alcohol and polyethylene glycol (added as a plasticizer) or butadiene-acrylonitrile copolymer rubber latex. The included CMC was considered to serve solely as a "thickener" in order to optimize the slurry viscosity. Nevertheless, as reported in another study by Porcher et al.,[124] the choice of the "thickener" played an important role, since the use of hydroxypropylmethyl cellulose (HPMC) instead of CMC led to inferior electrode microstructure homogeneity and, consequently, to lower specific capacities. The authors concluded that the uncharged HPMC polymer adsorbs to a greater extent to the LFP and carbon black particle surface than the negatively charged CMC. While greater adsorption of HPMC would favour the flocculation of LFP and carbon black agglomerates, lesser adsorption, i.e., the presence of "dangling" parts of the CMC polymer surrounding the particles, may favour bridging between the LFP and conductive carbon particles, thus, eventually resulting in a very homogenous dispersion of the different components. Similarly, Li and Lin[125] reported the stepwise addition of CMC and SBR to the electrode slurry was of great importance, since the more adsorbing SBR, if added first, favours the formation of particle agglomerates. On the contrary, adding CMC first, which adsorbs less to the LFP particle surface, causes a steric and electrostatic repulsion between the active material particles and, hence, results in a more homogenous electrode morphology and thus, enhanced cycling stability and de-/lithiation kinetics. These results nicely illustrate that the replacement of PVdF and NMP is not an easy task – even if the active material is essentially inert vs. water – and that all components and their corresponding interactions need to be considered (and understood) in order to obtain the best possible electrochemical performance for the final electrodes. As a matter of fact, Li et al.[126,127] reported that also cationic surfactants like polyethyleneimine may be suitable to enhance the electrode microstructure (in their study used together with xanthan gum as the binder), if carefully considering the isoelectric point of the electrode components (pH = 4.3 and 3.4 for LFP and carbon black, respectively). In fact, the increased repulsive potential between the particles supports their homogenous dispersion in water and, accordingly, the realization of well-structured coated electrodes. Focusing as well on the importance of well dispersed particles in an aqueous suspension, Tsai et al.[128] highlighted the importance of homogeneously coated LFP in order to prevent their
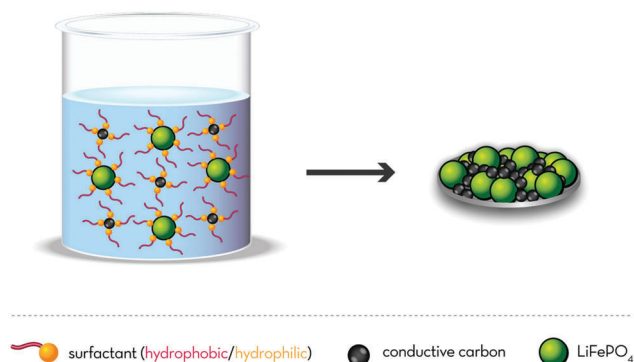

Fig. 4 Schematic illustration of the working principle of surfactants in aqueous electrode slurries, ensuring the homogenous dispersion of the hydrophobic carbon–coated LFP active material and carbon black particles (left panel) and, thus, allowing for the realization of a percolating network of the conductive agent throughout the electrode coating layer (right panel).

surfactant (hydrophobic/hydrophilic)   conductive carbon   LiFePO$_4$

3108 | Energy Environ. Sci., 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

agglomeration – or as they referred to it, "the gelation" of the electrode slurry – as a result of the hydrogen bonding between non-coated surfaces. As a matter of fact, such gelation may also occur for carbonaceous surfaces with a high density of hydroxyl, carboxyl, or carbonyl groups – not least due to the insulating character of sp³-hybridized carbon.[129] On the contrary, the presence of these surface functional groups eventually allows for the favourable interaction with water-soluble binding agents like CMC (potentially used also as a binding agent by itself),[122] PAA,[130–133] xanthan gum,[134] or carboxymethyl chitosan derivatives.[135–137] In turn, this advantageous interaction leads to advanced cycling stability, rate capability, and apparent lithium ion diffusion coefficients as well as frequently higher specific capacities of the electrodes made using such binders rather than PVdF, as a result of the more uniform electrode microstructure and the increased adhesion to the aluminium current collector, favouring the de-/lithiation kinetics and lowering the cell polarization.[122,131–134] One key feature enabling this enhanced electrode performance is the low swellability of most aqueous binders compared to PVdF.[135,138] Another highly advantageous characteristic, found by Zhang et al. for PAA, is that the binder does not only ensure the mechanical integrity of the electrode, but moreover forms a protective surface coating for the active material, which stabilizes the electrode/electrolyte interface and, thus, prevents or at least dramatically reduces detrimental side reactions like the dissolution of iron – especially for elevated operational temperatures such as, for instance, 55 °C.[132]

To further optimize the electrochemical performance of aqueous processed lithium-ion cathodes, Li et al.[139] have also considered the aluminium current collector/electrode coating interface. They found that the application of proper surface treatments of the aluminium foil such as, for instance, a corona plasma treatment and the resulting partial oxidation and functionalization of the aluminium surface (e.g., by –ROOH or –RO₂R) leads to better wettability by polar aqueous dispersions and, as a result, to substantially increased specific capacities by about 20 mA h g⁻¹ relative to the untreated samples.

With respect to these great achievements in the past few years, it does not appear surprising that also lithium-ion full-cells, incorporating exclusively aqueous processed electrodes, have been reported. Using PAA in combination with a small amount of SBR, for instance, Chong et al.[133] studied LFP/graphite cells and achieved a remarkable capacity retention of 70% after about 850 cycles. Kim et al.[140] reported a LFP/LTO full-cell, employing CMC as the binder for both electrodes and an ionic liquid-based electrolyte (i.e., N-butyl-N-methyl-pyrrolidinium bis(fluorosulfonyl)imide-lithium bis(trifluoromethanesulfonyl)-imide; PYR₁₄FSI-LiTFSI). These cells were stably cycling for more than 150 cycles and the observed, very minor fading was assigned to detrimental interfacial reactions at the anode rather than at the cathode.

Before continuing with the next subsection, we would like to highlight two more approaches reported for LFP to enhance the electrochemical performance and sustainability of these cathodes. The first concerns the replacement of the nanoparticulate carbon by electronically conductive polymers, which may facilitate the electrode preparation and material handling. The most prominent (water-soluble) polymer in this regard is certainly PEDOT:PSS. This conductive polymer has been combined with CMC[141,142] and carboxymethyl chitosan.[136] In combination with CMC, Eliseeva et al.[141] reported very remarkable specific capacities at lower and higher dis-/charge rates, i.e., 148 and 126 mA h g⁻¹ at 0.2C and 5C, respectively, as well as excellent cycling stability with only 1% decay over 100 cycles at 1C. Equally impressive, Zhong et al.[136] reported prototype-like prismatic 10 A h cells, including a combination of PEDOT:PSS and carboxymethyl chitosan as an electronically conductive binder matrix, providing a capacity retention of about 90% after 1000 cycles (charge/discharge = 1C/2C) and around 98% of the 1C capacity remaining when dis-/charging the cell at 7C.

The second approach was reported by Jeong et al.,[143] who introduced natural cellulose as the binder for LFP/graphite full-cells, achieving stable cycling for around 120 cycles. As cellulose is not water-soluble, they utilized an ionic liquid as the solvent/dispersant (1-ethyl-3-methylimidazolium acetate; EMIMAc). This may, at first sight, appear less "green" than simply using water, but the facile recuperation by applying a simple phase inversion process using water as a co-solvent provides the great chance to establish a completely "closed" recycling loop.

(b) High energy vs. water sensitivity – lithium transition metal oxides. The high chemical inertness of LFP largely originates from its structural stability, which is, in turn, related to the strong Fe–P–O bonding. With regard to energy density, however, the rather bulky and heavy nature of the PO₄³⁻ anion is less favourable, rendering LFP more suitable for stationary or PHEV applications rather than full EVs, for instance.[3,144] In contrast, the "blank" O²⁻ oxygen anion provides generally a relatively higher charge density, i.e., smaller volume and mass with respect to the overall charge, but the corresponding cathode materials are commonly less stable chemically – though these characteristics are not least determined also by the crystalline structure. Spinel LiMn₂O₄ (LMO) and its high-voltage derivative LiNi_xMn₂₋_xO₄ (LNMO; with $x \leq 0.5$), for instance, provide specific capacities of "only" 148 and 147 mA h g⁻¹, respectively, but their relatively higher operational potentials of about 4.0 and 4.8 V vs. Li/Li⁺ somewhat counterbalance the lower capacity. Moreover, both materials provide the substantial advantages of being cobalt-free and an intrinsic high rate capability due to the 3D lithium transport channels within the spinel structure[145] and an inherent high electronic conductivity.[146] Particularly LMO, however, suffers from a rather rapid capacity decay upon cycling, especially at elevated temperatures,[147,148] which originates from the dissolution of manganese into the liquid organic electrolyte as a result of the Jahn–Teller distortion occurring at about 3 V[145,149–153] and the disproportionation reaction of Mn³⁺_(solid) to Mn⁴⁺_(solid) and Mn²⁺_(solution).[145,154] In this regard, Ryou et al.[155] recently reported a highly interesting study on the impact of alginate as a potential binder for LMO-based electrodes. They showed that the cycling stability in both the half- and the full-cell
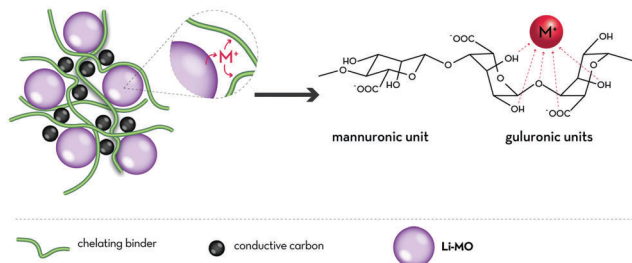
This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, 11, 3096–3127 | 3109

Fig. 5 Generalized illustration of the (potential) metal cation scavenging effect of chelating polysaccharide derivatives serving as binders; as reported for sodium alginate and the scavenging of divalent manganese cations dissolved from spinel-structured LiMn$_2$O$_4$ by Ryou et al.[155] [M = (transition) metal].

configuration (LMO/graphite for the latter) can be substantially enhanced compared to PVdF-containing electrodes, in particular at elevated temperature (i.e., 55 °C), as the alginate acts a manganese scavenger and, hence, prevents its diffusion to the graphite anode – a characteristic that is, in fact, well known from waste water purification.[156,157] Since this mechanism may very well be extended also to other transition metals that are dissolved into the electrolyte (see, for instance, the previous Section 2.3(a)), we have generalized this finding in Fig. 5, hoping that this will motivate future research studies to consider and evaluate this beneficial effect also for other cathode materials that are prone to suffer transition metal dissolution. In another study, reported by Zhang et al.,[158] a comparison of several water-soluble binding agents has been conducted, i.e., CMC and PAA in comparison to PVdF as a reference. In excellent agreement with those studies focusing on LFP, their findings revealed a more homogeneous microstructure for the aqueous processed electrodes and increased adhesion strength to the aluminium current collector – before and after cycling – as well as reduced thermal expansion of these two polymers compared to PVdF. It is worth noting that their results on PAA also showed uniform LMO particle coverage, indicating that this behaviour is not unique for LFP.

Nonetheless, the perspective for commercial applications of LMO remains limited at present, due to its comparably low energy density. Accordingly, also the number of studies towards this direction is rather low. Instead, a greater number of studies has been reported for its high voltage derivative, LNMO, initially reported by Amine et al.[159] and Dahn and co-workers.[160] In fact, the partial replacement of manganese by nickel allows for (theoretically) fixing the oxidation state of manganese to 4+, so that essentially only nickel is electrochemically active. By this, the aforementioned issues like Jahn–Teller distortion and Mn^{3+} disproportionation are ideally avoided.

We may, first, briefly review the rather performance-oriented studies now concerning aqueous electrode processing with LNMO as the active material, before focusing on the general issues, which are, as a matter of fact, of great importance also for all other lithium transition metal oxides, presently employed already or suggested to be employed soon in commercial lithium-ion batteries. To the best of our knowledge, the

use of water-soluble binders for LNMO has been reported for the first time by Wang et al.[161] in 2012, investigating the utilization of CMC and comparing the performance with reference electrodes comprising PVdF. They showed that the electrodes including CMC provided superior capacities over all dis-/charge rates and reduced self-discharge, while the cycling stability was roughly comparable, maybe slightly inferior to PVdF-based electrodes. This generally beneficial effect of water-soluble binders on the electrochemical performance of LNMO cathodes was supported by several studies, revealing further enhanced performance when using CMC[162] and extending the findings of Wang et al.[161] to CMC crosslinked via citric acid,[163] sodium alginate,[164,165] carboxymethyl chitosan,[166,167] poly(vinyl acetate),[168] PAA,[169] or TRD202A.[22] As for LFP, the main reasons for such improved performance were identified to be the well maintained electrode microstructure, a lower internal resistance and faster de-/lithiation kinetics, a higher peeling strength, and less swelling of the binder by the liquid organic electrolyte,[162,164–166] while the proper drying of in-water-processed electrodes is apparently crucial.[18,170] Once more, the use of PAA was reported to result in the formation of a very homogeneous surface coating of the active material particles,[169] which is, in light of the high lithium de-/insertion potential of LNMO and the rather limited oxidative stability of common organic-carbonate-based electrolytes, of even greater relevance compared to LFP and LMO, since it turned out to stabilize the electrode/electrolyte interface, thus preventing or at least lowering the continuous electrolyte decomposition. Another very interesting aspect of the study of Pieczonka et al.[169] was that the therein utilized Li-PAA may also as a Li$^+$ reservoir, which simultaneously allows for buffering the acidity of the electrolyte due to the corresponding exchange of lithium cations (from the binder) and protons (from the electrolyte), which mitigates parasitic side reactions at the interface.
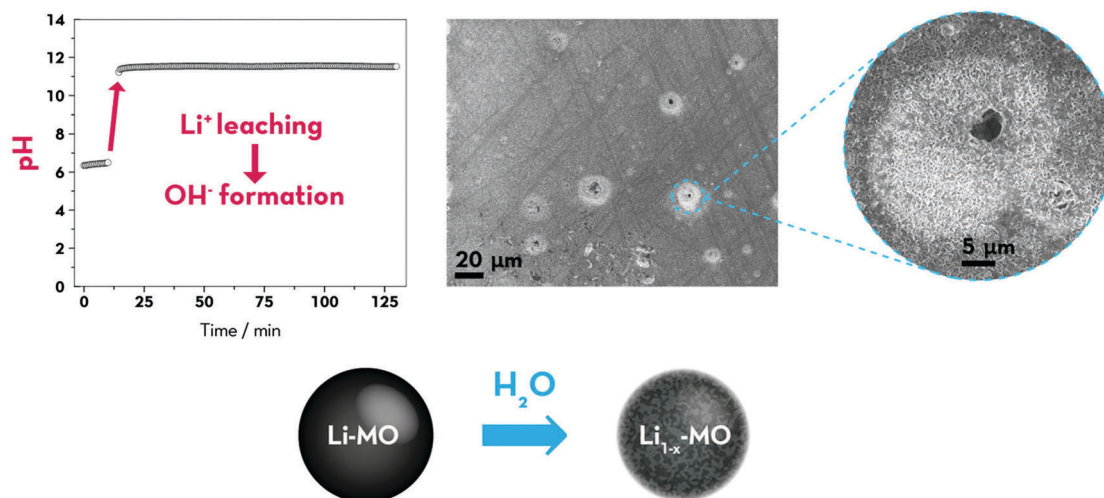
Nevertheless, the general issues when dispersing lithium transition metal oxides (including LNMO, LiCoO$_2$, Li[Ni$_{1-x-y}$Co$_x$Mn$_y$]O$_2$ (NCM), Li[Ni$_{1-x-z}$Co$_x$Al$_z$]O$_2$ (NCA, with $1 - x - z \geq 0.85$), or LiMn$_2$O$_3$·NCM (Li-rich NCM or LR-NCM)) in water remain: (i) the leaching of lithium out of the active material host structure, (ii) the concurrent formation of LiOH$_{aq}$ and structural degradation of the particle surface (i.e., the outer $\sim$3–10 nm), (iii) the subsequent increase in pH and, eventually, (iv) the corrosion of the aluminium current collector due to the breakdown of the native alumina surface layer – as summarized in Fig. 6a.[22,145,171–179] While it is still not comprehensively elucidated whether this lithium leaching is accompanied by the concomitant leaching and/or oxidation of the comprised transition metals[22] or by Li$^+$/H$^+$ exchange[180] or potentially both reactions, it is clear that the amount of electrochemically available lithium inside the active material is reduced, thus, lowering the overall reversible capacity – at least in lithium-ion full-cells, for which the cathode is the only lithium source.[175,176,178]

The strategies that have been so far pursued to overcome this great challenge are schematically illustrated in Fig. 6b. A rather easily implementable approach, the protection of the aluminium current collector surface by applying suitable

3110 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

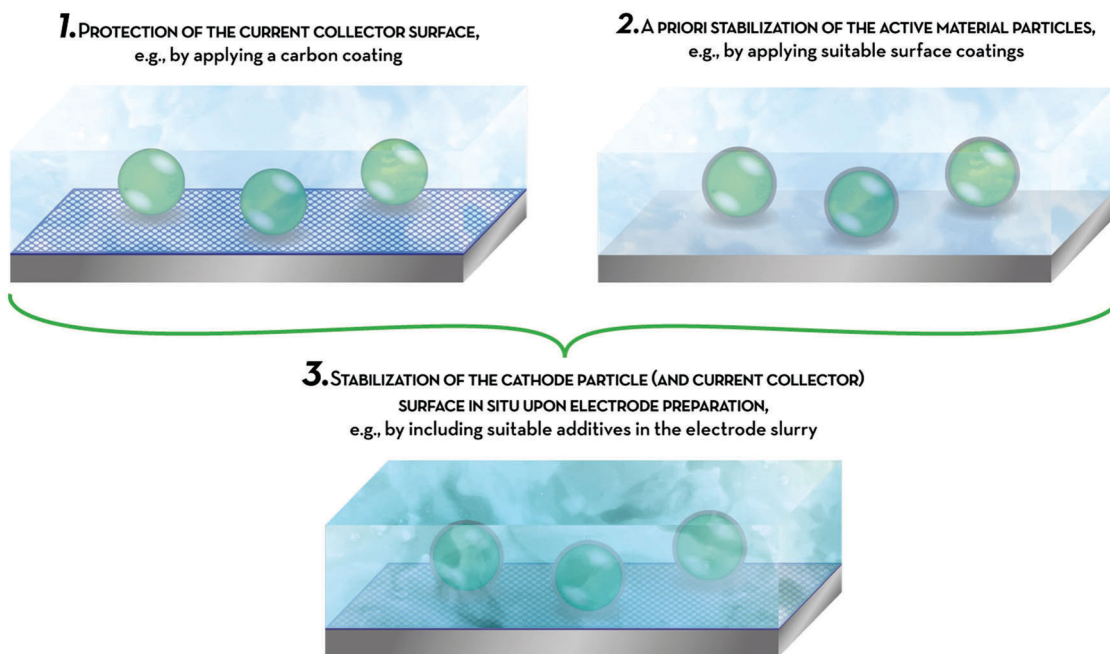This journal is © The Royal Society of Chemistry 2018

Fig. 6 (a) General challenges for the aqueous electrode processing of water-sensitive electrode materials like NCM, LR-NCM, or LNMO and (b) potential strategies to overcome these issues, including (1) the protection of the current collector surface, (2) the *a priori* stabilization of the active material particle surface, and (3) the stabilization and protection of potentially both surfaces *in situ* upon electrode preparation.

coating layers such as, for example, carbon, in order to physically prevent the contact between the electrode coating layer and the aluminium foil (1), has led to a substantial improvement in terms of cycling stability and achievable capacity, while also leading to decreased charge transfer resistances.[181,182] As a result, lab-scale lithium-ion full-cells, employing NCM and

graphite – both prepared by using CMC as the binder – showed very stable cycling for more than 2000 dis-/charge cycles and a final capacity retention of around 70%.[182] Nevertheless, the application of such coatings requires an additional processing step, lowers the overall energy density of the cell, and special care has to be taken to avoid detrimental defects in the coating

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | **3111**

layer, as these might still serve as nucleation sites for aluminium corrosion. Maybe even more importantly, this strategy does not really address the issue's origin, but instead its negative outcome. Similarly, the addition of mild (organic) acids (e.g., formic acid) during electrode preparation has been reported,[179,183] which, however, once again, addresses the detrimental effects of the lithium leaching by keeping the pH value of the electrode slurry well within the aluminium passivation regime, but not its origin. In fact, the addition of such mild acids may even have a negative impact on the active material integrity, since the transition metal dissolution significantly increases.[184] On the contrary, an approach that addresses the issue at its origin is the application of protective surface coatings for the active material itself (2). Tanabe et al.,[22] for example, prepared water-resistant LNMO by coating the particles with carbon, Al_2O_3, or Nb_2O_5. Employing TRD202A as an aqueous binder, the thus prepared electrodes showed a slightly worsened rate capability, but stable cycling and no aluminium current collector corrosion was detected – even though the pH still increased to values around 10 upon long-term storage of the active material in water, indicating that the lithium leaching was not fully prevented, yet. Slightly better results were obtained by the same group[185] when coating NCA with TiO_x, providing a comparable rate capability and cycling stability as for the PVdF-containing reference electrodes – presumably due to the realization of a really thin coating layer with a thickness of only 2–3 nm. Also the application of a vanadium oxide coating for LR-NCM successfully prevented the aluminium current collector corrosion, while moreover allowing for substantially increased specific capacities (+30 mA h g^{-1}) at moderate rates.[186] As a matter of fact, these coatings do not necessarily have to consist of inorganic materials. Instead, the use of, for instance, PAA[169] or crosslinked polyurethane in combination with CMC[187] – both resulting in the formation of polymer films, which homogenously cover/encapsulate the particle surface – may be employed as well. This approach possesses the great advantage that no additional, potentially costly processing step is needed and the surface coating is obtained in situ upon electrode preparation.

A different approach, essentially combining all the aforementioned strategies, was very recently reported by Loeffler et al.[188] Rather than adding a mild organic acid during the electrode fabrication process, the authors added a minor amount of phosphoric acid (PA) to buffer the otherwise dramatically increasing pH of the electrode slurry. Remarkably, the added PA spontaneously reacts at the NCM particle surface, resulting in a (very thin) metal (nickel/cobalt/manganese/lithium) phosphate surface coating, which stabilizes the active material/electrolyte interface and, thus, allows for less transition metal dissolution compared to the addition of formic acid, higher specific capacities, enhanced de-/lithiation kinetics, and advanced cycling stability. In addition, the current collector corrosion is suppressed, as the pH remains well in the aluminium passivation regime. As a result, NCM/graphite lithium-ion full-cells – both incorporating CMC as the binder – showed stable cycling for more than 300 cycles with an excellent capacity retention of 96%. The general applicability of this easily implementable approach has subsequently been confirmed by studying its effect also for the aqueous electrode preparation of NCM$_{424}$ (i.e., NCM with a relatively higher nickel and manganese content),[189] LNMO,[163] and LR-NCM.[190] The latter included moreover a comparison of three different binding agents, i.e., CMC, sodium alginate, and TRD202A, revealing slightly superior performance for CMC compared to alginate – in good agreement with an earlier study by Xu et al.[191] – and inferior cycling stability for TRD202A. Concerning the addition of PA, interestingly, the beneficial effect was more pronounced for CMC and alginate compared to TRD202A and it was found that the first two binders remain chemically unaffected by the addition of PA – at least in the presence of LR-NCM. Contrarily, TRD202A reacts with PA, indicating that this reaction and the reaction of the active material with PA are competitive and, hence, highlighting that the electrode preparation may be far more complex than simply mixing an inert binder, a conductive agent, and the active material in a suitable solvent/dispersant – an aspect that is frequently overlooked in the literature.

When investigating the impact of adding PA for LNMO-based cathodes using CMC as the binding agent, Kuenzel et al.[163] addressed also the issue of finding a suitable binder combination for high-voltage cathodes. While graphite anodes commonly contain a combination of CMC and SBR to ensure the flexibility and adhesion of high mass loading electrode coatings[192–195] (see also Section 2.1), the latter cannot be used in this case because of its limited electrochemical stability towards oxidation.[194–199] Nevertheless, it is worth mentioning in this context that two studies on LiCoO$_2$,[200,201] implementing a mixture of CMC and SBR, have reported its general suitability – even for anodic cut-off potentials as high as 4.5 V.[201] In fact, it appears that the initial oxidation of SBR leads, indeed, to a higher initial irreversibility, but benefits the stability of the cathode/electrolyte interface, resulting in less polarization upon cycling and an improved capacity retention compared to PVdF-based electrodes.

Kuenzel et al.,[163] however, followed another approach and crosslinked CMC using citric acid as the crosslinking agent, as this had been reported to be advantageous for low-voltage sulphur cathodes[202] and phosphorus-based sodium-ion anodes.[203] In combination with the addition of PA, substantially enhanced cycling stability and increased capacities were observed compared to the simple CMC reference. Beside the stabilization of the LNMO particle surface and suppressing the aluminium current collector corrosion, the addition of PA also led to the formation of a thin AlPO$_4$ layer on the current collector surface, presumably further contributing to the advantageous impact of adding PA to the electrode slurry.

Before eventually highlighting a few studies on prototype-like lithium-ion full-cells, which nicely illustrate the advanced development stage of aqueous cathode processing technologies, we may point at one more, initially maybe surprising advantageous effect of employing water-soluble binding agents. LR-NCM is an attractive candidate for next generation, high-energy LIBs, theoretically providing energy densities as high as 1000 W h kg^{-1} and commonly characterized by relatively low cobalt content.[204–206] Its application in commercial cells, however, is so far hindered

3112 | Energy Environ. Sci., 2018, 11, 3096–3127

This journal is © The Royal Society of Chemistry 2018

by the continuous voltage decay upon cycling, which is suggested to be the result of ongoing structural changes – although the precise reason remains to be comprehensively understood.[3,204,206] In this regard, it appears noteworthy that several recent studies investigating CMC,[207] alginate,[208] or guar gum[209] as binders for LR-NCM-based electrodes revealed reduced voltage fading in addition to generally improved electrochemical performance. These findings may, thus, pave the way for eventually employing LR-NCM in future LIBs without the need for expensive and extensive particle coatings to overcome the detrimental surface-driven changes upon continuous de-/lithiation.[210,211]

Finally, as mentioned earlier, we would like to highlight two studies that have reported the successful realization of prototype LIBs including aqueous processed cathodes. The first of these two was published by Wood et al.[117] in 2017. The authors assembled 1.5 A h full-cells, using NCM_{532} and graphite as the cathode and the anode, respectively, and CMC as the binder. Providing a capacity retention of around 80% after 900 cycles, comparable to the therein studied reference cells incorporating PVdF, these results render the completely water-based processing of lithium-ion electrodes feasible. Even larger cells, i.e., NCM_{111}/graphite full-cells with a total capacity of 15–18 A h, were reported by Loeffler et al.[212] – also in 2017. The graphite anode was based on a combination of CMC and SBR as the binder and the cathode contained a mixture of CMC and an acrylic waterborne latex. These cells showed a remarkable capacity retention of 99% after 500 dis-/charge cycles – or in other words a capacity fading of only 0.004% per cycle – rendering the realization of completely aqueous processed LIBs more than feasible, in fact.

(c) **The next generation – sulphur.** Sulphur as a potential alternative cathode material provides substantial advantages in terms of its theoretical specific capacity (1672 mA h g^{-1}), energy density (2.6 kW h kg^{-1}, if coupled with metallic lithium), environmental benignity, non-toxicity, and low cost.[213] In fact, S_8 is a by-product of the petroleum refining process[214] and, thus, theoretically an ideal candidate for the realization of fully sustainable lithium batteries, particularly if processed using aqueous electrode preparation routes and bio-derived binding agents. The challenges concerning the implementation of S_8 in commercial, long-lasting lithium batteries, however, are still significant. In fact, the shuttle mechanism of the formed polysulfides (Li_2S_x, $3 \leq x \leq 6$), resulting from their pronounced solubility in common electrolyte systems, the electronically insulating nature of S_8 and Li_2S, and the almost mandatory use of metallic lithium as the anode with all of its inherent issues still remain to be solved,[213,215–219] even though great progress has been achieved recently, e.g., by introducing solid ionic conductors[220] or advanced separators[221,222] to prevent the polysulfide shuttling. Another issue concerns the volume variation of the sulphur-based cathode, which varies by around 22% upon de-/lithiation,[223] thus requiring the employment of binding agents providing both relatively high elasticity combined with a strong binding force in order to withstand the occurring volume variations, while allowing the composite electrode to maintain electronic and ionic pathways. In this

regard, the implementation of water-soluble binders has led to substantial improvements compared to the commonly used PVdF or PEO. The use of gelatine, for instance, allows for a more homogeneous distribution of the active material, also upon cycling, and, as a result, higher discharge capacities and enhanced cycling stability compared to PEO-based electrodes,[224–229] which was assigned to the facilitated reconversion of Li_2S to S_8.[225] Similarly, also the utilization of CMC + SBR has resulted in improved discharge capacities, coulombic efficiencies, cycle life, and rate capability,[230,231] attributed to a lower internal resistance and charge transfer impedance.[232] As a matter of fact, comparable improvements have been reported for PAA[233] and alginate[234,235] and were ascribed to enhanced reaction kinetics and lowered internal resistances. We may, at this point, refer the interested reader to a very extensive review that has very recently been published by Li et al.,[236] covering also several rather "exotic" binding agents. One additional example, however, appears especially noteworthy. Wang et al.[237] reported the use of carbonyl-β-cyclodextrin, a modified cyclic oligosaccharide, as a potential binder for sulphur-based lithium cathodes and achieved a remarkable sulphur activity of more than 92% and a capacity retention of almost 95% after 50 cycles. Although there is certainly further work required to eventually commercialize sulphur-based cathodes for room temperature lithium batteries, these results nicely show that the transition to sustainable binders and electrode preparation procedures does not only have a beneficial impact concerning cost and environmental friendliness, but moreover allows for enhanced performance, thus potentially paving the way towards this promising battery technology.

3. Sodium-ion batteries

Non-aqueous Na-ion batteries (SIBs) are, indeed, very similar to LIBs, but promise lower prices as well as higher sustainability.[238] Obviously, the use of cheap and environmentally friendly materials and processes is crucial to achieve very low costs. In light of this, the use of natural binders and aqueous electrode processing is especially appealing if not fundamental for the future success of non-aqueous SIBs. However, SIBs and LIBs show some peculiarities with respect to the binder, due to (i) the larger ionic radius of Na^+, leading to different volume change upon reversible uptake and release; (ii) the use of Al instead of Cu as the negative current collector; and (iii) the somehow higher water sensitivity of the positive and negative active materials.

The large ionic radius of the Na^+ cation leads to higher volume changes upon sodiation and desodiation. In consequence, the careful selection and optimization of the binder is of great importance in order to maintain the mechanical integrity of the composite electrode and its adhesion to the current collector, especially for those active materials undergoing conversion and/or alloying reactions with Na^+.[239–242] In fact, the use of Al as the negative current collector is one of the fundamental advantages of SIB technology.[243–245] However, it also represents

an additional challenge to be addressed for the aqueous processing of negative electrodes because of the earlier mentioned Al corrosion (see Section 2.3).

The most prominent active material classes in SIBs are essentially similar to those in LIBs. Nevertheless, they exhibit different intrinsic properties, such as water sensitivity and volume changes upon cycling in SIBs, which strongly affects aqueous processing and binder selection.

3.1 Aqueous electrode processing of positive electrode materials for SIBs

Generally, not many studies specifically target the implementation and investigation of aqueous electrode processing for positive electrode materials in SIBs. In fact, the large majority of cathode materials are still processed with a PVdF binder.[245]

The use of a CMC binder has been reported for the $Na_{0.44}MnO_2$ material, which exhibits rather low water sensitivity.[246] The electrolyte (optimized: 1 M $NaPF_6$ in EC : DEC 3 : 7 (v/v) + 2 wt% FEC; fluoroethylene carbonate) was found to be important to prevent the anodic dissolution of Al upon long-term cycling. Like $Na_{0.44}MnO_2$, polyanionic materials show typically low water sensitivity. For example, the aqueous electrode processing of carbon-coated Na_2FePO_4F with a polyacrylic latex binder[247] and of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$[248] and $Na_3V_2(PO_4)_2F_3$[249] with a CMC binder has been reported. These electrodes showed enhanced and more stable performance in comparison to those made using PVdF resulting from better electronic conductivity,[247,248] enhanced electrode adhesion,[247–249] and facilitated Na^+ ion diffusion.[247,249] Furthermore, Zhao et al.[249] reported improved electrode integrity for $Na_3V_2(PO_4)_2F_3$ with CMC after cycling, negligible electrode swelling in contact with the liquid electrolyte, and the formation of a protective, solid and permeable interface film limiting the electrode resistance increase.

Na-Based hexacyanometalates $Na_xM_1[M_2(CN)_6]_y \cdot zH_2O$ (M_1, M_2 = transition metal; $0 \leq x \leq 2$; $y \leq 1$) contain interstitial water whose removal leads to improved electrochemical performance.[250] Aqueous electrode processing with a CMC binder was reported for the sodium iron hexacyanoferrates $Na_2Fe_2(CN)_6 \cdot 2H_2O$ and $Na_{1+x}Fe_2(CN)_6 \cdot 3.1H_2O$.[251,252] The effect of PVdF, Na-CMC, PTFE, and ethylene propylene diene monomer (EPDM) rubber binders on the performance of $Na_{0.75}Fe_{2.08}(CN)_6 \cdot 3.4H_2O$ was investigated very recently.[253] The best electrochemical performance, especially at low current rates, was observed with a PVdF binder although electrodes with CMC delivered comparable electrochemical performance at high current rates (10C). Partial solubility and instability of the active material in water were reported to aggravate the electrode processing and adhesion of the coated electrode to the current collector.

The aqueous processing of layered oxide cathode materials is connected with several challenges. Layered oxides are typically categorized into P2- or O3-type according to the structural classification reported by Delmas et al.[254] Both differ with respect to the number of transition metal layers per unit cell and the coordination of the Na-cation, being either octahedral (O) or trigonal prismatic (P). Most layered oxides are sensitive

towards moisture and air, undergoing side reactions with water and carbon dioxide leading to the formation of sodium hydroxide and sodium carbonate, respectively.[245,255] Hence, aqueous electrode processing of layered oxides can lead to active material degradation leading to poor electrochemical performance. As a result, increasing efforts are focusing on the development of air and moisture stable layered oxides. Air-stable and Co/Ni-free O3-type $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$ with high water stability has been reported.[256] Improved air and water stability was also reported for O3-type $NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2$, synthesized via Cu/Ti-doping of $NaNi_{0.5}Mn_{0.5}O_2$.[257] Lu and Dahn[258] studied the intercalation of water in different P2-$Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ materials in 2001 and found increased water sensitivity at higher cobalt contents. They assumed the super-lattice ordering in the transition metal layer to aggravate water intercalation and to be suppressed by addition of cobalt. Interestingly, P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ was found not to be hygroscopic and stable towards moisture. In fact, Kubota and Komaba[259] reported the enhanced electrochemical performance for this material with a CMC binder in comparison to PVdF. Recently, the aqueous electrode processing with a CMC binder has also been reported for P2-type $Na_{2/3}Ni_{1/3}Mn_{5/9}Al_{1/9}O_2$.[260]

3.2 Aqueous electrode processing of negative electrode materials for SIBs

In comparison to cathode materials, many studies report the aqueous processing of anode materials in SIBs, but often with copper as the current collector. In the very recent review of Bommier and Ji,[261] the binders most commonly used for carbon-, alloying-, conversion- and insertion-based anode materials in SIBs are evaluated. The most commonly used binder is PVDF, but in particular for alloying- and conversion-based anode materials, i.e., those materials showing higher volume changes upon reversible Na^+ storage, CMC and other aqueous binders were found to be preferentially used. In that review, the effect of the binder on the initial coulombic efficiency was statistically evaluated as well. With the exception of carbonaceous materials, all anodes made utilizing a CMC binder showed substantially higher initial coulombic efficiencies, frequently above 75%.

The most commonly used anode materials in SIBs are, however, hard carbons. Several studies, focusing on the hard carbon material design and/or de-/sodiation mechanism, report aqueous processing with, e.g., CMC,[262,263] Na-alginate,[264,265] or sodium polyacrylate,[259,266] sometimes employing Al as the current collector.[263,265,266] Dahbi et al.[263] demonstrated superior performance of hard carbon electrodes on Al current collectors made with CMC, rather than PVdF, in 1 M $NaPF_6$ in PC with 2 vol% of FEC as an additive. An XPS study revealed that the hard carbon particles are initially covered by a thin layer of CMC, which contributes to the formation of a uniform and thin passivation film upon sodiation. In contrast, the PVdF-based electrodes show the formation of thick surface films, and of binder de-fluorination, resulting in the formation of NaF. In turn, the binder decomposition led to loosened

3114 | Energy Environ. Sci., 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

composite electrodes and increasing resistance. The study by Vogt et al.[267] confirmed the partial decomposition of PVdF and formation of NaF when using 1 M NaClO$_4$ in PC as the electrolyte, indicating that these processes negatively affect the initial coulombic efficiency and the long-term cycling performance of the cell.

Fan et al.[268] reported the effect of the binder on the performance of nitrogen doped hollow carbon nanotubes and found improved performance and higher initial coulombic efficiency with a sodium polyacrylate (Na-PAA) binder in comparison to PVdF. This was explained via the electrochemical activity of Na-PAA, the lower internal resistance of the electrode, and the formation of a homogeneous passivation layer covering the active material particles. The binding capability of Na-PAA was found to drop, however, with decreasing molecular weight.

For insertion-based anode materials such as titanates, e.g., Li$_4$Ti$_5$O$_{12}$,[269] Na-doped Li$_4$Ti$_5$O$_{12}$,[270] and the sodium titanate Na$_2$Ti$_6$O$_{13}$,[271] similar results like for hard carbons have been observed. In detail, a more stable long-term cycling performance has been obtained with sodium alginate and CMC in comparison to a PVdF binder on a Cu current collector. Zarrabeitia et al.[272] investigated the moisture and water stability of Na$_2$Ti$_3$O$_7$.

The importance of proper binder selection for alloying based materials such as Sn[267,273–275] or Sb[276] is illustrated by several studies, reporting improved electrochemical performance with aqueous binders in comparison to PVdF. In detail, Komaba et al.[273] reported an improved electrochemical performance and enhanced initial coulombic efficiency of Sn electrodes made with PAA (polyacrylic acid) in comparison to those made with PVdF. Dai et al.[274] inter alia evaluated the performance of Sn nanoparticles with PVdF or CMC as the binder. The use of CMC enabled an improved performance because of its higher binding ability due to the formation of strong H-bonds between the carboxylic groups in CMC and the Sn nanoparticles. Yui et al.[275] investigated the effect of PVdF, PAA, sodium polyacrylate, CMC, and polyimide on the electrochemical performance of Sn–Co based anodes. Confirming previous observations, these authors obtained very good performance with PAA and CMC in comparison to the other binders. The improved electrochemical behaviour is due to the enhanced electrode adhesion for the PAA (0.72 kN m^{-1}) and CMC (0.62 kN m^{-1}) based electrodes with respect to those based on PVdF (0.60 kN m^{-1}) as well as the decreased electrode swelling after the initial cycle, i.e., 111% for PAA and 125% for CMC compared to 198% for PVdF.

The electrochemical reaction of sodium with black or red phosphorous leads to the formation of sodium phosphide (Na$_3$P), which is associated with the strong volume expansions occurring, ranging from 292% (red phosphorous) to 390% (black phosphorous), i.e., in the same range as Sb (Na$_3$Sb: ≈293%) and Sn (Na$_{3.75}$Sn: ≈423%). Thus, P-based electrodes require binders that have elastic moduli, e.g., oxygen containing functional groups, capable of buffering the large volume changes to maintain mechanical integrity and adhesion to the current collector. In fact, electrodes with phosphorous

and Na-PAA,[277,278] PAA,[279] or CMC[280] show much better performance than those based on PVdF as the binder.

For FeP, the combination of CMC and PAA as the binder was reported to enable enhanced performance as compared to electrodes with PVdF or CMC only.[281] The formation of the earlier mentioned CMC/PAA cross-linked structure, capable of buffering the mechanical stresses generated by large volume changes, was assumed as the possible origin. The results correlated well with the previous work by Sun and co-workers,[282] reporting strongly improved electrochemical performance of Co$_3$O$_4$ and NiO–C electrodes made with CMC/PAA (5 wt% each) in comparison with PVdF as the binder. The same observation was made by Zhou et al.[283] for a SnS–graphene hybrid anode material with PAA/CMC. The use of crosslinked chitosan as the binder (dissolved in 1 wt% acetic acid in aqueous solution) has been reported for Sb.[284] The authors argued that crosslinked polymer binders may offer a stronger, more rigid network and, thus, better mechanical integrity for materials undergoing large volume changes during cycling in comparison to regular non-crosslinked polymers. The latter, in fact, may go through plastic deformation upon repeated extraction and uptake of sodium, eventually failing in maintaining the electrode integrity.

Recently, Luo et al.[285] reported the use of a hydroxyl-rich Na-alginate binder with an organic oxygen-rich sodium rhodizonate active material and observed that the binder filled the cracks in the coated electrode, which resulted from the large volume changes of the active material because of the formation of strong H-bonds between the binder and the active material. This led to improved adhesion and mechanical stability as well as lower resistance and, in consequence, enhanced electrochemical performance. Similar observations were made for α-Fe$_2$O$_3$ with natural hydroxyl-rich arabic gum,[286] demonstrating the importance of binder–active material bond formation for the achievement of improved performance.

4. Electrochemical double-layer capacitors

Among the different electrochemical devices covered in this review, EDLCs are those where the role of the binder has been, so far, more neglected. The quite scarce literature available on the topic reflects the limited interest of the scientific community; reasons being the relatively easy charge storage mechanism (double layer charging does not involve breaking/creation of chemical bonds, phase transitions, nor considerable volume changes) and, probably, the more limited market demand of such devices. Nevertheless, the binder may have a significant impact on the performance, cycle life, and environmental impact of EDLCs as well. An ideal binder should, indeed, provide sufficient mechanical and electrochemical stability without impeding wettability, ion mobility in the electrode pores, and electron conduction. Therefore, besides being "greener", alternatives binders should provide physicochemical properties of the electrode layer as close as possible, if not superior, to those obtained by conventional F-containing polymers.

The first attempt to replace conventional PTFE was done in 1998 by Bonnefoi et al.[287] They targeted CMC as an alternative, mostly to reduce cost. As the aim of their work was to increase the volumetric capacitance of the electrode, raising the activated carbon (AC) content was mandatory. Unfortunately, though, when using only CMC, they could not exceed 80 wt% AC without greatly decreasing the mechanical properties of the electrodes. Whereas, PTFE allowed mechanically stable electrodes with an AC content up to 95 wt%, without affecting the electrode resistivity nor their frequency behaviour. As the use of CMC appeared to be incompatible with high AC loading, to accomplish their target (i.e., fabricating an economical 2 V, 300 F supercapacitor in a total volume of 100 cm^{-3}) they decided to only partially replace PTFE with CMC. Although the composition of the two investigated PTFE/CMC ratios was not specified, in both cases a reduction of the resistivity was observed compared to the PTFE counterpart for the same electrode density (ca. 0.4 $g\ cm^{-3}$) and composition (95 wt% AC, 5 wt% binder).

Beck and Dolata extended the exploration of greener binders for EDLCs by evaluating commercially available aqueous dispersions of PS, SBR and ethylene-acrylic acid copolymers for electrode preparation.[288] In an acidic electrolyte (12 M H_2SO_4), however, none of the chosen binders could deliver the same capacitance as the PTFE-based electrodes. Stability over prolonged cycling also appeared to need improvements, with the loss of capacitance attributed to the low molecular weight of the F-free binders which could be transported into the pores and block them. Overall, the closest performance to PTFE could be achieved with Butonal LS 133, which is a styrene–butadiene copolymer. A similar binder was also proposed by Sun et al.[289] An organic solvent-free solution/dispersion, mainly constituted by an SBR–PAN (polyacrylonitrile) mixture, was used to fabricate electrodes with 10 wt% binder content. An interesting feature provided by this novel binder is its thermal stability. In fact, it shows minimal to no mass loss upon heating up to 300 °C in an inert atmosphere (N_2). Nevertheless, the fast heating rate (10 °C min^{-1}) used for the thermogravimetric analysis may have led to an overestimation of the performance. Compatibility with both organic (Et_4NBF_4 in PC and acetonitrile; ACN) and IL ($EMIMBF_4$) electrolytes was also proven by CV, galvanostatic cycling, and float voltage tests.
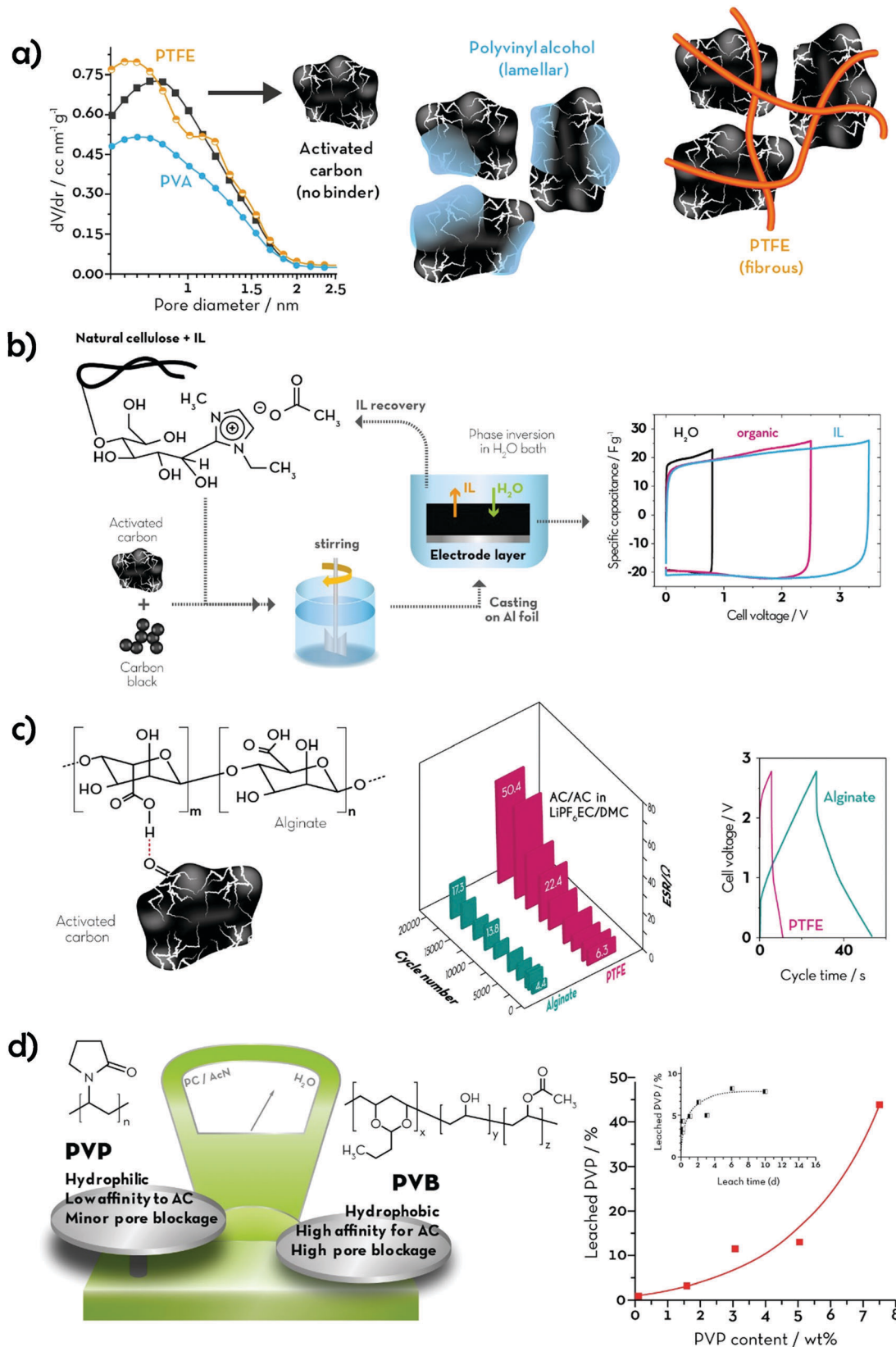
In an attempt to develop a green supercapacitor exclusively composed of environmentally friendly materials, Dyatkin et al.[290] explored alternative binders. Unfortunately, the large majority of investigated polymers (and mixtures thereof) did not enable sufficient mechanical stability, impeding the fabrication of robust freestanding electrodes. This was attributed, mainly, to the poor elasticity, molecular mass, and number of polar bonds capable of binding the activated carbon particles.[290] The only two viable alternatives resulted to be a 1 : 1 blend of poly(vinyl acetate) and polyisoprene (PVAc–PIpr) and a crosslinked PVA-based glue. They provided comparable malleability to PTFE, resulting in flexible, but freestanding electrodes. However, the curing step necessary to crosslink the hydroxyl groups with BO_4 (in sodium borate solution) substantially affected the specific surface area and pore volume of the PVA-based electrode. The decreased available surface was also attributed to the morphological properties of the different binders – with PTFE creating a fibrous network entangling the carbon particles – while PVA shows lamellar deposits on the carbon surface (Fig. 7a). Also in terms of the obtained capacitance, none of the greener binders could outperform PTFE. Additionally, a substantial decrease of the rate capability was observed as a result of the higher resistance. Overall, the authors concluded that no readily available polymer could offer, to date, the same features as PTFE.

In the early stage of binder research for EDLCs, CMC has certainly been the most popular choice, with the group of Balducci extensively reporting its use as an alternative to fluorinated polymers.[291–294] Nevertheless, CMC is far from being the ideal binder for this application. From one side, it is not a "universal" binder. CMC-based electrodes can certainly operate in the majority of organic (propylene carbonate or acetonitrile) and IL-based electrolytes, but cannot be employed in aqueous environments due to the high solubility of CMC. This is a pretty restricting feature, as aqueous EDLCs would benefit from enhanced power performance enabled by the high conductivity of the water-based electrolyte. In order to overcome this issue, Böckenfeld et al.[295] proposed natural cellulose (NC) as a potentially universal binder for EDLCs. NC is, in fact, insoluble in water as well as in most organic solvents. This does complicate the electrode fabrication method, but substantially decreases cost and environmental impact. NC is, indeed, cheaper than CMC (0.5–1.5 EUR kg^{-1} vs. 1–2 EUR kg^{-1}) and is not subject to any chemical treatment.[296] Böckenfeld et al.[295] exploited the solubility of NC in an imidazolium-based IL for obtaining a homogeneous slurry that could be cast on Al foil and, finally, the IL was completely recovered by phase inversion with water. Such a clever approach, which was previously proven for LIB electrodes by Jeong et al.,[143] led to NC-based AC electrodes compatible with aqueous (neutral, 1 M Na_2SO_4), organic (1 M Et_4NBF_4), and IL-based electrolytes (PC-PYR_{14}TFSI, 1 : 1 w/w; Fig. 7b). The same technique was adopted by Murashko et al.[297] to fabricate free-standing AC electrodes for aqueous EDLCs. The AC–NC weight ratio 6 : 1 was found to be optimal in terms of internal resistance, rate capability, and stability upon prolonged cycling. Interestingly, Varzi et al.[298] also demonstrated that NC provides enhanced stability at high voltages. Extended float voltage tests performed at 3.7 V in the pure IL electrolyte (PYR_{14}TFSI) showed reduced capacitance fading and less pronounced ESR (equivalent series resistance) growth compared to analogous electrodes containing PVdF. The improved performance was ascribed to the higher cathodic stability of NC, which, in such demanding conditions, does not suffer from the dehydrofluorination occurring with PVdF.

A further limitation of CMC is the difficulty to obtain sufficiently flexible and mechanically stable electrodes. Indeed, CMC-based electrodes become extremely brittle after drying, resulting in easier cracking and peeling of the electrode layer.[299] To address this issue, other naturally occurring polysaccharides have been proposed. Alginate, for example, a major constituent of brown algae and a copolymer of 1 → 4-linked β-D-mannuronic

Fig. 7 Effect of different binders on EDLC electrode properties and performance. (a) Possible pore blockage caused by a lamellar PVA binder compared to fibrous PTFE.[290] (b) Method for producing universal EDLC electrodes based on natural cellulose. These can be employed, indeed, with aqueous, organic and IL-based electrolytes.[295,298,314] (c) Hydrogen bonds formed by the interaction of carboxylic groups of alginate and basic moieties on the activated carbon surface, resulting in longer cycling life and reduced resistance growth.[300] (d) PVP/PVB mixtures as binders for aqueous EDLCs. By tuning the ratio of the two components it is possible to tune the affinity towards activated carbon and the porosity and, at the same time, minimize the PVP leaching.[307]

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | **3117**

and α-L-guluronic acid, has been reported as an EDLC binder for the first time by Yamagata *et al.*[299] Similarly to the initial report of Kovalenko *et al.*[84] with Si electrodes for LIBs, they observed a strong affinity of alginate with activated carbon too. This leads to substantially reduced impedance, which is fundamental to achieve the high power density expected from EDLCs.[299] As explained later by Tran *et al.*,[300] the advantage of alginate is the high content of carboxylic moieties (from the pyranose ring of α-L-guluronic acid) that can interact with the basic groups on the AC surface and establish stable H-bonds (Fig. 7c). These guarantee superior cycling stability in a lithium containing electrolyte (1 M LiPF$_6$ in EC:DMC) for Li-ion capacitors, despite the high residual water content due to the aqueous electrode processing (*ca.* 597 ppm compared to 43 and 69 ppm of PTFE and PVdF, respectively). Also, alginate-based electrodes showed a larger accessible porosity (mostly in the mesoporous region), resulting in faster energy delivery and uptake. The same group (Tran *et al.*[300]) also studied PAA and Na-PAA as water-soluble binders. Although these enable more compact electrodes and better adhesion to the current collector, higher pore blockage was observed in the case of Na-PAA (attributed to the presence of 0.5% SBR, necessary for the electrode fabrication) and increasing ESR upon cycling for PAA (probably related to the current collector corrosion due to the acidic slurry, *i.e.*, pH = 3.3). They concluded that, overall, alginate is the most promising green binder among those investigated. Additionally, according to stress relaxation tests, alginate-based slurries possess very promising rheological properties. In fact, they can maintain a rather stable viscosity over time, which renders alginate the best candidate to obtain stable and, therefore, up-scalable slurries.[300]

Recently, Varzi *et al.*[301] reported the benefits of a further polysaccharide binder, namely starch. Being highly abundant and extractable from renewable sources (*e.g.*, non-edible potatoes growing in marginal areas), starch would be a perfect candidate for replacing the fluorinated polyolefin. Starch is mostly composed of a mixture of amylose and amylopectin. Similar to NC, CMC and alginate, amylose is a linear polymer, whereas amylopectin has moderately branched chains instead. Depending on the source, the ratio between the two components can vary, but the branched amylopectin is often the main component (>80%).[302] This appears to be the key for overcoming the brittleness and shrinkage upon drying typical of CMC, which become particularly problematic when aiming at high active material loading for high areal capacitance. The use of potato starch enabled the fabrication of homogeneous and crack-free electrode layers with thicknesses as high as 240 μm and AC loadings up to 9.3 mg cm^{-2}, whereas, the analogous slurry based on CMC showed fractures and poor adhesion to the current collector already at 88 μm and 5.1 mg cm^{-2}. This behaviour is attributed to the branched structure of amylopectin capable of better releasing the stress upon drying compared to the linear CMC chains. Potato starch also demonstrated cycling stability and electrochemical stability comparable with those of other previously reported polysaccharides (*e.g.*, NC) and superior to those of conventional PVdF.

The same group also proposed casein as a further green alternative binder for EDLC electrodes.[303] Protein-based binders have been known since ancient times for their excellent adhesive power and have been extensively employed in mural paintings and wood crafting. However, their role in the electrochemical energy storage field was never explored. Among the possible choices (*e.g.*, collagen, egg white, *etc.*), Varzi *et al.*[303] selected casein because it is water soluble, biodegradable, and F-free. Furthermore, it can be easily extracted from food leftovers and, specifically, milk products. Interestingly, as evidenced in a recent study, a huge amount of milk is poured down the drains each year, mostly because it has passed its sell-by date or become sour.[304] This does not only represent a waste of edible resources but, when released in water streams, could cause serious harm to the environment providing food for bacteria and algae, which will deplete the oxygen levels in the water, ultimately affecting the aquatic life.[305] Therefore, using milk leftovers as a source for binder production would have multiple beneficial environmental impacts. Compared to PVdF, the study by Varzi *et al.* evidenced that casein can provide (i) one order of magnitude higher adhesion strength to the Al foil and (ii) reduced pore clogging. Its thermal stability, proven in both dynamic and static mode, showed no degradation up to at least 180 °C. Casein appears to be compatible with both PC- and acetonitrile (ACN)-based electrolytes offering capacitance values comparable with those of CMC- and PVdF-based electrodes for over 10 000 cycles. Unfortunately, though, casein-based electrodes also showed relatively higher resistivity, which affected the power capability. Reducing the binder content and pressing/calendaring the electrodes was found to be beneficial to mitigate this issue.

Recently, polyvinylpyrrolidone (PVP) was also proposed as an alternative binder.[306,307] Although synthetic, PVP is F-free, non-toxic, and water/ethanol soluble. Therefore, it might be easily implemented into casting and/or spray coating electrode manufacturing. By means of micro scratch measurements, Aslan *et al.*[306] demonstrated that the mechanical stability of AC electrodes increases with the polymer molecular weight (MW), resulting in a maximum penetration force of 475 mN for 1 300 000 g mol^{-1} PVP. As a result, coherent films with superior mechanical stability were achieved with PVP, yet using much less binder with respect to PVdF (3.5 wt% *vs.* 10 wt%). Differently from PVdF, PVP appears to strongly glue the AC particles together (and to the current collector) without substantially affecting the total surface area or the pore volume of the carbon. This was ascribed, mostly, to the low affinity of the hydrophilic PVP towards the hydrophobic AC surface, thus hindering the binder easily spreading into the pores. The highly hygroscopic character of PVP (due to the tertiary amide group), however, may result in the issue that water may be easily trapped in the electrode. This has no detrimental effect in PC but, as shown by FTIR, water residues can trigger the decomposition of ACN-based electrolytes to form acetamide, H$_2$ and CO$_2$.[306,308] Careful drying of PVP-based electrodes should therefore be considered in that case. Besides that, no degradation of PVP itself was observed. The electrochemical

3118 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

performance evaluated in symmetric EDLCs evidenced higher capacitance with respect to PVdF, as expectable from the previously discussed pore clogging of the latter. Comparable performance to PTFE-based electrodes was found in both PC- and ACN-based electrolytes (1 M Et_4NBF_4). However, most interestingly, a slightly improved rate capability could be achieved with PVP despite the much larger electrical resistance (a factor of 5–7). This result, which may appear contradictory, was attributed to the better electrode/current collector interface obtained by casting compared to rolling.

In order to extend the applicability of PVP to aqueous EDLCs, the same authors proposed a strategy involving its mixture with polyvinyl butyral (PVB),[307] a hydrophobic resin extensively used for lamination of safety glasses and solar modules. PVB can be homogeneously blended with PVP in ethanol without phase separation in a wide range of compositions, accordingly tuning the hydrophobic/hydrophilic character of the electrode.[307] Finding the optimal PVP/PVB ratio is fundamental to balance mechanical stability, electrode porosity, and wettability (Fig. 7d). High PVP contents enable better adhesion to the current collector, increase the wettability (owing to the hydrophilicity of PVP), and minimize pore blockage (due to the easy spreading of the hydrophobic PVB on the AC surface), while large PVB loads guarantee enhanced mechanical stability in water. The best balance was found to be a PVP/PVB ratio of 1 : 4 (specifically 1.5 wt% PVP and 6 wt% PVB). Interestingly, the authors determined that below 2 wt% PVP, less than 5% of its total content was leached out from the electrode into the electrolyte, as measured by high pressure liquid chromatography (HPLC). Even after prolonged storage of 10 days, a maximum of 8% PVP was lost. This was not found to negatively affect the electrochemical performance of symmetric EDLCs, employing a 1 M NaCl aqueous electrolyte. On the contrary, the capacitance and rate capability substantially improved after 78 days of operation, probably due to the improved wetting of PVB over time. A stable electrochemical response was also observed in acidic (H_2SO_4) and basic (KOH) electrolytes. However, the PVP/PVB mixture appears to be incompatible with a neutral Na_2SO_4 solution. This interesting aspect is certainly worth further investigation.

5. Summary and outlook

Although rapidly growing, the aqueous processing of battery and EDLC electrodes is still a much-unexplored field compared to, e.g., the development of new active materials. Recently though, the importance of greener battery production is being recognized and, in turn, the central role of the binder is becoming more and more relevant.

With graphite anodes based on CMC/SBR mixtures already representing the state of the art, the field of LIBs is definitively the most advanced in terms of aqueous processing. Nonetheless, with the advent of high-energy density materials like silicon new challenges have to be faced – especially related to the tremendous volume changes occurring upon de-/lithiation.

Focusing increasingly on the binder chemistry and its interaction with the active material rather than solely considering rather basic characteristics like stiffness or flexibility, considerable steps forward have been made in the cyclability of such alloying-type materials, particularly for silicon-based anodes. As a matter of fact, the interplay of covalent and non-covalent interactions, including inter alia the self-healing properties of hydrogen bonds, between the binder and the particle surface appears to be the key factor to achieve long-term stable cycling, while, still, further understanding of the underlying mechanisms is required to fully exploit the potential benefits of highly functional binding agents.

Similarly, the implementation of water-soluble binders for lithium-ion cathodes, especially for water-sensitive, high-energy transition metal oxides, appears to be far from being completely exploited. In fact, the first studies on this subject have been published just a few years ago. But even though being a rather unexplored field, the work reported so far has already shown great promise, as nicely highlighted by the suppressed voltage decay for LR-NCM, the scavenging effect for dissolved manganese ions, or the realization of 15–18 A h full-cells, providing a capacity retention of 99% after 500 cycles.

This great promise holds true also for sodium-ion batteries, even though this field has been opened up even more recently. Just like for lithium-ion anodes, remarkable improvements have been reported for active materials like tin, antimony, or phosphorus, which undergo severe volume variations. Specifically, crosslinked CMC and PAA have shown substantial advances in this regard and also in the case of sodium-ion batteries it appears that the impact of the binder chemistry on the electrode/electrolyte interface plays a decisive role in addition to the overall mechanical integrity of the electrode. In this context, we may anticipate that also an understanding of the interface with the aluminium current collector at the negative electrode will be crucial for further moving this technology forward.

Eventually, despite being highly underrated, the role of novel binders is slowly emerging also in the EDLC field. Interestingly though, some of the features considered beneficial for LIBs and SIBs are found to be detrimental for EDLCs. In fact, the high particle coverage observed for some aqueous binders, which provides protection towards exfoliation (graphite) and active material pulverization (silicon), can effectively block the porosity of EDLC electrodes, resulting in higher resistance and reduced capacitance. However, similarities can also be found. As a matter of fact, interactions between the basic surface group of the activated carbon and the acidic alginate chains lead to longer cycle life and a minor resistance increase upon cycling.

In general, the large majority of studies covered in this review are only lab-scale studies, usually limited to a few grams of material and/or low loading and simple electrode preparation. In order to fully assess the applicability of novel binders, these remain to be validated on a larger scale. Indeed, whenever a new binder is introduced in the electrode formulation, the rheological properties of the slurry must be fully evaluated, as well as the impact of the electrode tape post-processing

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, 11, 3096–3127 | 3119

(*e.g.*, drying, calendaring) on the final electrode architecture and its mechanical properties. This evaluation ideally also includes the volumetric changes occurring on a micro- and macro-scale upon cycling, *e.g.*, by employing techniques like *in situ* dilatometry,[309–311] X-ray tomography,[312] or *in situ* hydro-dynamic spectroscopy,[313] as such volume changes have a sub-stantial impact on the eventual cycling performance and lifetime of the resulting electrodes.

List of abbreviations

AC	Activated carbon
ACN	Acetonitrile
CMC	Carboxymethyl cellulose
EC	Ethylene carbonate
EDLC	Electrochemical double-layer capacitor
EV	Electric vehicle
DEC	Diethyl carbonate
DMAC	*N*,*N*-Dimethylacetamide
DMC	Dimethyl carbonate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DS	Degree of substitution
DSC	Differential scanning calorimetry
EMIMAc	1-Ethyl-3-methylimidazolium acetate
FEC	1-Fluoroethylene carbonate
FSI	Bis(fluorosulfonyl)imide
GG	Guar gum
HEV	Hybrid electric vehicle
HPMC	Hydroxypropylmethyl cellulose
ICL	1st cycle irreversible capacity loss
LCA	Life cycle assessment
LFP	Lithium iron phosphate ($LiFePO_4$)
LIB	Lithium-ion battery
LMO	Lithium manganese oxide ($LiMn_2O_4$)
LR-NCM	$LiMn_2O_3 \cdot NCM$
LTO	Lithium titanate ($Li_4Ti_5O_{12}$)
NC	Natural cellulose
NCA	$Li[Ni_{1-x-z}Co_xAl_z]O_2$ (with $1 - x - z \geq 0.85$)
NCM	$Li[Ni_{1-x-y}Co_xMn_y]O_2$
NMP	*N*-Methyl-2-pyrrolidone
PA	Phosphoric acid
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PANi	Polyaniline
PC	Propylene carbonate
PE	Polyethylene
PEDOT:PSS	Poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate)
PEO	Poly(ethylene oxide)
Pipr	Polyisoprene
PMA	Poly(methyl acrylate)
PS	Polystyrene
PTFE	Poly(tetrafluoroethylene)
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
PVB	Polyvinyl butyral
PVdF	Poly(vinylidene difluoride)
PVP	Polyvinylpyrrolidone
PYR_{14}	*N*-Butyl-*N*-methyl-pyrrolidinium
SBR	Styrene butadiene rubber
SEI	Solid electrolyte interphase
SIB	Sodium-ion battery
TEM	Transmission electron microscopy
TFSI	Bis(trifluoromethanesulfonyl)imide

Author contributions

D. Br. wrote Sections 1.0 and 2.3 and conceived Fig. 4–6. D. Bu. wrote Section 3. A. M. wrote Sections 1.1, 2.1, and 2.2 and conceived Fig. 3. A. V. wrote Sections 1.2 and 4 and conceived Fig. 1, 2 and 7. S. P. supervised the writing and revised the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928–935.

2 Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577–3613.

3 D. Andre, S.-J. Kim, P. Lamp, S. F. Lux, F. Maglia, O. Paschos and B. Stiaszny, *J. Mater. Chem. A*, 2015, **3**, 6709–6732.

4 D. Bresser, K. Hosoi, D. Howell, H. Li, H. Zeisel, K. Amine and S. Passerini, *J. Power Sources*, 2018, **382**, 176–178.

5 K. P. Lee, N. C. Chromey, R. Culik, J. R. Barnes and P. W. Schneider, *Fundam. Appl. Toxicol.*, 1987, **9**, 222–235.

6 D. E. Malek, L. A. Malley, T. W. Slone, G. S. Elliott, G. L. Kennedy, W. Mellert, K. Deckardt, C. Gembardt, B. Hildebrand, S. R. Murphy, D. B. Bower and G. A. Wright, *Drug Chem. Toxicol.*, 1997, **20**, 63–77.

7 W. Zhu, D. R. Schmehl, C. A. Mullin and J. L. Frazier, *PLoS One*, 2014, **9**, e77547.

8 F. M. Courtel, S. Niketic, D. Duguay, Y. Abu-Lebdeh and I. J. Davidson, *J. Power Sources*, 2011, **196**, 2128–2134.

3120 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

9 T. S. Poet, C. R. Kirman, M. Bader, C. van Thriel, M. L. Gargas and P. M. Hinderliter, *Toxicol. Sci.*, 2010, **113**, 468–482.

10 V. Haufroid, V. K. Jaeger, S. Jeggli, R. Eisenegger, A. Bernard, D. Friedli, D. Lison and P. Hotz, *Int. Arch. Occup. Environ. Health*, 2014, **87**, 663–674.

11 https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-n-methylpyrrolidone-nmp#advic, accessed in June 2018, EPA, 2018.

12 European Parliament and the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), 2006.

13 G. Berckmans, M. Messagie, J. Smekens, N. Omar, L. Vanhaverbeke and J. Van Mierlo, *Energies*, 2017, **10**, 1314.

14 D. L. Wood Iii, J. Li and C. Daniel, *J. Power Sources*, 2015, **275**, 234–242.

15 M. Valvo, A. Liivat, H. Eriksson, C.-W. Tai and K. Edström, *ChemSusChem*, 2017, **10**, 2431–2448.

16 J. Li, Z. Du, R. E. Ruther, S. J. An, L. A. David, K. Hays, M. Wood, N. D. Phillip, Y. Sheng, C. Mao, S. Kalnaus, C. Daniel and D. L. Wood, *JOM*, 2017, **69**, 1484–1496.

17 D. L. Wood, J. D. Quass, J. Li, S. Ahmed, D. Ventola and C. Daniel, *Drying Technol.*, 2017, 1–11.

18 J. Li, C. Daniel, S. J. An and D. Wood, *MRS Adv.*, 2016, **1**, 1029–1035.

19 N. Susarla, S. Ahmed and D. W. Dees, *J. Power Sources*, 2018, **378**, 660–670.

20 S. Feng, Z. Zhong, Y. Wang, W. Xing and E. Drioli, *J. Membr. Sci.*, 2018, **549**, 332–349.

21 K. Notake, T. Gunji, H. Kokubun, S. Kosemura, Y. Mochizuki, T. Tanabe, S. Kaneko, S. Ugawa, H. Lee and F. Matsumoto, *J. Appl. Electrochem.*, 2016, **46**, 267–278.

22 T. Tanabe, T. Gunji, Y. Honma, K. Miyamoto, T. Tsuda, Y. Mochizuki, S. Kaneko, S. Ugawa, H. Lee, T. Ohsaka and F. Matsumoto, *Electrochim. Acta*, 2017, **224**, 429–438.

23 O. E. Bankole, C. Gonc and L. Lei, *J. Environ. Ecol.*, 2013, **4**, 14–28.

24 G. Jiang and S. J. Pickering, *Waste Manage.*, 2016, **48**, 465–470.

25 J. Drofenik, M. Gaberscek, R. Dominko, F. W. Poulsen, M. Mogensen, S. Pejovnik and J. Jamnik, *Electrochim. Acta*, 2003, **48**, 883–889.

26 J.-H. Lee, S. Lee, U. Paik and Y.-M. Choi, *J. Power Sources*, 2005, **147**, 249–255.

27 C. Clasen and W. M. Kulicke, *Prog. Polym. Sci.*, 2001, **26**, 1839–1919.

28 T. Heinze and A. Koschella, *Macromol. Symp.*, 2005, **223**, 13–40.

29 J.-H. Lee, U. Paik, V. A. Hackley and Y.-M. Choi, *J. Electrochem. Soc.*, 2005, **152**, A1763.

30 H. Buqa, M. Holzapfel, F. Krumeich, C. Veit and P. Novák, *J. Power Sources*, 2006, **161**, 617–622.

31 M. Gaberscek, M. Bele, J. Drofenik, R. Dominko and S. Pejovnik, *Electrochem. Solid-State Lett.*, 2000, **3**, 171–173.

32 M. Gaberšček, M. Bele, J. Drofenik, R. Dominko and S. Pejovnik, *J. Power Sources*, 2001, **97**, 67–69.

33 M. Bele, M. Gaberscek, R. Dominko, J. Drofenik, K. Zupan, P. Komac, K. Kocevar, I. Musevic and S. Pejovnik, *Carbon*, 2002, **40**, 1117–1122.

34 L. El Ouatani, R. Dedryvère, J. B. Ledeuil, C. Siret, P. Biensan, J. Desbrières and D. Gonbeau, *J. Power Sources*, 2009, **189**, 72–80.

35 T. Zhang, I. de Meatza, X. Qi and E. Paillard, *J. Power Sources*, 2017, **356**, 97–102.

36 J.-H. Lee, U. Paik, V. A. Hackley and Y.-M. Choi, *J. Power Sources*, 2006, **161**, 612–616.

37 S. Komaba, T. Ozeki and K. Okushi, *J. Power Sources*, 2009, **189**, 197–203.

38 S. Komaba, K. Okushi, T. Ozeki, H. Yui, Y. Katayama, T. Miura, T. Saito and H. Groult, *Electrochem. Solid-State Lett.*, 2009, **12**, A107–A110.

39 S. Komaba, N. Yabuuchi, T. Ozeki, K. Okushi, H. Yui, K. Konno, Y. Katayama and T. Miura, *J. Power Sources*, 2010, **195**, 6069–6074.

40 F. Jeschull, M. J. Lacey and D. Brandell, *Electrochim. Acta*, 2015, **175**, 141–150.

41 J. Chong, S. Xun, H. Zheng, X. Song, G. Liu, P. Ridgway, J. Q. Wang and V. S. Battaglia, *J. Power Sources*, 2011, **196**, 7707–7714.

42 F. Jeschull, D. Brandell, M. Wohlfahrt-Mehrens and M. Memm, *Energy Technol.*, 2017, **5**, 2108–2118.

43 Y.-S. Park, E.-S. Oh and S.-M. Lee, *J. Power Sources*, 2014, **248**, 1191–1196.

44 D. Shin, H. Park and U. Paik, *Electrochem. Commun.*, 2017, **77**, 103–106.

45 N. Cuesta, A. Ramos, I. Cameán, C. Antuña and A. B. García, *Electrochim. Acta*, 2015, **155**, 140–147.

46 D. Versaci, R. Nasi, U. Zubair, J. Amici, M. Sgroi, M. A. Dumitrescu, C. Francia, S. Bodoardo and N. Penazzi, *J. Solid State Electrochem.*, 2017, **21**, 3429–3435.

47 L. Zhang, L. Chai, Q. Qu, L. Zhang, M. Shen and H. Zheng, *Electrochim. Acta*, 2013, **105**, 378–383.

48 D. V. Carvalho, N. Loeffler, M. Hekmatfar, A. Moretti, G. T. Kim and S. Passerini, *Electrochim. Acta*, 2018, **265**, 89–97.

49 A. García, M. Culebras, M. N. Collins and J. J. Leahy, *J. Appl. Polym. Sci.*, 2018, **135**, 46217.

50 Z. Chen, I. Belharouak, Y. K. Sun and K. Amine, *Adv. Funct. Mater.*, 2013, **23**, 959–969.

51 M. He, E. Castel, A. Laumann, G. Nuspl, P. Novák and E. J. Berg, *J. Electrochem. Soc.*, 2015, **162**, A870–A876.

52 N. J. J. de Klerk, A. Vasileiadis, R. B. Smith, M. Z. Bazant and M. Wagemaker, *Phys. Rev. Mater.*, 2017, **1**, 25404.

53 G. T. Kim, S. S. Jeong, M. Joost, E. Rocca, M. Winter, S. Passerini and A. Balducci, *J. Power Sources*, 2011, **196**, 2187–2194.

54 S.-L. Chou, J.-Z. Wang, H.-K. Liu and S.-X. Dou, *J. Phys. Chem. C*, 2011, **115**, 16220–16227.

55 B.-R. Lee and E.-S. Oh, *J. Phys. Chem. C*, 2013, **117**, 4404–4409.

56 B.-R. Lee, S. Kim and E.-S. Oh, *J. Electrochem. Soc.*, 2014, **161**, A2128–A2132.

57 D. Carvalho, N. Loeffler, G.-T. Kim, M. Marinaro, M. Wohlfahrt-Mehrens and S. Passerini, *Polymers*, 2016, **8**, 276.

58 S. J. Rezvani, M. Pasqualini, A. Witkowska, R. Gunnella, A. Birrozzi, M. Minicucci, H. Rajantie, M. Copley, F. Nobili and A. Di Cicco, *Appl. Surf. Sci.*, 2018, **435**, 1029–1036.

59 M. Mancini, F. Nobili, R. Tossici, M. Wohlfahrt-Mehrens and R. Marassi, *J. Power Sources*, 2011, **196**, 9665–9671.

60 A. Moretti, G.-T. Kim, D. Bresser, K. Renger, E. Paillard, R. Marassi, M. Winter and S. Passerini, *J. Power Sources*, 2013, **221**, 419–426.

61 M. Mancini, F. Nobili, R. Tossici and R. Marassi, *Electrochim. Acta*, 2012, **85**, 566–571.

62 M. N. Obrovac and V. L. Chevrier, *Chem. Rev.*, 2014, **114**, 11444–11502.

63 K. Rhodes, N. Dudney, E. Lara-Curzio and C. Daniel, *J. Electrochem. Soc.*, 2010, **157**, A1354–A1360.

64 K. Feng, M. Li, W. Liu, A. G. Kashkooli, X. Xiao, M. Cai and Z. Chen, *Small*, 2018, **14**, 1702737.

65 J. Li, R. B. Lewis and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2007, **10**, A17.

66 B. Koo, H. Kim, Y. Cho, K. T. Lee, N.-S. Choi and J. Cho, *Angew. Chem., Int. Ed.*, 2012, **51**, 8762–8767.

67 W.-R. Liu, M.-H. Yang, H.-C. Wu, S. M. Chiao and N.-L. Wu, *Electrochem. Solid-State Lett.*, 2005, **8**, A100.

68 J. S. Bridel, T. Azaïs, M. Morcrette, J. M. Tarascon and D. Larcher, *Chem. Mater.*, 2010, **22**, 1229–1241.

69 A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C. F. Huebner, T. F. Fuller, I. Luzinov and G. Yushin, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3004–3010.

70 M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami and M. Ohwada, *J. Appl. Phys.*, 1990, **68**, 1272–1281.

71 N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wöhrle, C. Wurm and M. Winter, *Electrochem. Solid-State Lett.*, 2008, **11**, A76–A80.

72 U. Maver, A. Znidarsic and M. Gaberscek, *J. Mater. Chem.*, 2011, **21**, 4071–4075.

73 N. Delpuech, D. Mazouzi, N. Dupré, P. Moreau, M. Cerbelaud, J. S. Bridel, J. C. Badot, E. De Vito, D. Guyomard, B. Lestriez and B. Humbert, *J. Phys. Chem. C*, 2014, **118**, 17318–17331.

74 D. Mazouzi, B. Lestriez, L. Roué and D. Guyomard, *Electrochem. Solid-State Lett.*, 2009, **12**, A215–A218.

75 J.-S. Bridel, T. Azaïs, M. Morcrette, J.-M. Tarascon and D. Larcher, *J. Electrochem. Soc.*, 2011, **158**, A750–A759.

76 M. Cerbelaud, B. Lestriez, D. Guyomard, A. Videcoq and R. Ferrando, *Langmuir*, 2012, **28**, 10713–10724.

77 B. Lestriez, S. Bahri, I. Sandu, L. Roué and D. Guyomard, *Electrochem. Commun.*, 2007, **9**, 2801–2806.

78 S. Komaba, K. Shimomura, N. Yabuuchi, T. Ozeki, H. Yui and K. Konno, *J. Phys. Chem. C*, 2011, **115**, 13487–13495.

79 W. Porcher, S. Chazelle, A. Boulineau, N. Mariage, J. P. Alper, T. Van Rompaey, J.-S. Bridel and C. Haon, *J. Electrochem. Soc.*, 2017, **164**, A3633–A3640.

80 C. Erk, T. Brezesinski, H. Sommer, R. Schneider and J. Janek, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7299–7307.

81 Z. Karkar, D. Guyomard, L. Roué and B. Lestriez, *Electrochim. Acta*, 2017, **258**, 453–466.

82 C. R. Hernandez, A. Etiemble, T. Douillard, D. Mazouzi, Z. Karkar, E. Maire, D. Guyomard, B. Lestriez and L. Roué, *Adv. Energy Mater.*, 2018, **8**, 1701787.

83 J. Song, M. Zhou, R. Yi, T. Xu, M. L. Gordin, D. Tang, Z. Yu, M. Regula and D. Wang, *Adv. Funct. Mater.*, 2014, **24**, 5904–5910.

84 I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, **334**, 75–79.

85 L. Zhang, L. Zhang, J. Zhang, W. Hao and H. Zheng, *J. Mater. Chem. A*, 2015, **3**, 15432–15443.

86 Z.-Y. Wu, L. Deng, J.-T. Li, Q.-S. Huang, Y.-Q. Lu, J. Liu, T. Zhang, L. Huang and S.-G. Sun, *Electrochim. Acta*, 2017, **245**, 371–378.

87 L. Yue, L. Zhang and H. Zhong, *J. Power Sources*, 2014, **247**, 327–331.

88 C. Chen, S. H. Lee, M. Cho, J. Kim and Y. Lee, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2658–2665.

89 Z.-H. Wu, J.-Y. Yang, B. Yu, B.-M. Shi, C.-R. Zhao and Z.-L. Yu, *Rare Met.*, DOI: 10.1007/s12598-016-0753-0.

90 Y. K. Jeong, T. Kwon, I. Lee, T.-S. Kim, A. Coskun and J. W. Choi, *Nano Lett.*, 2014, **14**, 864–870.

91 Y. K. Jeong, T. Kwon, I. Lee, T.-S. Kim, A. Coskun and J. W. Choi, *Energy Environ. Sci.*, 2015, **9**, 1224–1230.

92 J. Liu, Q. Zhang, T. Zhang, J.-T. Li, L. Huang and S.-G. Sun, *Adv. Funct. Mater.*, 2015, **25**, 3599–3605.

93 S. Klamor, M. Schroder, G. Brunklaus, P. Niehoff, F. Berkemeier, F. M. Schappacher and M. Winter, *Phys. Chem. Chem. Phys.*, 2015, **17**, 5632–5641.

94 Y. Bie, J. Yang, Y. Nuli and J. Wang, *J. Mater. Chem. A*, 2017, **5**, 1919–1924.

95 D.-E. Yoon, C. Hwang, N.-R. Kang, U. Lee, D. Ahn, J.-Y. Kim and H.-K. Song, *ACS Appl. Mater. Interfaces*, 2016, **8**, 4042–4047.

96 P. E. Marszalek, A. F. Oberhauser, Y.-P. Pang and J. M. Fernandez, *Nature*, 1998, **396**, 661.

97 M.-H. Ryou, J. Kim, I. Lee, S. Kim, Y. K. Jeong, S. Hong, J. H. Ryu, T.-S. Kim, J.-K. Park, H. Lee and J. W. Choi, *Adv. Mater.*, 2013, **25**, 1571–1576.

98 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426–430.

99 H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat. Commun.*, 2013, **4**, 1943.

100 L. Wang, T. Liu, X. Peng, W. Zeng, Z. Jin, W. Tian, B. Gao, Y. Zhou, P. K. Chu and K. Huo, *Adv. Funct. Mater.*, 2018, **28**, 1704858.

101 D. Shao, H. Zhong and L. Zhang, *ChemElectroChem*, 2014, **1**, 1679–1687.

102 T. M. Higgins, S.-H. Park, P. J. King, C. Zhang, N. McEvoy, N. C. Berner, D. Daly, A. Shmeliov, U. Khan, G. Duesberg, V. Nicolosi and J. N. Coleman, *ACS Nano*, 2016, **10**, 3702–3713.

103 P.-F. Cao, M. Naguib, Z. Du, E. Stacy, B. Li, T. Hong, K. Xing, D. N. Voylov, J. Li, D. L. Wood, A. P. Sokolov, J. Nanda and T. Saito, *ACS Appl. Mater. Interfaces*, 2018, **10**, 3470–3478.

104 T. Kwon, Y. K. Jeong, I. Lee, T.-S. Kim, J. W. Choi and A. Coskun, *Adv. Mater.*, 2014, **26**, 7979–7985.

3122 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

105 J. Cabana, L. Monconduit, D. Larcher and M. R. Palacín, *Adv. Mater.*, 2010, **22**, E170–E192.

106 D. Bresser, S. Passerini and B. Scrosati, *Energy Environ. Sci.*, 2016, **9**, 3348–3367.

107 J. Li, D.-B. Le, P. P. Ferguson and J. R. Dahn, *Electrochim. Acta*, 2010, **55**, 2991–2995.

108 S. Mitra, P. S. Veluri, A. Chakraborthy and R. K. Petla, *ChemElectroChem*, 2014, **1**, 1068–1074.

109 F. Maroni, S. Gabrielli, A. Palmieri, E. Marcantoni, F. Croce and F. Nobili, *J. Power Sources*, 2016, **332**, 79–87.

110 K. Zhou, M. Kang, X. He, Z. Hong, Z. Huang and M. Wei, *J. Mater. Chem. A*, 2017, **5**, 18138–18147.

111 C. Li, X. Wang, S. Li, Q. Li, J. Xu, X. Liu, C. Liu, Y. Xu, J. Liu, H. Li, P. Guo and X. S. Zhao, *Appl. Surf. Sci.*, 2017, **416**, 308–317.

112 D. Bresser, E. Paillard, R. Kloepsch, S. Krueger, M. Fiedler, R. Schmitz, D. Baither, M. Winter and S. Passerini, *Adv. Energy Mater.*, 2013, **3**, 513–523.

113 A. Varzi, D. Bresser, J. von Zamory, F. Müller and S. Passerini, *Adv. Energy Mater.*, 2014, **4**, 1400054.

114 M.-H. Lee, T.-H. Kim, C. Hwang, J. Kim and H.-K. Song, *Electrochim. Acta*, 2017, **225**, 78–85.

115 L. Yin, S. Chai, J. Ma, J. Huang, X. Kong, P. Bai and Y. Liu, *J. Alloys Compd.*, 2017, **698**, 828–834.

116 J. Chen, W. Liu, S. Liu, H. Wang, Y. Zhang and S. Chen, *Chem. Eng. J.*, 2017, **308**, 1200–1208.

117 D. L. Wood, J. D. Quass, J. Li, S. Ahmed, D. Ventola and C. Daniel, *Drying Technol.*, 2017, 1–11.

118 W.-J. Zhang, *J. Power Sources*, 2011, **196**, 2962–2970.

119 A. Guerfi, M. Kaneko, M. Petitclerc, M. Mori and K. Zaghib, *J. Power Sources*, 2007, **163**, 1047–1052.

120 W. Porcher, P. Moreau, B. Lestriez, S. Jouanneau, F. L. Cras and D. Guyomard, *Ionics*, 2008, **14**, 583–587.

121 W. Porcher, P. Moreau, B. Lestriez, S. Jouanneau and D. Guyomard, *Electrochem. Solid-State Lett.*, 2008, **11**, A4–A8.

122 S. F. Lux, F. Schappacher, A. Balducci, S. Passerini and M. Winter, *J. Electrochem. Soc.*, 2010, **157**, A320–A325.

123 W. Porcher, B. Lestriez, S. Jouanneau and D. Guyomard, *J. Power Sources*, 2010, **195**, 2835–2843.

124 W. Porcher, B. Lestriez, S. Jouanneau and D. Guyomard, *J. Electrochem. Soc.*, 2009, **156**, A133–A144.

125 C.-C. Li and Y.-S. Lin, *J. Power Sources*, 2012, **220**, 413–421.

126 J. Li, B. L. Armstrong, J. Kiggans, C. Daniel and D. L. Wood, *Langmuir*, 2012, **28**, 3783–3790.

127 J. Li, B. L. Armstrong, J. Kiggans, C. Daniel and D. L. Wood, *J. Electrochem. Soc.*, 2013, **160**, A201–A206.

128 J.-C. Tsai, F.-Y. Tsai, C.-A. Tung, H.-W. Hsieh and C.-C. Li, *J. Power Sources*, 2013, **241**, 400–403.

129 F.-Y. Tsai, J.-H. Jhang, H.-W. Hsieh and C.-C. Li, *J. Power Sources*, 2016, **310**, 47–53.

130 J.-H. Lee, J.-S. Kim, Y. C. Kim, D. S. Zang and U. Paik, *Ultramicroscopy*, 2008, **108**, 1256–1259.

131 Z. P. Cai, Y. Liang, W. S. Li, L. D. Xing and Y. H. Liao, *J. Power Sources*, 2009, **189**, 547–551.

132 Z. Zhang, T. Zeng, H. Lu, M. Jia, J. Li and Y. Lai, *ECS Electrochem. Lett.*, 2012, **1**, A74–A76.

133 J. Chong, S. Xun, H. Zheng, X. Song, G. Liu, P. Ridgway, J. Q. Wang and V. S. Battaglia, *J. Power Sources*, 2011, **196**, 7707–7714.

134 J. He, H. Zhong, J. Wang and L. Zhang, *J. Alloys Compd.*, 2017, **714**, 409–418.

135 M. Sun, H. Zhong, S. Jiao, H. Shao and L. Zhang, *Electrochim. Acta*, 2014, **127**, 239–244.

136 H. Zhong, A. He, J. Lu, M. Sun, J. He and L. Zhang, *J. Power Sources*, 2016, **336**, 107–114.

137 J. He, J. Wang, H. Zhong, J. Ding and L. Zhang, *Electrochim. Acta*, 2015, **182**, 900–907.

138 I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, **334**, 75–79.

139 J. Li, C. Rulison, J. Kiggans, C. Daniel and D. L. Wood, *J. Electrochem. Soc.*, 2012, **159**, A1152–A1157.

140 G. T. Kim, S. S. Jeong, M. Joost, E. Rocca, M. Winter, S. Passerini and A. Balducci, *J. Power Sources*, 2011, **196**, 2187–2194.

141 S. N. Eliseeva, O. V. Levin, E. G. Tolstopjatova, E. V. Alekseeva, R. V. Apraksin and V. V. Kondratiev, *Mater. Lett.*, 2015, **161**, 117–119.

142 P. R. Das, L. Komsiyska, O. Osters and G. Wittstock, *J. Electrochem. Soc.*, 2015, **162**, A674–A678.

143 S. S. Jeong, N. Böckenfeld, A. Balducci, M. Winter and S. Passerini, *J. Power Sources*, 2012, **199**, 331–335.

144 E. A. Olivetti, G. Ceder, G. G. Gaustad and X. Fu, *Joule*, 2017, **1**, 229–243.

145 M. M. Thackeray, *J. Am. Ceram. Soc.*, 1999, **82**, 3347–3354.

146 M. Thackeray, *Nat. Mater.*, 2002, **1**, 81.

147 D. Guyomard and J. M. Tarascon, *J. Electrochem. Soc.*, 1992, **139**, 937–948.

148 Y. Xia and M. Yoshio, *J. Power Sources*, 1997, **66**, 129–133.

149 M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mater. Res. Bull.*, 1983, **18**, 461–472.

150 T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.*, 1990, **137**, 769–775.

151 M. M. Thackeray, *Prog. Solid State Chem.*, 1997, **25**, 1–71.

152 M. M. Thackeray, Y. Shao-Horn, A. J. Kahaian, K. D. Kepler, E. Skinner, J. T. Vaughey and S. A. Hackney, *Electrochem. Solid-State Lett.*, 1998, **1**, 7–9.

153 P. Ramadass, B. Haran, R. White and B. N. Popov, *J. Power Sources*, 2002, **111**, 210–220.

154 R. J. Gummow, A. de Kock and M. M. Thackeray, *Solid State Ionics*, 1994, **69**, 59–67.

155 M.-H. Ryou, S. Hong, M. Winter, H. Lee and J. W. Choi, *J. Mater. Chem. A*, 2013, **1**, 15224–15229.

156 T. Gotoh, K. Matsushima and K.-I. Kikuchi, *Chemosphere*, 2004, **55**, 57–64.

157 T. S. Pathak, J.-H. Yun, S.-J. Lee, D.-J. Baek and K.-J. Paeng, *Carbohydr. Polym.*, 2009, **78**, 717–724.

158 Z. Zhang, T. Zeng, Y. Lai, M. Jia and J. Li, *J. Power Sources*, 2014, **247**, 1–8.

159 K. Amine, H. Tukamoto, H. Yasuda and Y. Fujita, *J. Power Sources*, 1997, **68**, 604–608.

160 Q. Zhong, *J. Electrochem. Soc.*, 1997, **144**, 205.

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | 3123

161 Z. Wang, N. Dupré, A.-C. Gaillot, B. Lestriez, J.-F. Martin, L. Daniel, S. Patoux and D. Guyomard, *Electrochim. Acta*, 2012, **62**, 77–83.

162 F. De Giorgio, N. Laszczynski, J. von Zamory, M. Mastragostino, C. Arbizzani and S. Passerini, *ChemSusChem*, 2017, **10**, 379–386.

163 M. Kuenzel, D. Bresser, T. Diemant, D. Viera Carvalho, G.-T. Kim, R. J. Behm and S. Passerini, *ChemSusChem*, 2018, **11**, 562–573.

164 W.-Y. Chou, Y.-C. Jin, J.-G. Duh, C.-Z. Lu and S.-C. Liao, *Appl. Surf. Sci.*, 2015, **355**, 1272–1278.

165 F. Bigoni, F. De Giorgio, F. Soavi and C. Arbizzani, *J. Electrochem. Soc.*, 2017, **164**, A6171–A6177.

166 H. Zhong, J. He and L. Zhang, *Mater. Res. Bull.*, 2017, **93**, 194–200.

167 H. Zhong, J. Lu, A. He, M. Sun, J. He and L. Zhang, *J. Mater. Sci. Technol.*, 2017, **33**, 763–767.

168 P. P. Prosini, M. Carewska and A. Masci, *Solid State Ionics*, 2015, **274**, 88–93.

169 N. P. W. Pieczonka, V. Borgel, B. Ziv, N. Leifer, V. Dargel, D. Aurbach, J.-H. Kim, Z. Liu, X. Huang, S. A. Krachkovskiy, G. R. Goward, I. Halalay, B. R. Powell and A. Manthiram, *Adv. Energy Mater.*, 2016, **6**, 1501010.

170 B. P. N. Nguyen, N. Mariage, R. Fredon, E. M. Kelder and B. Lestriez, *J. Electrochem. Soc.*, 2015, **162**, A1451–A1459.

171 A. Manthiram and J. B. Goodenough, *Can. J. Phys.*, 1987, **65**, 1309–1317.

172 J. Kim, Y. Hong, K. S. Ryu, M. G. Kim and J. Cho, *Electrochem. Solid-State Lett.*, 2006, **9**, A19–A23.

173 G. V. Zhuang, G. Chen, J. Shim, X. Song, P. N. Ross and T. J. Richardson, *J. Power Sources*, 2004, **134**, 293–297.

174 K. Matsumoto, R. Kuzuo, K. Takeya and A. Yamanaka, *J. Power Sources*, 1999, **81–82**, 558–561.

175 X. Zhang, W. J. Jiang, X. P. Zhu, A. Mauger, Qilu and C. M. Julien, *J. Power Sources*, 2011, **196**, 5102–5108.

176 T. Tanabe, T. Gunji, Y. Honma, K. Miyamoto, T. Tsuda, Y. Mochizuki, S. Kaneko, S. Ugawa, H. Lee, T. Ohsaka and F. Matsumoto, *Electrochim. Acta*, 2016, **224**, 429–438.

177 R. Moshtev, P. Zlatilova, S. Vasilev, I. Bakalova and A. Kozawa, *J. Power Sources*, 1999, **81–82**, 434–441.

178 G. E. Brown, V. E. Henrich, W. H. Casey, D. L. Clark, C. Eggleston, A. Felmy, D. W. Goodman, M. Grätzel, G. Maciel, M. I. McCarthy, K. H. Nealson, D. A. Sverjensky, M. F. Toney and J. M. Zachara, *Chem. Rev.*, 1999, **99**, 77–174.

179 N. L. Sukiman, X. Zhou, N. Birbilis, A. E. Hughes, J. M. C. Mol, S. J. Garcia and G. E. Thompson, *Aluminium Alloys – New Trends in Fabrication and Applications*, Intech, 2012, pp. 47–97.

180 I. A. Shkrob, J. A. Gilbert, P. J. Phillips, R. Klie, R. T. Haasch, J. Bareño and D. P. Abraham, *J. Electrochem. Soc.*, 2017, **164**, A1489–A1498.

181 I. Doberdò, N. Löffler, N. Laszczynski, D. Cericola, N. Penazzi, S. Bodoardo, G. T. Kim and S. Passerini, *J. Power Sources*, 2014, **248**, 1000–1006.

182 N. Loeffler, J. Von Zamory, N. Laszczynski, I. Doberdo, G. T. Kim and S. Passerini, *J. Power Sources*, 2014, **248**, 915–922.

183 A. Moretti, G. T. Kim, D. Bresser, K. Renger, E. Paillard, R. Marassi, M. Winter and S. Passerini, *J. Power Sources*, 2013, **221**, 419–426.

184 N. Loeffler, G. T. Kim, F. Mueller, T. Diemant, J. K. Kim, R. J. Behm and S. Passerini, *ChemSusChem*, 2016, **9**, 1112–1117.

185 T. Tanabe, Y. Liu, K. Miyamoto, Y. Irii, F. Maki, T. Gunji, S. Kaneko, S. Ugawa, H. Lee, T. Ohsaka and F. Matsumoto, *Electrochim. Acta*, 2017, **258**, 1348–1355.

186 N. Laszczynski, J. von Zamory, J. Kalhoff, N. Loeffler, V. S. K. Chakravadhanula and S. Passerini, *ChemElectroChem*, 2015, **2**, 1768–1773.

187 N. Loeffler, T. Kopel, G.-T. Kim and S. Passerini, *J. Electrochem. Soc.*, 2015, **162**, A2692–A2698.

188 N. Loeffler, G. T. Kim, F. Mueller, T. Diemant, J. K. Kim, R. J. Behm and S. Passerini, *ChemSusChem*, 2016, **9**, 1112–1117.

189 Z. Chen, G.-T. Kim, D. Chao, N. Loeffler, M. Copley, J. Lin, Z. Shen and S. Passerini, *J. Power Sources*, 2017, **372**, 180–187.

190 A. Kazzazi, D. Bresser, A. Birrozzi, J. von Zamory, M. Hekmatfar and S. Passerini, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17214–17222.

191 J. Xu, S.-L. Chou, Q. Gu, H.-K. Liu and S.-X. Dou, *J. Power Sources*, 2013, **225**, 172–178.

192 J. H. Lee, S. Lee, U. Paik and Y. M. Choi, *J. Power Sources*, 2005, **147**, 249–255.

193 W.-R. Liu, M.-H. Yang, H.-C. Wu, S. M. Chiao and N.-L. Wu, *Electrochem. Solid-State Lett.*, 2005, **8**, A100–A103.

194 M. Ling, J. Qiu, S. Li, H. Zhao, G. Liu and S. Zhang, *J. Mater. Chem. A*, 2013, **1**, 11543.

195 H. Buqa, M. Holzapfel, F. Krumeich, C. Veit and P. Novák, *J. Power Sources*, 2006, **161**, 617–622.

196 S. Chou, Y. Pan, J. Wang, H. Liu and S. Dou, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20347–20359.

197 S. F. Lux, F. Schappacher, A. Balducci, S. Passerini and M. Winter, *J. Electrochem. Soc.*, 2010, **157**, A320.

198 Q. Wu, S. Ha, J. Prakash, D. W. Dees and W. Lu, *Electrochim. Acta*, 2013, **114**, 1–6.

199 H. Yamamoto and H. Mori, *Lithium-Ion Batteries: Science and Technologies*, Springer, 2009, pp. 163–179.

200 C.-C. Li and Y.-W. Wang, *J. Power Sources*, 2013, **227**, 204–210.

201 N. Yabuuchi, Y. Kinoshita, K. Misaki, T. Matsuyama and S. Komaba, *J. Electrochem. Soc.*, 2015, **162**, A538–A544.

202 Q. Pang, X. Liang, C. Y. Kwok, J. Kulisch and L. F. Nazar, *Adv. Energy Mater.*, 2016, 1601630.

203 J. Song, Z. Yu, M. L. Gordin, X. Li, H. Peng and D. Wang, *ACS Nano*, 2015, **9**, 11933–11941.

204 M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li and S. A. Hackney, *J. Mater. Chem.*, 2005, **15**, 2257–2267.

205 H. Chen, M. Chen, C. Du, Y. Cui, P. Zuo, X. Cheng and G. Yin, *Mater. Chem. Phys.*, 2016, **171**, 6–10.

206 J. Wang, X. He, E. Paillard, N. Laszczynski, J. Li and S. Passerini, *Adv. Energy Mater.*, 2016, **6**, 1600906.

207 J. Li, R. Klöpsch, S. Nowak, M. Kunze, M. Winter and S. Passerini, *J. Power Sources*, 2011, **196**, 7687–7691.

208 Z. Han, H. Zhan and Y. Zhou, *Mater. Lett.*, 2014, **114**, 48–51.

3124 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

209 T. Zhang, J.-T. Li, J. Liu, Y.-P. Deng, Z.-G. Wu, Z.-W. Yin, D. Guo, L. Huang and S.-G. Sun, *Chem. Commun.*, 2016, **52**, 4683–4686.

210 L. Baggetto, D. Mohanty, R. A. Meisner, C. A. Bridges, C. Daniel, D. L. Wood III, N. J. Dudney and G. M. Veith, *RSC Adv.*, 2014, **4**, 23364–23371.

211 S. Hy, F. Felix, J. Rick, W.-N. Su and B. J. Hwang, *J. Am. Chem. Soc.*, 2014, **136**, 999–1007.

212 N. Loeffler, G.-T. Kim, S. Passerini, C. Gutierrez, I. Cendoya, I. De Meatza, F. Alessandrini and G. B. Appetecchi, *ChemSusChem*, 2017, **10**, 3581–3587.

213 D. Bresser, S. Passerini and B. Scrosati, *Chem. Commun.*, 2013, **49**, 10545–10562.

214 W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, Á. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char and J. Pyun, *Nat. Chem.*, 2013, **5**, 518–524.

215 D. Lin, Y. Liu and Y. Cui, *Nat. Nanotechnol.*, 2017, **12**, 194–206.

216 K. Zhang, G.-H. Lee, M. Park, W. Li and Y.-M. Kang, *Adv. Energy Mater.*, 2016, **6**, 1600811.

217 Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Angew. Chem., Int. Ed.*, 2013, **52**, 13186–13200.

218 A. Manthiram, Y. Fu, S.-H. Chung, C. Zu and Y.-S. Su, *Chem. Rev.*, 2014, **114**, 11751–11787.

219 M. Wild, L. O'Neill, T. Zhang, R. Purkayastha, G. Minton, M. Marinescu and G. J. Offer, *Energy Environ. Sci.*, 2015, **8**, 3477–3494.

220 D. Moy and S. R. Narayanan, *J. Electrochem. Soc.*, 2017, **164**, A560–A566.

221 J.-Y. Hwang, H. M. Kim, S. Shin and Y.-K. Sun, *Adv. Funct. Mater.*, 2017, **28**, 1704294.

222 C. Sheng-Heng and M. Arumugam, *Adv. Mater.*, 2014, **26**, 7352–7357.

223 X. He, J. Ren, L. Wang, W. Pu, C. Jiang and C. Wan, *J. Power Sources*, 2009, **190**, 154–156.

224 J. Sun, Y. Huang, W. Wang, Z. Yu, A. Wang and K. Yuan, *Electrochim. Acta*, 2008, **53**, 7084–7088.

225 Y. Huang, J. Sun, W. Wang, Y. Wang, Z. Yu, H. Zhang, A. Wang and K. Yuan, *J. Electrochem. Soc.*, 2008, **155**, A764–A767.

226 Y. Wang, Y. Huang, W. Wang, C. Huang, Z. Yu, H. Zhang, J. Sun, A. Wang and K. Yuan, *Electrochim. Acta*, 2009, **54**, 4062–4066.

227 J. Sun, Y. Huang, W. Wang, Z. Yu, A. Wang and K. Yuan, *Electrochem. Commun.*, 2008, **10**, 930–933.

228 W. Zhang, Y. Huang, W. Wang, C. Huang, Y. Wang, Z. Yu and H. Zhang, *J. Electrochem. Soc.*, 2010, **157**, A443.

229 Q. Wang, W. Wang, Y. Huang, F. Wang, H. Zhang, Z. Yu, A. Wang and K. Yuan, *J. Electrochem. Soc.*, 2011, **158**, A775–A779.

230 M. Rao, X. Song, H. Liao and E. J. Cairns, *Electrochim. Acta*, 2012, **65**, 228–233.

231 M. Rao, X. Song and E. J. Cairns, *J. Power Sources*, 2012, **205**, 474–478.

232 M. He, L.-X. Yuan, W.-X. Zhang, X.-L. Hu and Y.-H. Huang, *J. Phys. Chem. C*, 2011, **115**, 15703–15709.

233 Z. Zhang, W. Bao, H. Lu, M. Jia, K. Xie, Y. Lai and J. Li, *ECS Electrochem. Lett.*, 2012, **1**, A34–A37.

234 W. Bao, Z. Zhang, Y. Gan, X. Wang and J. Lia, *J. Energy Chem.*, 2013, **22**, 790–794.

235 S. Zhu, J. Yu, X. Yan, E. Zhao, Y. Wang, D. Sun, Y. Jin and K. Kanamura, *J. Appl. Electrochem.*, 2016, **46**, 725–733.

236 J.-T. Li, Z.-Y. Wu, Y.-Q. Lu, Y. Zhou, Q.-S. Huang, L. Huang and S.-G. Sun, *Adv. Energy Mater.*, 2017, **7**, 1701185.

237 J. Wang, Z. Yao, C. W. Monroe, J. Yang and Y. Nuli, *Adv. Funct. Mater.*, 2013, **23**, 1194–1201.

238 C. Vaalma, D. Buchholz, M. Weil and S. Passerini, *Nat. Rev. Mater.*, 2018, **3**, 18013.

239 H. Kang, Y. Liu, K. Cao, Y. Zhao, L. Jiao, Y. Wang and H. Yuan, *J. Mater. Chem. A*, 2015, **3**, 17899–17913.

240 S.-L. Chou, Y. Pan, J.-Z. Wang, H.-K. Liu and S.-X. Dou, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20347–20359.

241 M. Lao, Y. Zhang, W. Luo, Q. Yan, W. Sun and S. X. Dou, *Adv. Mater.*, 2017, **29**, 1–23.

242 W. Zhang, M. Dahbi and S. Komaba, *Curr. Opin. Chem. Eng.*, 2016, **13**, 36–44.

243 J. Peters, D. Buchholz, S. Passerini and M. Weil, *Energy Environ. Sci.*, 2016, **9**, 1744–1751.

244 D. Buchholz, A. Moretti, R. Kloepsch, S. Nowak, V. Siozios, M. Winter and S. Passerini, *Chem. Mater.*, 2013, **25**, 142–148.

245 J.-Y. Hwang, S.-T. Myung and Y.-K. Sun, *Chem. Soc. Rev.*, 2017, **46**, 3529–3614.

246 V. Dall'Asta, D. Buchholz, L. G. Chagas, X. Dou, C. Ferrara, E. Quartarone, C. Tealdi and S. Passerini, *ACS Appl. Mater. Interfaces*, 2017, **9**, 34891–34899.

247 X. Deng, W. Shi, J. Sunarso, M. Liu and Z. Shao, *ACS Appl. Mater. Interfaces*, 2017, **9**, 16280–16287.

248 P. R. Kumar, Y. H. Jung, S. A. Ahad and D. K. Kim, *RSC Adv.*, 2017, **7**, 21820–21826.

249 J. Zhao, X. Yang, Y. Yao, Y. Gao, Y. Sui, B. Zou, H. Ehrenberg, G. Chen and F. Du, *Adv. Sci.*, 2018, 1700768.

250 J. Song, L. Wang, Y. Lu, J. Liu, B. Guo, P. Xiao, J. J. Lee, X. Q. Yang, G. Henkelman and J. B. Goodenough, *J. Am. Chem. Soc.*, 2015, **137**, 2658–2664.

251 A. Rudola, K. Du and P. Balaya, *J. Electrochem. Soc.*, 2017, **164**, A1098–A1109.

252 W. J. Li, S. L. Chou, J. Z. Wang, Y. M. Kang, J. L. Wang, Y. Liu, Q. F. Gu, H. K. Liu and S. X. Dou, *Chem. Mater.*, 2015, **27**, 1997–2003.

253 M. J. Piernas-Muñoz, E. Castillo-Martínez, J. L. Gómez-Cámer and T. Rojo, *Electrochim. Acta*, 2016, **200**, 123–130.

254 C. Delmas, C. Fouassier and P. Hagenmuller, *Phys. B+C*, 1980, **99**, 81–85.

255 N. Ortiz-Vitoriano, N. E. Drewett, E. Gonzalo and T. Rojo, *Energy Environ. Sci.*, 2017, **10**, 1051–1074.

256 L. Mu, S. Xu, Y. Li, Y.-S. S. Hu, H. Li, L. Chen and X. Huang, *Adv. Mater.*, 2015, **27**, 6928–6933.

257 H. R. Yao, P. F. Wang, Y. Gong, J. Zhang, X. Yu, L. Gu, C. Ouyang, Y. X. Yin, E. Hu, X. Q. Yang, E. Stavitski,

This journal is © The Royal Society of Chemistry 2018

Energy Environ. Sci., 2018, **11**, 3096–3127 | 3125

Y. G. Guo and L. J. Wan, *J. Am. Chem. Soc.*, 2017, **139**, 8440–8443.

258 Z. Lu and J. R. Dahn, *Chem. Mater.*, 2001, **13**, 1252–1257.

259 K. Kubota and S. Komaba, *J. Electrochem. Soc.*, 2015, **162**, A2538–A2550.

260 X. H. Zhang, W. L. Pang, F. Wan, J. Z. Guo, H. Y. Lü, J. Y. Li, Y. M. Xing, J. P. Zhang and X. L. Wu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20650–20659.

261 C. Bommier and X. Ji, *Small*, 2018, 1703576.

262 X. Dou, I. Hasa, M. Hekmatfar, T. Diemant, R. J. Behm, D. Buchholz and S. Passerini, *ChemSusChem*, 2017, **10**, 2668–2676.

263 M. Dahbi, T. Nakano, N. Yabuuchi, T. Ishikawa, K. Kubota, M. Fukunishi, S. Shibahara, J. Y. Son, Y. T. Cui, H. Oji and S. Komaba, *Electrochem. Commun.*, 2014, **44**, 66–69.

264 Y. Li, Y. S. Hu, M. M. Titirici, L. Chen and X. Huang, *Adv. Energy Mater.*, 2016, **6**, 1–9.

265 Y. Li, Y.-S. Hu, H. Li, L. Chen and X. Huang, *J. Mater. Chem. A*, 2016, **4**, 96–104.

266 M. Dahbi, M. Kiso, K. Kubota, T. Horiba, T. Chafik, K. Hida, T. Matsuyama and S. Komaba, *J. Mater. Chem. A*, 2017, **5**, 9917–9928.

267 L. O. Vogt, M. El Kazzi, E. Jämstorp Berg, S. Pérez Villar, P. Novák and C. Villevieille, *Chem. Mater.*, 2015, **27**, 1210–1216.

268 Q. Fan, W. Zhang, J. Duan, K. Hong, L. Xue and Y. Huang, *Electrochim. Acta*, 2015, **174**, 970–977.

269 Y. Sun, L. Zhao, H. Pan, X. Lu, L. Gu, Y.-S. Hu, H. Li, M. Armand, Y. Ikuhara, L. Chen and X. Huang, *Nat. Commun.*, 2013, **4**, 1870.

270 F. Zhao, P. Xue, H. Ge, L. Li and B. Wang, *J. Electrochem. Soc.*, 2016, **163**, A690–A695.

271 Y. Zhang, H. Hou, X. Yang, J. Chen, M. Jing, Z. Wu, X. Jia and X. Ji, *J. Power Sources*, 2016, **305**, 200–208.

272 M. Zarrabeitia, E. Castillo-Martínez, J. M. López Del Amo, A. Eguía-Barrio, M. A. Muñoz-Márquez, T. Rojo and M. Casas-Cabanas, *J. Power Sources*, 2016, **324**, 378–387.

273 S. Komaba, Y. Matsuura, T. Ishikawa, N. Yabuuchi, W. Murata and S. Kuze, *Electrochem. Commun.*, 2012, **21**, 65–68.

274 K. Dai, H. Zhao, Z. Wang, X. Song, V. Battaglia and G. Liu, *J. Power Sources*, 2014, **263**, 276–279.

275 Y. Yui, M. Hayashi, K. Hayashi and J. Nakamura, *Solid State Ionics*, 2015, **288**, 219–223.

276 M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp and Y. Shao-Horn, *J. Phys. Chem. Lett.*, 2015, **6**, 4653–4672.

277 N. Yabuuchi, Y. Matsuura, T. Ishikawa, S. Kuze, J. Y. Son, Y. T. Cui, H. Oji and S. Komaba, *ChemElectroChem*, 2014, **1**, 580–589.

278 M. Dahbi, N. Yabuuchi, M. Fukunishi, K. Kubota, K. Chihara, K. Tokiwa, X. Yu, H. Ushiyama, K. Yamashita, J.-Y. Son, Y.-T. Cui, H. Oji and S. Komaba, *Chem. Mater.*, 2016, **28**, 1625–1635.

279 Y. Kim, Y. Park, A. Choi, N. S. Choi, J. Kim, J. Lee, J. H. Ryu, S. M. Oh and K. T. Lee, *Adv. Mater.*, 2013, **25**, 3045–3049.

280 J. Qian, X. Wu, Y. Cao, X. Ai and H. Yang, *Angew. Chem., Int. Ed.*, 2013, **52**, 4633–4636.

281 W.-J. Li, S.-L. Chou, J.-Z. Wang, H.-K. Liu and S.-X. Dou, *Chem. Commun.*, 2015, **51**, 3682–3685.

282 J. Ming, H. Ming, W.-J. Kwak, C. Shin, J. Zheng and Y.-K. Sun, *Chem. Commun.*, 2014, **50**, 13307–13310.

283 T. Zhou, W. K. Pang, C. Zhang, J. Yang, Z. Chen, H. K. Liu and Z. Guo, *ACS Nano*, 2014, **8**, 8323–8333.

284 H. Gao, W. Zhou, J. H. Jang and J. B. Goodenough, *Adv. Energy Mater.*, 2016, **6**, 1–7.

285 C. Luo, X. Fan, Z. Ma, T. Gao and C. Wang, *Chem*, 2017, **3**, 1050–1062.

286 L. Xu, H. Sitinamaluwa, H. Li, J. Qiu, Y. Wang, C. Yan, H. Li, S. Yuan and S. Zhang, *J. Mater. Chem. A*, 2017, **5**, 2102–2109.

287 L. Bonnefoi, P. Simon, J. Fauvarque, C. Sarrazin, J. Sarrau and A. Dugast, *J. Power Sources*, 1999, **80**, 149–155.

288 F. Beck and M. Dolata, *J. Appl. Electrochem.*, 2001, **31**, 517–521.

289 X. Sun, X. Zhang, H. Zhang, B. Huang and Y. Ma, *J. Solid State Electrochem.*, 2013, **17**, 2035–2042.

290 B. Dyatkin, V. Presser, M. Heon, M. R. Lukatskaya, M. Beidaghi and Y. Gogotsi, *ChemSusChem*, 2013, **6**, 2269–2280.

291 A. Krause and A. Balducci, *Electrochem. Commun.*, 2011, **13**, 814–817.

292 A. Krause, P. Kossyrev, M. Oljaca, S. Passerini, M. Winter and A. Balducci, *J. Power Sources*, 2011, **196**, 8836–8842.

293 N. Böckenfeld, R.-S. Kühnel, S. Passerini, M. Winter and A. Balducci, *J. Power Sources*, 2011, **196**, 4136–4142.

294 A. Brandt, P. Isken, A. Lex-Balducci and A. Balducci, *J. Power Sources*, 2012, **204**, 213–219.

295 N. Böckenfeld, S. S. Jeong, M. Winter, S. Passerini and A. Balducci, *J. Power Sources*, 2013, **221**, 14–20.

296 H. A. Ambjörnsson, K. Schenzel and U. Germgård, *BioResources*, 2013, **8**, 1918–1932.

297 K. Murashko, D. Nevstrueva, A. Pihlajamäki, T. Koiranen and J. Pyrhönen, *Energy*, 2017, **119**, 435–441.

298 A. Varzi, A. Balducci and S. Passerini, *J. Electrochem. Soc.*, 2014, **161**, A368–A375.

299 M. Yamagata, S. Ikebe, K. Soeda and M. Ishikawa, *RSC Adv.*, 2013, **3**, 1037–1040.

300 H. Y. Tran, M. Wohlfahrt-Mehrens and S. Dsoke, *J. Power Sources*, 2017, **342**, 301–312.

301 A. Varzi and S. Passerini, *J. Power Sources*, 2015, **300**, 210–222.

302 M. Murase, N. Yabuuchi, Z.-J. Han, J.-Y. Son, Y.-T. Cui, H. Oji and S. Komaba, *ChemSusChem*, 2012, **5**, 2307–2311.

303 A. Varzi, R. Raccichini, M. Marinaro, M. Wohlfahrt-Mehrens and S. Passerini, *J. Power Sources*, 2016, **326**, 672–679.

304 D. S. Reay, E. A. Davidson, K. A. Smith, P. Smith, J. M. Melillo, F. Dentener and P. J. Crutzen, *Nat. Clim. Change*, 2012, **2**, 410–416.

305 B. S. Shete and N. P. Shinkar, *Int. J. Curr. Eng. Technol.*, 2013, **3**, 1611–1615.

306 M. Aslan, D. Weingarth, N. Jäckel, J. S. Atchison, I. Grobelsek and V. Presser, *J. Power Sources*, 2014, **266**, 374–383.

3126 | *Energy Environ. Sci.*, 2018, **11**, 3096–3127

This journal is © The Royal Society of Chemistry 2018

307 M. Aslan, D. Weingarth, P. Herbeck-Engel, I. Grobelsek and V. Presser, *J. Power Sources*, 2015, **279**, 323–333.

308 P. Kurzweil and M. Chwistek, *J. Power Sources*, 2008, **176**, 555–567.

309 M. Winter, G. H. Wrodnigg, J. O. Besenhard, W. Biberacher and P. Novák, *J. Electrochem. Soc.*, 2000, **147**, 2427–2431.

310 M. M. Hantel, V. Presser, R. Kötz and Y. Gogotsi, *Electrochem. Commun.*, 2011, **13**, 1221–1224.

311 D. Sauerteig, S. Ivanov, H. Reinshagen and A. Bund, *J. Power Sources*, 2017, **342**, 939–946.

312 M. Ebner, F. Marone, M. Stampanoni and V. Wood, *Science*, 2013, **342**, 716–720.

313 N. Shpigel, M. D. Levi, S. Sigalov, O. Girshevitz, D. Aurbach, L. Daikhin, P. Pikma, M. Marandi, A. Jänes, E. Lust, N. Jäckel and V. Presser, *Nat. Mater.*, 2016, **15**, 570.

314 A. Brandt, S. Pohlmann, A. Varzi, A. Balducci and S. Passerini, *MRS Bull.*, 2013, **38**, 554–559.