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Please cite this article as: C.A.F. Nason, Y. Xu, Pre-intercalation: A valuable approach for the improvement of post-lithium battery materials, *eScience*, https://doi.org/10.1016/j.esci.2023.100183.

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Improved charge storage

Improved electronic conductivity

Pre-intercalation

Improved cycling stability

Improved ionic conductivity
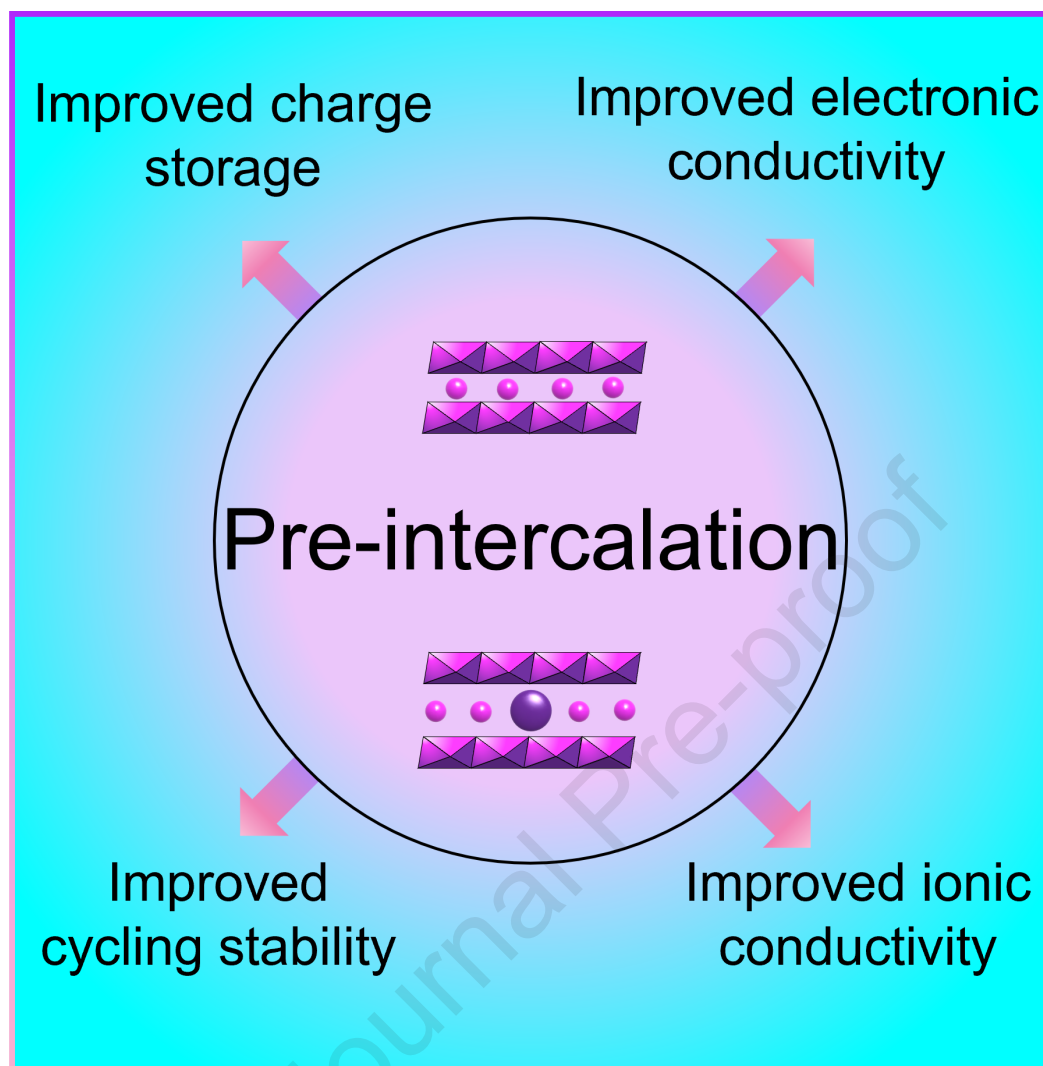
Pre-intercalation: A valuable approach for the improvement of post-lithium battery materials

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Abstract

With the growing concern around the sustainability and supply of lithium, the need for alternative rechargeable energy storage technologies has become ever more pressing. Sodium-, potassium-, magnesium-, and zinc-ion batteries are fast becoming viable alternatives but are held back by capacity, rate and stability problems that have not developed comparably to lithium-ion batteries. To overcome these shortcomings and reduce the reliance on lithium, electrode materials used for these post-lithium batteries must be improved. Pre-intercalation of foreign species into the lattice of promising electrode materials can enhance their electrochemical performance in comparison to the un-pre-intercalated counterparts, closing the performance gap with lithium-ion batteries. This review article covers the common methods of pre-intercalating foreign species into electrode materials, the resulting structural effects and the improvements that are observed in the materials' electrochemical performance for post-lithium batteries. Timely and impactful work reported previously are summarised as examples of these improvements, demonstrating the value and ever-growing importance of pre-intercalation in today's battery landscape.

Keywords: Intercalation; Post-Lithium; Batteries; Energy Storage; Electrode Materials;

Ion Diffusion; Active Sites

1. Introduction

Of the current energy storage technologies, lithium-ion batteries (LIBs) are

among the most suited for tackling the current energy crisis and are one of the

most important energy storage technologies of the 21st century [1]. They have

permeated the lives of most people living in developed countries, being

ubiquitous in handheld electronic devices, electric vehicles and home energy

storage. However, the success of LIBs has also created a problem. The

34   production of lithium hydroxide, a precursor for many lithium electrodes, is very

35   slow and can take up to 24 months from start to finish [2]. This creates a huge

36   production bottleneck and results in rising prices, with lithium hydroxide costing

37   £20,000 ton^{-1} in Nov 2017 to now £69,000 ton^{-1} in Nov 2022 [3]. Viable

38   alternatives are needed. These come in the form of sodium-ion batteries (NIBs),

39   potassium-ion batteries (KIBs), magnesium-ion batteries (MIBs) and zinc-ion

40   batteries (ZIBs). Each of the alternatives to lithium (Li) have their own individual

41   challenges and benefits when applied as charge carriers in batteries. To begin

42   with, the most mature of these is sodium (Na) (Fig. 1b). The main benefits of Na^+

43   arise from its much higher crustal abundance, 2.3% vs 0.002%, and its smaller

44   stokes radius, 4.6 Å vs 4.8 Å, than Li^+. Crustal abundance is a reliable indicator

45   of lower price, which is the largest factor in NIB's viability [4]. Na^+ also does

46   not alloy with aluminum at low voltages, allowing for the more expensive and

47   denser copper to be replaced as the anode current collector, raising the energy

48   density of the battery and saving on material costs [5]. However, it does suffer

49   from some downsides when compared to Li. Firstly, many common carbon anode

50   materials require further modification to store Na^+ ions at any appreciable level.

51   This is due to Na^+ poorly intercalating into graphite, forming NaC_{64} and NaC_{186},

52   which is very poor utilization when compared to LiC_6 or KC_8 [6, 7]. Secondly,

53   while the stokes radius of Na^+ in propylene carbonate (PC) is smaller than Li^+,

54   its ionic radius is larger, 1.02 Å vs 0.76 Å [8]. Not only does this result in slower

55   ion diffusion within the host lattice but also results in greater expansion and

56 contraction, promoting cracking and expulsion of the active material into the

57 electrolyte, rendering it electrochemically inert. It is also more reactive than Li,

58 making it difficult utilizing metal anodes on a commercial scale.

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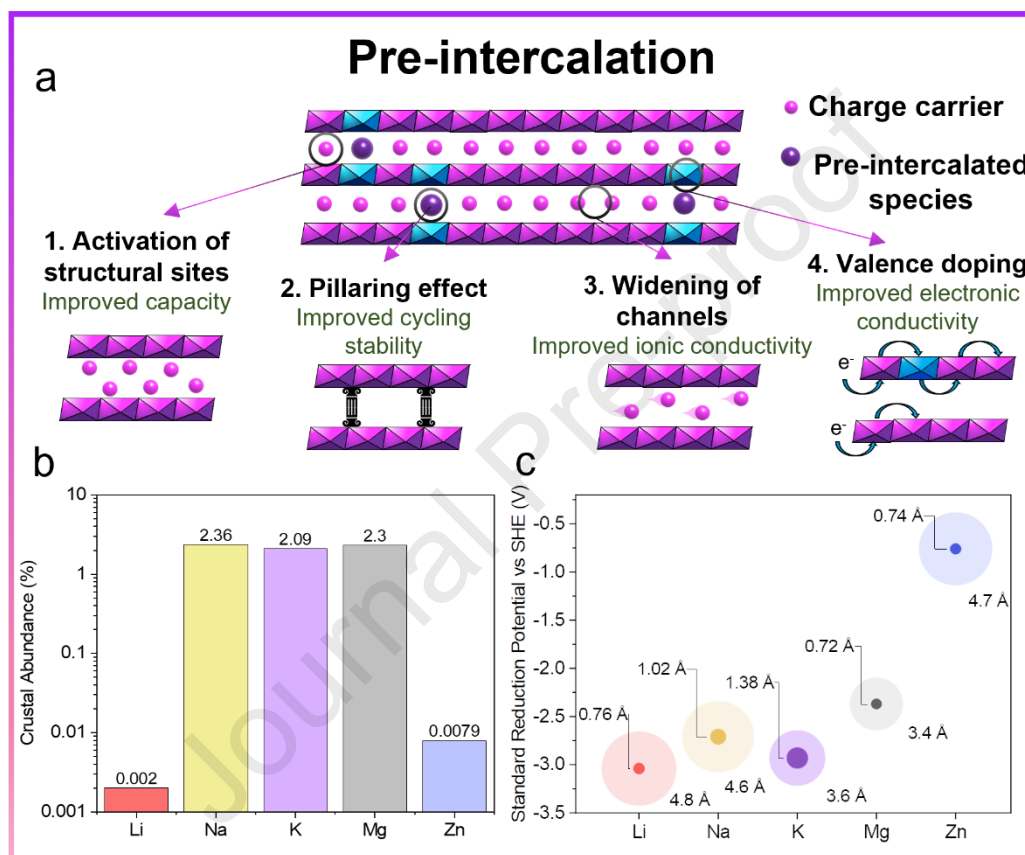
Fig. 1. (a) Schematic of pre-intercalation and its effects, along with the corresponding
benefits for battery materials. (b) Crustal abundance of lithium, sodium, potassium,
magnesium and zinc [9]. (c) Comparison of the M^+/M redox couple against the
Standard Hydrogen Electrode (SHE), the Stokes and ionic radii of Li^+, Na^+, K^+, Mg^{2+}
and Zn^{2+}.

66

67 KIBs are another key alternative to LIBs. From their first reporting in 2004, KIBs

68 have significantly advanced in terms of capacity, energy density, cycling stability

69 and rate performance [10]. Potassium (K) has a similar crustal abundance to Na,

70 making it a good fit for large scale applications where cost plays an even larger

71 factor. Its redox potential in propylene carbonate (PC) is even lower than Li^+, at

72 -2.88 V vs SHE. This could realize higher volumetric energy density cells than

73 even LIBs, as the operating voltage is a key metric in energy density. In addition,

74 the stokes radii of K^+ in PC is even smaller than Li^+ or Na^+, 3.6 Å, indicating that

75 KIBs could be a good candidate for fast charging and discharging [11]. However,

76 this may be misleading, as KIBs suffer from problems associated with its larger

77 ionic radius, 1.43 Å. This large size results in poorer ionic diffusion, greater

78 expansion and contraction of the host lattice, lower energy density and lower

79 specific capacity as fewer active sites have the space to accommodate it,

80 compared to LIBs. It is also even more reactive to H_2O and O_2 than Na, resulting

81 in the obvious problems associated with having kilograms of highly reactive K

82 in a highly mobile platform such as a vehicle, assuming a metal anode is used.

83 Despite these drawbacks for mobile applications, both KIBs and NIBs show

84 promise in the stationary energy storage sector and could be the key to realizing

85 a fully renewable energy consuming society.

86 Moving away from alkali metals, ZIBs and MIBs are two other developing

87 battery technologies. These ions benefit from being multivalent, as they can

88 theoretically transport charge far more efficiently than monovalent ion. However,

89 this benefit also appears as a problem, as because these ions are multivalent and

90 they have a higher mass to charge ratios than Li^+, diffusion through electrolytes

91 and materials are sluggish, due to larger hydration shells than Na^+ or K^+ (Fig. 1c)

92 and stronger attraction/repulsion with the chemical environment within the host

4

93 lattice. Even with this problem, zinc in particular benefits from being able to

94 utilize aqueous electrolytes, using water soluble zinc salts. This makes aqueous

95 ZIBs far safer than alkali metal batteries, both because of the replacement of

96 carbonate electrolyte and the reactivity of the metal anode [12]. Magnesium, in

97 contrast, suffers mainly from electrolyte problems as the passivation layer

98 formed on the surface of the magnesium hinders its stripping and plating,

99 resulting in poor coulombic efficiency and rapid capacity decay [13]. As with Na

100 and K, both magnesium and zinc are cheap and abundant, making them strong

101 candidates for large scale energy storage.

102 When analysing the weaknesses of the LIB alternatives, some common themes

103 start to emerge. In all cases, while the metals used are cheaper and/or more

104 abundant than Li, the capacity or the stability of the electrode materials results in

105 the practical energy density per £ to be lower than LIBs, rendering them currently

106 unviable. Their larger size or charge to size ratio vs Li^+ also means that their

107 diffusion in electrode hosts is more difficult, due to increased sterics and

108 increased interactions with the surrounding atoms in the lattice. To become a

109 practical alternative to LIBs, improvements to capacity, rate performance,

110 stability, ionic and electronic conductivity are needed. This review highlights

111 pre-intercalation as a valuable approach to tackle some of the problems faced by

112 post-LIBs (Fig. 1a), by discussing the fundamental effects that are associated

113 with pre-intercalation and the performance for NIBs, KIBs, ZIBs and MIBs.

114 Recent and impactful advances that have been made utilizing pre-intercalation

115 are summarized and future perspectives are provided.

116 **2. Pre-intercalation Background**

117 Since its first reporting in 1974, pre-intercalation has become an increasingly

118 valuable approach to alter the properties of materials. This was followed by the

119 pioneering work by Worrel in 1981, who investigated the pre-intercalation of

120 alkali metal ions into TiS_2 for LIBs [14]. In general, pre-intercalation involves

121 the insertion of foreign ions or molecules into the host structure to assist the

122 intercalation of further ions or molecules. Through a combination of steric and

123 electronic effects, the pre-intercalated species modulates the structure-

124 performance relationship of the material. Specifically for battery applications,

125 pre-intercalation is primarily to alter the host structure to better accommodate the

126 ions that are going to be cycled via the rocking chair mechanism, i.e., the charge

127 carriers [15]. These alterations are performed to improve one or multiple of the

128 problems associated with post-lithium-ion batteries, namely low capacity, poor

129 performance at faster charge/discharge rates, and capacity loss on cycling.

130

131 **2.1 Methods of Pre-intercalation**

132 There are two ways to pre-intercalate species into a host material, chemical and

133 electrochemical pre-intercalation, each with their own benefits and drawbacks

134 (Fig. 2). Chemical pre-intercalation commonly refers to the type of pre-

135 intercalation performed during the synthesis of the material, such as during a

136 solvo/hydrothermal, sol-gel, precipitation, ion-exchange or solid-state reaction

137 [16-19]. Out of these, solvo/hydrothermal is the most commonly used method

138 due to its simplicity of use and the ability to form meta-stable phases under the

139 high pressure and high temperature conditions, along with its industrial

140 applicability. The pre-intercalated species may be added in the initial formation

141 as a dopant or in a subsequent step, with the former providing greater control to

142 the degree of pre-intercalation and the latter generally avoiding possible phase

143 impurities.

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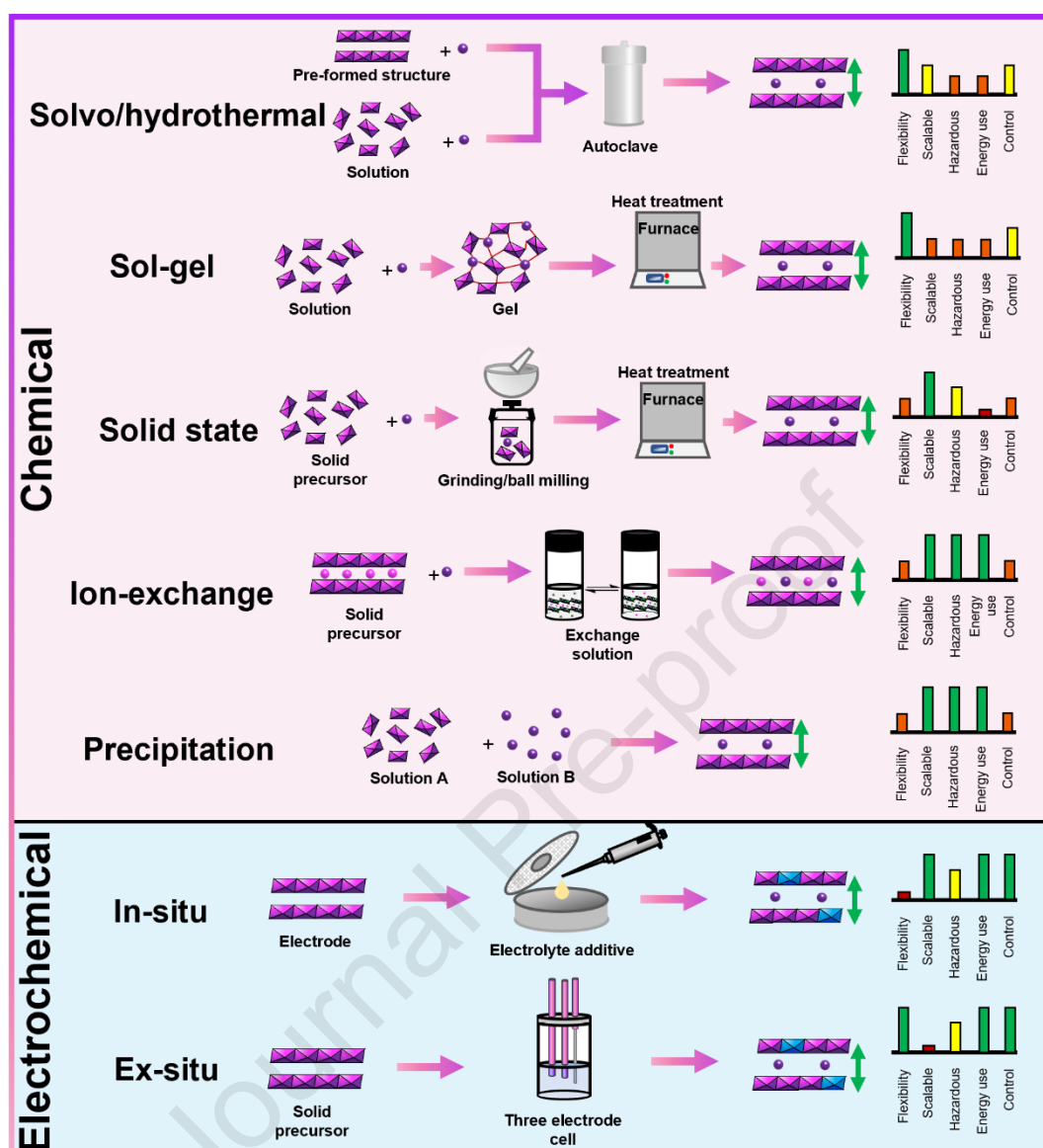
Fig. 2. Summary of the common methods of pre-intercalation, along with a qualitative analysis of their relative performance in several areas of industrial relevance.

147

Sol-gel synthesis has gained significant popularity in recent years, due to its

flexibility and low energy usage. However, a major hurdle is the reagents

commonly used (e.g., titanium isopropoxide and niobium ethoxide), which are

expensive and difficult to manufacture and handle, partially due to their

propensity to react with moisture. This is currently limiting sol-gels industrial

applicability. Ion-exchange, a large and distinct field of chemistry, has seen little

154 application in the battery industry, with no commercial materials utilising the

155 process. This is understandable, as it has some significant hidden limitations. To

156 perform ion-exchange, cations present in the material must be exchanged with

157 cations in a surrounding media, which limits its use on cathodes, as any cations

158 exchanged would likely not be de-intercalated upon charging, reducing the

159 number of charge carriers and thus the capacity. Secondly, to perform ion-

160 exchange, the material must already contain cations, thus ruling out many anode

161 materials, such as carbonaceous materials and transition metal oxides (e.g., Ti

162 and Nb oxides). Therefore, while ion-exchange is extremely attractive from a

163 green chemistry point of view as it is often performed at room temperature and

164 aqueous conditions, the pool of materials that can benefit from it are extremely

165 limited [20]. In contrast, solid-state synthesis, is the most industrially relevant

166 type of synthesis, as it is currently used in the manufacturing process of lithium

167 cobalt oxide [21]. However, it suffers from poor energy use, often operating in

168 excess of 800 °C, and is extremely limited in terms of morphology, secondary

169 particle size, and pre-intercalation control. Finally, electrochemical pre-

170 intercalation uses the driving force of the electric field generated by an applied

171 voltage or current to insert species into the structure of the material [22, 23]. This

172 can be done *ex-situ*, before cell assembly, or *in-situ*, using an additive to the

173 electrolyte [24]. *Ex-situ* electrochemical pre-intercalation allows for maximum

174 control over the pre-intercalation degree, but is difficult to perform and scale. *In-*

175 *situ* pre-intercalation is significantly simpler, as the pre-intercalating species is

176 added directly to the electrolyte. However, this has much less control over the

177 pre-intercalation degree than *ex-situ*, and the complication of additional species

178 in the electrolyte can affect electrochemical stability and other unforeseen

179 interactions, which potentially affects the SEI composition and growth.

180 Both the chemical and electrochemical approaches have different benefits and

181 drawbacks, with the former being far more scalable and mature but having far

182 less control over the degree of pre-intercalation than the latter [23]. However,

183 electrochemical pre-intercalation provides access to synthetically challenging

184 structures but results in greater structural damage to the electrode when compared

185 to chemical pre-intercalation due to the lattice expansion, as its performed after

186 fabrication of the electrode.

187

188 **2.2 Pre-intercalated Species**

189 Throughout the literature, there is a wide and diverse range of pre-intercalated

190 species, which each has a unique effect on the particular structure type it is pre-

191 intercalated into. There are several key attributes to pre-intercalated species, each

192 with their own effects on the electrochemical attributes of the host lattice. The

193 first attribute is the size of the species (left part of Fig. 3).

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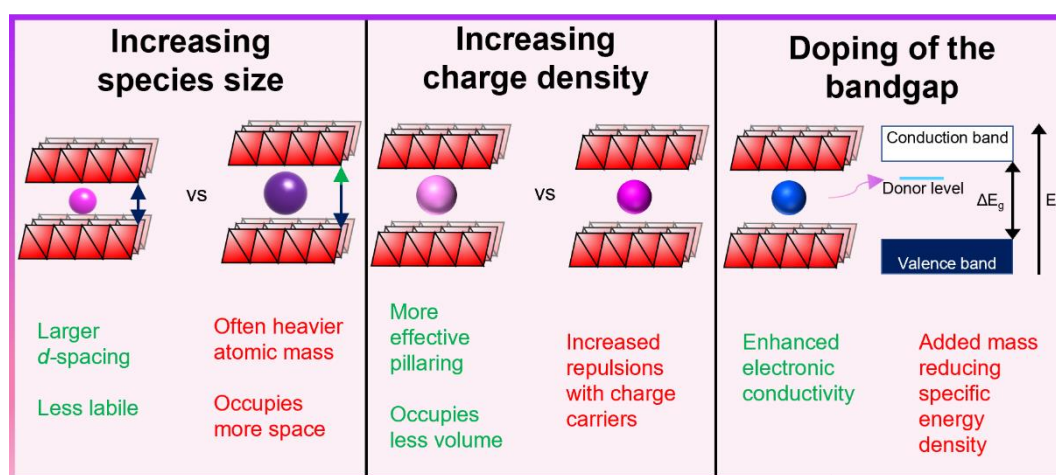
Fig. 3. Schematic displaying the effects of altering a pre-intercalating species size and charge density, along with doping effects.

With large species, for example K^+, Rb^+ and Cs^+, it has been well observed to increase the lattice spacing in layered structures, as they occupy larger volume with increasing atomic radius and have longer M–O bond lengths, directly increasing the d-spacing [25]. The increase in the d-spacing could help reducing cation–cation repulsion on charge and discharge, allowing for enhanced capacity and rate performance. However, intercalating large species consequentially takes up space that could otherwise be used for charge carriers, potentially resulting in a reduced capacity. This may also inactivate previously active sites, as the favourability of large species in relative to charge carriers may be preferred [26]. The second attribute is the charge density of the species (centre part of Fig. 3). These can range from the commonly found monovalent ions (Na^+ and K^+), to divalent ions (Mg^{2+} and Ca^{2+}), trivalent ions (Al^{3+}, Ti^{3+} and Fe^{3+}) and charge-neutral species (anthraquinone and benzoquinone) [24, 27]. The species charge density and the associated hard–soft interactions with the host lattice polarise the local electronic environment to varying degrees, particularly for the higher

11

214 valance cations e.g., Fe^{3+}, Ti^{3+} and Al^{3+}, potentially resulting in enhanced

215 electron affinity of the redox active cations (Fig. 4) [28].

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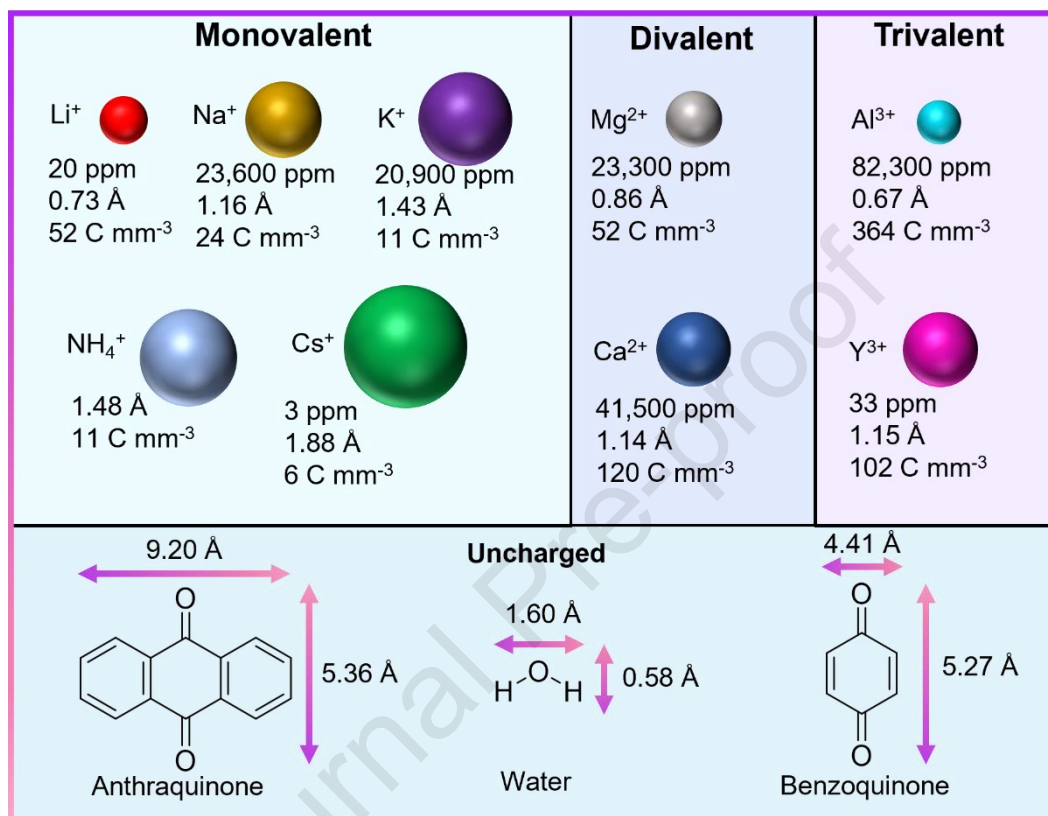
218 **Fig. 4.** Representation of the species covered in this review, including size, charge
219 density and crustal abundance (ppm) where applicable [9].

220

221 Furthermore, as the charge density of the pre-intercalated ions increases, the

222 electrostatic repulsion with the charge carriers increases. This can have either

223 positive or negative effects, depending on the level of pre-intercalation. With a

224 low level (<0.1 per formula), the increased electrostatic interaction has been

225 shown to be beneficial, with Sawangphruk *et al.* demonstrating that Zn^{2+} had a

226 reduced binding energy to the lattice in pre-intercalated δ-MnO$_2$ when the species

227 was the charge dense Al^{3+}, rather than Ca^{2+} or Na^+ [29]. However, when the pre-

228 intercalation level is high, these electrostatic repulsions may result in more

229 hindered diffusion and thus worsen rate performance [30].

230 The third attribute is the doping effect and orbital configuration of the pre-

231 intercalated species (right part of Fig. 3). Species like alkali metals, which only

232 have valence s orbitals, are not high enough in energy to mix with the d orbitals

233 of transition metals, likely adding no extra levels in the bandgap of the host

234 structure. However, they bring additional electrons into the host structure, acting

235 as n-type dopants [31]. For example, through angle-resolved photoemission

236 spectroscopy (ARPES), Takahashi *et al.* demonstrated that when Ca^{2+} was pre-

237 intercalated into graphite, there were significant downfield shifts in the C *2p* π

238 and σ bands, resulting in significantly enhanced charge transfer kinetics [32]. In

239 addition, through electrostatic and steric interactions they distort the surrounding

240 lattice, and even slight deviations caused by the distortion can result in dramatic

241 changes in the band structure, significantly improving conductivity relative to the

242 non-pre-intercalated structure [33]. However, other transition metals like

243 titanium and iron do have d orbitals available for such mixing, allowing for more

244 traditional doping and additional levels within the band structure to improve

245 electronic conductivity. Finally, the lability of the species must be considered

246 carefully. In general, the greater the interaction of the pre-intercalated species

247 with the surround host lattice, the higher the diffusion barriers are, and the less

248 labile the species is. This aspect of pre-intercalation is significantly

249 underdeveloped, but some general considerations can be made. While there are

13

250 a multitude of factors that determine a species bonding strength, it can be roughly

251 judged via the predicted bond length between the atoms in the host lattice and

252 the pre-intercalated species, as bond length is a reasonable proxy for bond

253 strength [34]. In many cases, it is a metal–oxygen bond that is formed, as many

254 of the examples are metal cations intercalating into oxygen containing lattices.

255 The stronger the metal–oxygen bond is, the less the likelihood of the species is

256 to be highly labile than the charge carrier is [25]. In addition, the larger the cation

257 is, the more oxygens it is able to interact with, further reducing its lability, which

258 is the root cause of many problems with KIBs and NIBs. However, in-depth

259 research is required in this aspect of pre-intercalation, as very little conclusive

260 evidence has been produced on the lability and effects of the de-intercalation of

261 these species after long term cycling.

262

263 **2.3 Pre-intercalated Hosts**

264 As vital as pre-intercalated species, the crystal and electronic structures of the

265 host lattice must be analysed carefully when pre-intercalation is considered. With

266 the vast number of crystal structures under investigation in the energy storage

267 literature, a comprehensive coverage would be near futile, but general themes

268 can undoubtedly be gleamed. The crystal structures can be generally categorised

269 into two types, layered and tunnelled.

270 Layered materials, in this context, are comprised of two-dimensional (2D) sheets

271 with space in between the sheets for charge carriers to intercalate into. These 2D

272 interlayer spaces allow intercalating ions to diffuse in a plane, speeding up

273 diffusion through the structure and reducing overpotential, despite some slight

274 preferential diffusion directions that have been observed in some materials [35].

275 The stacking arrangement of these sheets gives rise to the three most common

276 layered intercalation based active materials with the formula A_yMX_2 ($0 \leq y \leq 1$),

277 which are O1, O3 and P3 respectively [36]. These are so named for the octahedral

278 and prismatic sites that they contain, with significant differences in ion selectivity

279 between them. As the octahedral sites are larger, forming longer M–X bond

280 lengths with the intercalating charge carriers, these preferentially intercalate

281 larger cations, such as Na^+ and K^+ that are more able to fill the site and stabilise

282 the structure [36]. While the P-type structures can still intercalate the larger ions,

283 they are less favoured, resulting in reduced capacity. This expands upon the

284 structure–performance relationship of the material, as by modulating the

285 interlayer spacing via pre-intercalation, the volume of these sites can be altered,

286 improving their selectivity towards larger ions, thus improving their performance

287 (Fig. 5).

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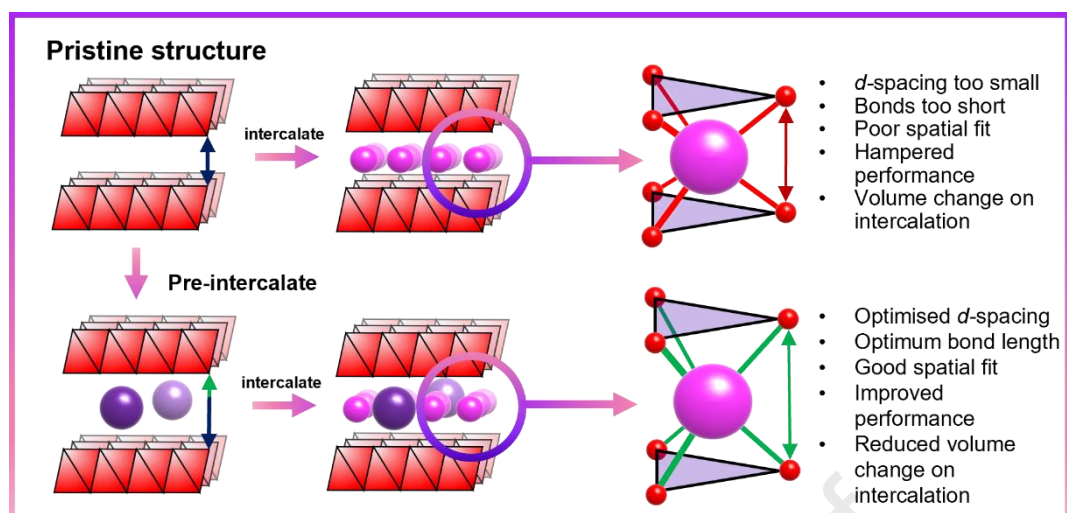
Fig. 5. Schematic displaying the effect of optimized d-spacing on the local environment of the charge carriers, resulting in enhanced electrochemical performance.

This logic extends to other layered materials such as α-V_2O_5 or $Na_2Ti_3O_7$. For tunnelled-type structures, the structure–performance relationship between the pre-intercalated species and host lattice is much harder to predict. The size of the channel is a significant limiting factor here, as pre-intercalating a species with greater interactions with the lattice than the charge carriers may block channels, effectively making the channel unusable for ion diffusion. However, it has been demonstrated that large channels such as those in α-MnO_2, can benefit pre-intercalation, as the ability of the pre-intercalated species to block channels is offset by the absolute size of the channel vs the size of the charge carriers [37]. The difference in applicability can be inferred from the most common structures for pre-intercalation, which are overwhelmingly layered type materials. There is a significant research deficiency in pre-intercalating tunnelled type structures, particularly spinel and NASICON structures. In one of the rare examples, Masquelier *et al.* described the electrochemical pre-intercalation of Na^+ into $Na_3FeV(PO_4)_3$ NASICON-type structure, but concluded that while initial cycles

16

306   were improved, the valence change of Fe^{3+} to Fe^{2+} to accommodate the pre-

307   intercalation resulted in significant capacity fading, as the reduction back to Fe^{2+}

308   was kinetically slow [22, 23]. Further studies into tunnelled structures would be

309   valuable additions to the pre-intercalation literature. While there is clearly

310   significant nuance and variation within these two groupings, most common

311   materials can be assigned to these two.

312

313   **Table 1:** Summary of pre-intercalated hosts covered, along with the pre-
314   intercalated ions and their effects.

Species	Material	Method	Structure type	Ion-battery	Δd (nm)	Stabilised performance	Ref
K^+/Na^+	C	Molten Salt	Soft Carbon	KIB	+0.018	325 mAh g^{-1} @ 100 mA g^{-1}	[44]
K^+	C	HEBM	Soft Carbon	KIB	–	302 mAh g^{-1} @ 50 mA g^{-1}	[46]
Na^+	δ-$Na_{0.36}V_2O_5$	Hydrothermal	Layered	NIB	+0.690	179 mAh g^{-1} @ 20 mA g^{-1}	[50]
K^+	δ-$K_{0.42}V_2O_5 \cdot nH_2O$	Hydrothermal	Layered	KIB	−0.185	167 mAh g^{-1} @ 20 mA g^{-1}	[53]
K^+	$K_{0.22}V_{1.74}O_{4.37}$ 0.82 H_2O	Precipitation	Layered	KIB	+0.350	183 mAh g^{-1} @ 5 mV s^{-1}	[54]
Na^+	$Na_{0.71}K_{0.29}MnO_2$	Hydrothermal	Layered	NIB	−0.04	130 mAh g^{-1} @ 1.5C	[41]
K^+	δ-$K_{0.42}MnO_2$	Precipitation	Layered	ZIB	increase	130 mAh g^{-1} @ 300 mA g^{-1}	[55]
$K^+/Na^+/Li^+$	$M_{0.7}Fe_{0.5}Mn_{0.5}O_2$	Precipitation	Layered	NIB	+0.221	181 mAh g^{-1} @ 100 mA g^{-1}	[56]
K^+	$K_{0.25}TiS_2$	Chemical Treatment	Layered	KIB	+0.193	135 mAh g^{-1} @ 24 mA g^{-1}	[60]
NH_4^+/K^+	$K_{0.5}V_2O_5$	Hydrothermal	Layered	KIB	+0.501	71 mAh g^{-1} @ 25 mA g^{-1}	[62]
H_2O	$V_2O_5 \cdot 0.6H_2O$	Hydrothermal	Layered	KIB	+0.888	103 mAh g^{-1} @ 50 mA g^{-1}	[63]
Y^{3+}	$Y_{0.06}V_2O_5$	Sol-gel	Layered	NIB	+0.25	119 mAh g^{-1} @ 100 mA g^{-1}	[30]
Al^{3+}	$H_{11}Al_2V_6O_{23.2}$	Hydrothermal	Layered	ZIB	+0.886	260 mAh g^{-1} @ 1 A g^{-1}	[64]
Al^{3+}	α-MnO_2	Hydrothermal	Tunnelled	ZIB	+0.05	401 mAh g^{-1} @ 100 mA g^{-1}	[37]
Al^{3+}, anthraquinone	V_2O_5	Hydrothermal	Layered	ZIB	+0.95	400 mAh g^{-1} @ 1 A g^{-1}	[24]
Al^{3+}, benzoquinone	V_2O_5	Hydrothermal	Layered	ZIB	+0.024	332 mAh g^{-1} @ 1 A g^{-1}	[27]
K^+	$Ti_3C_2T_x$ -MXene	Chemical Treatment	Layered	KIB	+0.02	70 mAh g^{-1} @ 1 A g^{-1}	[71]
Ca^{2+}	$CaV_8O_{20} \cdot 3H_2O$	Hydrothermal	Layered	NIB	+0.628	252 mAh g^{-1} @ 200 mA g^{-1}	[61]
K^+	TiS_2	Electrochemical	Layered	NIB	+0.122	124 mAh g^{-1} @ 5C	[73]
Cs^+/Na^+	$Na_{0.33}Cs_{0.03}V_2O_5$	Hydrothermal	Tunnelled	ZIB	+0.014	313 mAh g^{-1} @ 200 mA g^{-1}	[74]
Mg^{2+}/H_2O	$Mg_{0.3}V_2O_5$ 1.1H_2O	Hydrothermal	Layered	MIB	+0.12	164 mAh g^{-1} @ 100 mA g^{-1}	[75]
Na^+	$NaMnO_{2-y-\delta}(OH)_{2y}$	Hydrothermal	Layered	NIB	+0.18	137 mAh g^{-1} @ 10C	[82]
K^+	$K_{0.20}VS_4$	Electrochemical	Layered	MIB	increase	194 mAh g^{-1} @ 50 mA g^{-1}	[83]
Na^+	$Na_{0.33}V_2O_5$	Hydrothermal	Layered	ZIB	+0.374	341 mAh g^{-1} @ 100 mA g^{-1}	[84]
Na^+	$Na_3FeV(PO_4)_3$	Electrochemical	Tunnelled	NIB	increase	110 mAh g^{-1} @ C/20	[23]

315

316 **3. Effects of Pre-Intercalation**

317 **3.1 Activating Structural Sites**

318 Within the crystal structure of every intercalation-based active material, there are

319 active sites that can favourably accommodate the charge carrier ions. For

320 example, in O3 and P3 type layered metal oxides, these sites are the octahedral

321 and prismatic sites between the layers, respectively. By engineering the interlayer

322 spacing via pre-intercalation, the spatial volume of these sites can be increased

323 or decreased, optimising the site for improved interactions between the

324 intercalating charge carrier and the lattice. This concept is well applied in other

325 areas of research such as coordination chemistry, but is rarely applied in the

326 energy storage field [26]. As the size of the intercalating ion may be too large,

327 some sites may not be readily accessible or optimised for occupation, thus by

328 understanding this optimisation of spatial fit, the possible sites in a material may

329 be activated through enlarging or reducing their volume, thus improving

330 capacity.

331 In addition, common methods such as enhancing conductivity through carbon

332 coating or advanced electrolyte formulations will have no effect on the inherent

333 crystal structure of the material, thus providing no assistance to the activation or

334 optimisation of such active sites. Thus, pre-intercalation is ideally suited to

335 improve these inactive sites, as by pre-intercalating larger pillaring ions or

336 molecules, lattice spacing can be expanded, allowing for greater access to

337 favourable sites for charge storage [38, 39]. While this does occur during charge

338   and discharge, often the degree of volume change is very limited, <25%, whereas

339   pre-intercalation can produce dramatic d-spacing changes, up to 100% increases

340   [40, 41]. This can provide access to more active sites than is achieved through

341   the charge–discharge expansion and contraction. For active sites that are

342   oversized for the corresponding ion, interactions with the surrounding lattice can

343   improve the spatial fit of subsequent intercalating ions. By increasing the

344   distance between the layers of a material, the greater volume of free space there

345   is to store intercalating charge carriers, so an improvement to the specific

346   capacity of the pre-intercalated material is anticipated. This activation effect is

347   also more commonly seen in battery types that use cations with a larger radius,

348   such as Na^+ and K^+, as these cations are the most affected by the size of active

349   sites [42]. Smaller ions such as Li^+, Zn^{2+} and Mg^{2+}, are less sterically hindered

350   by the surrounding lattice, so pre-intercalation may not improve capacity to a

351   great extent, as there already exists adequate access to most of the active sites.

352   This is displayed in the number of recent reviews that display a focus on utilising

353   pre-intercalation to improve the specific capacity of a material, which are

354   primarily Na and K-based batteries [42, 43]. Due to the facile nature of pre-

355   intercalation, it can be applied to a wide variety of materials. Liu et al. utilised

356   pre-intercalation via a molten salt, a KCl/NaCl mix with a 1:1 molar ratio, which

357   was added to a mix of soft carbon, sulphur powder and urea to produce K^+

358   intercalated nitrogen and sulphur doped soft carbon (NSC) nanosheets for use as

359   an anode in KIBs [44]. The K content was estimated to be 1.23 at.%, by energy-

19

360 dispersive X-ray spectroscopy (EDS). As pre-intercalation content is an

361 important variable, further determination of K content via inductively coupled

362 plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron

363 spectroscopy (XPS), would be beneficial to fully emphasise the effect of pre-

364 intercalated K on performance. Transmission electron microscopy (TEM) results

365 revealed an interlayer distance of 0.378 nm, which was corroborated by X-ray

366 diffraction (XRD), whereas comparative literature values for non-potassiated

367 NSCs have been reported as 0.36 nm, a clear increase that can be clearly ascribed

368 to the pre-intercalated K^+ [45]. This increase was then demonstrated to increase

369 the capacity, as the pre-potassiated NSC averaged 325 mAh g^{-1} compared to an

370 average of 220 mAh g^{-1} for the non-pre-intercalated NSC, at the same rate of 100

371 mA g^{-1} over the first 10 cycles. Through density-functional theory (DFT)

372 calculations, the synergistic effect of K^+ pre-intercalation and heteroatom doping

373 were investigated, indicating that a combination of improved K-adsorption

374 energies, enlarged interlayer spacing and reduced migration barriers were the

375 reasons for the enhanced capacity and kinetics observed.

376 Further investigating carbon materials, pre-potassiated amorphized carbon black

377 (K-aCB) was investigated by Park *et al.* via high-energy ballmilling (HEM) with

378 metallic K, followed by the 500 °C annealing as an anode for KIBs [46]. The

379 level of pre-potassiation was only confirmed via electron energy loss

380 spectroscopy (EELS) and EDS. The interlayer spacing was observed to be

381 expanded. For performance, the K-aCB achieved a reversible capacity of 302

382   mAh g^{-1} over 200 cycles, as well as 337 mAh g^{-1} on the first discharge and 407

383   mAh g^{-1} on the first charge, corresponding to a 120.7% initial coulombic

384   efficiency. The aCB and CB showed a reversible capacity of 175 mAh g^{-1} and

385   74 mAh g^{-1}, respectively. With the amorphization control showing much lower

386   capacity, the increase in performance was ascribed to the pre-potassiation

387   reducing irreversible reactions common in the first cycle. However, due to the

388   partially amorphous nature of the carbon, any graphitic regions remaining would

389   have been expanded due to the pre-intercalation of K$^+$, allowing for greater

390   access to those sites, thus further increasing the capacity.

391   Utilizing pre-intercalation to boost access to active sites is not only limited to

392   carbonaceous materials, with layered vanadium oxides being a common subject

393   of pre-intercalation investigation. Vanadium oxides have been the subject of

394   intensive research for decades. Since the first successful demonstration in NIBs

395   in 2011, many avenues have been explored to improve the performance in line

396   with LIB benchmarks, such as phase optimization, nanostructural control, doping

397   and carbon coating [47-49]. Even with the success of these methods, pre-

398   intercalation stands out as a major factor in the improvement of vanadium oxides

399   as a cathode material for NIBs and KIBs. Pomerantseva *et al.*, utilising previous

400   work for LIBs, reported a chemically pre-intercalated δ-V$_2$O$_5$ as a cathode for

401   NIBs [50]. By optimising the aging times for the chemical pre-intercalation to

402   occur, a maximum ratio of Na:V of 0.36 was observed in a pure bilayered δ-

403   Na$_x$V$_2$O$_5$ phase, with a large interlayer spacing of 11.4 Å. This phase

21

404 rearrangement, from orthorhombic α-V_2O_5 to δ-$Na_xV_2O_5$, along with the

405 corresponding interlayer spacing increase, from 4.5 Å to 11.4 Å, provided far

406 greater access to the redox active sites for the intercalating Na^+ ions, which was

407 reflected in the capacity. The optimised δ-$Na_xV_2O_5$ achieved a 365 mAh g^{-1} first

408 discharge and a ~320 mAh g^{-1} 2nd charge, significantly larger than previous

409 capacities for vanadium oxides [47, 51, 52]. However, this capacity was poorly

410 retained, with it dropping to 179 mAh g^{-1} after 30 cycles, with no longer term

411 cycling characterisation performed, indicating that possibly the performance

412 continued to decrease on cycling. Pomerantseva *et al.* went on to repeat this work

413 for KIBs, demonstrating a potassiation of δ-$K_{0.42}V_2O_5$·nH_2O, with an interlayer

414 distance of 9.65 Å [53]. This is a reduction from pristine δ-V_2O_5, at 11.5 Å, which

415 was ascribed to a lower water content, with only 1 row of water molecules in the

416 interlayer spacing, rather than the usual 2 for other alkali metals. This is an

417 example of interlayer optimisation, as interactions with the pre-intercalated

418 species reduced the interlayer spacing, improving interactions for subsequently

419 intercalated species. This δ-$K_{0.42}V_2O_5$·nH_2O displayed a 1st discharge of 268

420 mAh g^{-1} with good stability, retaining 74% when cycling at 20 mA g^{-1}.

421 Analysing the structure–performance relationship demonstrates that reduction in

422 interlayer spacing can also improve performance, indicating that interlayer

423 spacing optimisation is more important to improvements in capacity, rather than

424 absolute size. In general, if the interlayer spacing is initially small, pre-

425 intercalation of larger species can expand the structure and provide more volume

22

426   for the charge carriers to occupy sites, thus activating them, while weakening

427   coulombic interactions with the negatively charged layers. If the *d*-spacing is

428   already very large, pre-intercalated species can contract the layers, shortening the

429   distance between the layers and stabilising the charge carriers.

430   Teng *et al.* demonstrated the improvement that pre-intercalated interlayer water

431   can have on amorphous materials in aqueous KIBs, with the disordered

432    $K_{0.22}V_{1.74}O_{4.37} \cdot 0.82\ H_2O$ out performing commercial V_2O_5, achieving 183 mAh

433   g^{-1} and ~43 mAh g^{-1} respectively [54]. This was ascribed to the pre-intercalated

434   water molecules interacting with the $[VO_6]$ octahdedra and inducing local

435   structural rearrangements, along with structural distortions caused by the K^+ ions.

436   A synergistic effect between the pre-intercalated water and K^+ was posited, that

437   the disordered structure allowed for a wider potential window for K^+

438   intercalation, improving storage. However, it is possible that the local

439   deformations caused by the pre-intercalated K^+, further stabilised by the water

440   molecules, also contributed to the increase in capacity.

441   Manganese oxide materials have also been demonstrated to show improvements

442   to capacity with pre-intercalation, with Shao *et al.* utilising pre-intercalation to

443   improve the capacity of Birnessite-type (A_xMnO_{2+y}) materials in NIBs [41].

444   Commonly, only one metal cation is intercalated into Birnessite-type manganese

445   oxides, but for this work, both Na^+ and K^+ were pre-intercalated. This has the

446   synergistic effect of reducing the amount of cations lost via irreversible

447   processes, as well as utilising the K^+ ions to provide adequate access to the active

448   sites. The 15:1 Na:K sample showed an improved discharge capacity of ~130

449   mAh g^{-1} when compared to the $KMnO_2$ that achieved ~80 mAh g^{-1}. However,

450   this effect was lost when the ratio of K^+ in the synthesis was reduced above 22.5:1

451   Na:K. This smaller interplanar spacing would reduce the availability of active

452   sites for the Na^+ ions, which had previously been kept available by the K^+ ions,

453   which would explain the decrease in performance. This effect was also observed

454   by Yu et al. using alkali ion pre-intercalated δ-MnO_2 in ZIBs, as the $K_{0.42}MnO_2$

455   out-performed the $Na_{0.43}MnO_2$ and $Li_{0.52}MnO_2$, in capacity, rate performance and

456   cycling stability and was attributed to the greater structural integrity the larger

457   K^+ provided [55]. The structure-performance relationship between the host and

458   the pre-intercalated species can be clearly indicated via the larger K^+ ions

459   expanding the interlayer spacing, increasing the volume of the active sites and

460   improving the capacity, despite also taking up more volume concurrently. The

461   lower charge density of the K^+ also results in less electrostatic repulsion, thus

462   enabling to store more Zn^{2+} in the available volume.

463
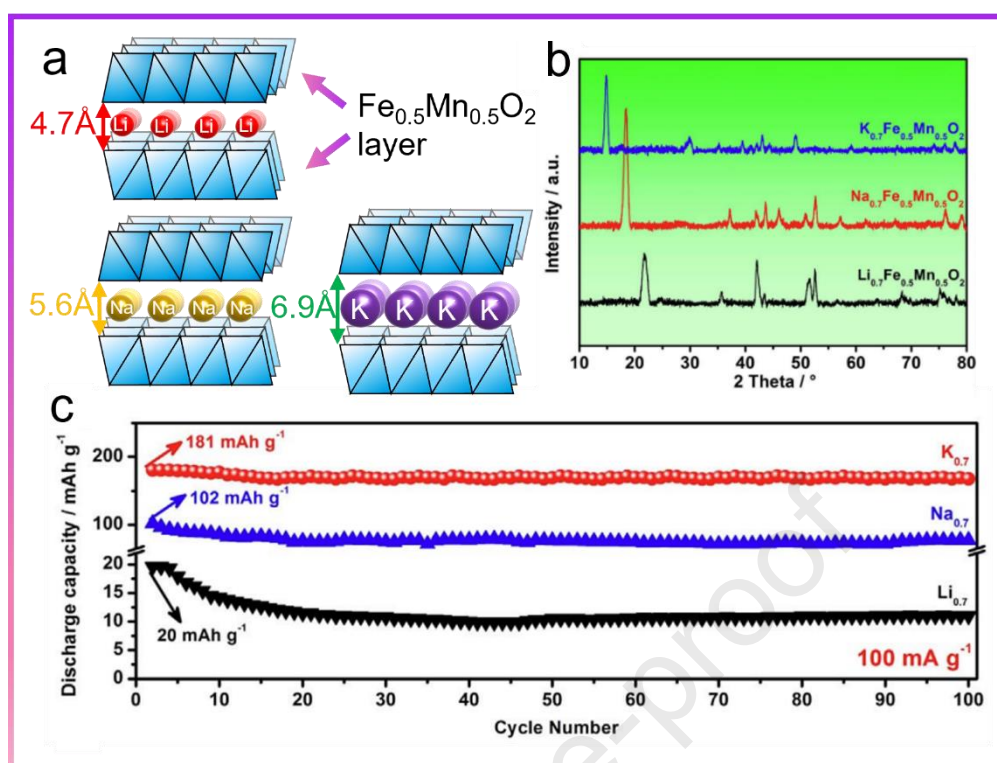
Fig. 6. (a) Schematic displaying the effects of varying the size of the pre-intercalated alkali ion on the *d*-spacing of crystal structure. (b) XRD patterns of iron manganese oxides pre-intercalated with various alkali metal ions, from K^+ to Li^+. (c) cycling performance of the pre-intercalated iron manganese oxides, at 100 mA g^{-1}. Reproduced with permission from Ref. [56]. Copyright © 2017 Elsevier Ltd.

Mai *et al.* reported a K^+ ion pre-intercalated iron-manganese oxide, $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ for NIBs [56]. They investigated the electrochemical performance of $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$, $Na_{0.7}Fe_{0.5}Mn_{0.5}O_2$ and $Li_{0.7}Fe_{0.5}Mn_{0.5}O_2$ (Figs. 6a and b) with each sample also being carbon coated. There was a stark difference between samples, with the Li^+ pre-intercalated sample producing 20 mAh g^{-1} of capacity on discharge at 100 mA g^{-1}, in comparison to the Na^+ and K^+ containing samples, that achieved 102 and 181 mAh g^{-1} respectively, at the same current density (Fig. 6c). Over 100 cycles this capacity was retained by 93%, 76% and 56% for the K, Na and Li containing material respectively. The K-containing

25

481   version also exhibited the highest interlayer spacing, at 6.94 Å, and the lowest

482   R_{ct} of the tested samples. This again reinforces both the structure-performance

483   relationship and the host-guest relationship, as widening the *d*-spacing results in

484   the increased volume of the active sites and thus increased capacity, despite

485   larger K^+ occupying more space than Na^+ or Li^+.

486   Pre-intercalation has been demonstrated to be an effective way to improve the

487   capacity of electrode materials in NIBs, KIBs and aqueous KIBs. The primary

488   mechanism by which pre-intercalation was observed to improved capacity was

489   generally through the expansion of the interlayer spacing. This allows for more

490   species to be incorporated into the structure, as the electrostatic repulsion

491   between the charge carriers could be reduced with increasing distance between

492   them. Exceptions to this rule were covered but were limited to vanadium

493   materials with exceptionally large *d*-spacings [54]. The type of species appears

494   to be an essential factor, as the species needs to be large enough to adequately

495   expand the interlayer spacing to optimise for further ion intercalation. However,

496   pre-intercalating too many species can have detrimental effects, as the larger pre-

497   intercalated species can block active sites if in excess, as seen with $KMnO_2$, so

498   optimisation is required. The primary beneficiaries of this effect are layered-type

499   materials, as Na^+ and K^+ can struggle to diffuse into the layers if they are not

500   sufficiently widened.

501

502   **3.2 Pillaring to Reduce Lattice Expansion and Contraction**

26

503   The pillaring effect of pre-intercalated species in layered structures is one of the

504   most beneficial and most studied effects of pre-intercalation [57]. The pre-

505   intercalating species fills the sites between the layers, holding the layers at a more

506   optimum distance for further ion intercalation, reducing expansion and

507   contraction of the lattice, which consequently minimises pulverisation of the

508   electrode and improves stability. Although this reduces the volumetric energy

509   density slightly, the improvement to the stability often outweighs the reduction

510   of volumetric energy density. The pillaring effect can expand or contract the

511   interlayer spacing, as discussed previously, as the d-spacing can decrease if the

512   intercalated species is positive, shielding the two negative layers more effectively

513   from each other. This pre-intercalation effect is vitally important in the post-LIB

514   types, as poor cycling stability is an almost ubiquitous problem, as the larger

515   sizes or larger charges of the cations vs Li^+ induce larger volume changes on

516   intercalation and deintercalation. Metal sulphides, in particular TiS_2, were some

517   of the first materials examined for use in LIBs, but have struggled to gain traction

518   commercially [58, 59]. This is because despite high capacity, TiS_2 is marred by

519   complex phase transitions, disproportionation reactions and sulphide shuttling,

520   which rapidly degrade battery performance on cycling [60]. Loh *et al.*

521   investigated TiS_2 as a cathode for KIBs by pre-potassiating it to form $K_{0.25}TiS_2$

522   (Fig. 7a) [60]. This was demonstrated to have improved cycling performance

523   than bulk TiS_2, retaining ~135 mAh g^{-1} after 120 cycles at 24 mA g^{-1}, compared

524   to ~80 mAh g^{-1} from the TiS_2. This was investigated via *in-situ* XRD, with an

525   unstable buffer phase observed when K content is between 0.1 and 0.25. This

526   buffer phase (2^k) is irreversible upon charging, being unable to be charged back

527   to TiS_2 and resulting in significant K^+ loss upon formation. By forming a phase

528   with a higher K content of 0.25 per formula chemically, the associated structural

529   deformation from pristine TiS_2 to the buffer phase is bypassed and much less K^+

530   is removed from the system, demonstrated by a lower irreversible initial

531   discharge capacity and a higher ICE (Figs. 7b and c). This phenomenon is likely

532   to occur in many other material, as irreversible phase transformations are very

533   common sources of initial capacity loss, but is rarely investigated in depth,

534   indicating a fruitful area of further research [61]. Vanadium oxides, while

535   concretely demonstrated to show higher capacity capability with pre-

536   intercalation, also show improved stability by pillaring the pre-intercalated ions

537   between the layers. The relationship between the size of interlayer spacing and

538   the performance has already been analysed, with a clear trend that optimisation

539   is better than absolute distance, but this had yet to be demonstrated from a

540   stability perspective. To investigate the pillaring effect on the stability of

541   vanadium oxides, Zhang *et al.* compared the stability of several pre-intercalated

542   vanadium oxides, $NH_4V_3O_8$, $(NH_4)_{0.5}V_2O_5$ and $K_{0.5}V_2O_5$ for KIB cathodes [62].
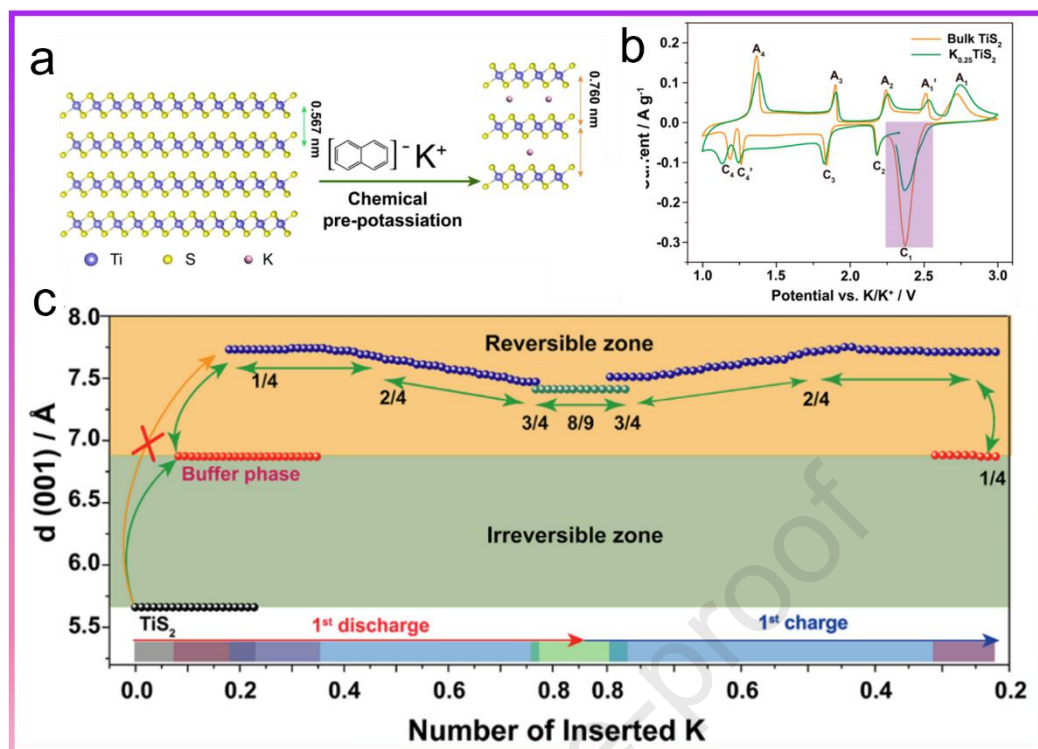
Fig. 7. (a) Schematic displaying the pre-intercalation of K^+ into the TiS_2 layers. (b) CV curves of TiS_2 and $K_{0.25}TiS_2$ demonstrating a skipping of C_1 on first discharge. (c) Schematic displaying the SOC versus the *d*-spacing of the (001) reflection, with irreversible phases indicated. Reproduced with permission from Ref. [60]. Copyright © 2017, American Chemical Society.

These were observed to have an interlayer spacing of 7.78 Å, 9.56 Å and 9.37 Å respectively, compared to 4.36 Å for the V_2O_5 control. Despite the presence of hydrogen bonding between the NH_4^+ and V-O layers, the stability of both $NH_4V_3O_8$ and $(NH_4)_{0.5}V_2O_5$ was far worse than the K^+ pre-intercalated $K_{0.5}V_2O_5$, as they achieved a capacity retention of 20.2 and 59.1% respectively, to the 83.5% the $K_{0.5}V_2O_5$ achieved. This result was attributed to layer collapse and irreversible structural destruction caused by the de-intercalation of the larger NH_4^+. This is a clear example of one of the major problems pre-intercalation faces, the retention of the pillaring species. If the pillaring species is too labile, it

559 can de-intercalate on cycling, causing both the pillaring effect to be reduced and

560 because it is often larger than the charge carrier ions, it causes more structural

561 damage than the charge carriers, leading to worse cycling stability. This is a

562 particular problem with water intercalated materials, as during cycling the

563 crystalline water can be de-intercalated into the electrolyte and undergo

564 electrolysis, which forms species that catalyse electrolyte breakdown and

565 severely reduce battery performance. This was observed for $V_2O_5 \cdot 0.6\ H_2O$ in

566 KIBs by Li *et al.*, that used pre-intercalated water to stabilise the interlayer space

567 of the V_2O_5 sheets [63]. The discharge capacity dropped from 225 mAh g^{-1} to

568 ~100 mAh g^{-1} over 50 cycles, only to rise back up to ~175 mAh g^{-1} by 250 cycles.

569 This inconsistent capacity was attributed to the water de-intercalating, increasing

570 side reactions and possibly forming KOH, but also making space for further K$^+$

571 intercalation. One strategy to stabilise these structural waters, while retaining

572 their layer widening effect, is to co-intercalate another pillaring ion. Cao *et al.*

573 demonstrated this in NIBs by pre-intercalating a Y^{3+} ion into hydrated V_2O_5 to

574 form $Y_{0.02}V_2O_5$ and $Y_{0.06}V_2O_5$ [30]. The Y^{3+} was observed to coordinate to the

575 structural oxygen and the crystalline water to form [YO$_6$] octahedra, increasing

576 the interlayer spacing from 11.78 Å to 12.03 Å and 12.22 Å for V_2O_5, $Y_{0.02}V_2O_5$

577 and $Y_{0.06}V_2O_5$ respectively. This is an excellent example of the pillaring effect,

578 as ideally, the pillaring species should be kept as minimal as possible, as too

579 many pre-intercalated species can start to block active sites that can be used by

580 the charge carriers. This is what was observed for the increasing amount of Y^{3+},

30

581 as $Y_{0.02}V_2O_5$ and $Y_{0.06}V_2O_5$ were cycled for 100 cycles and retained 119 and 95

582 mAh g^{-1} respectively, showing greater stability than the control V_2O_5 that

583 retained 84 mAh g^{-1}. The pre-intercalated $Y_xV_2O_5$ are also noticeably more

584 consistent in cycling performance, likely due to the stabilisation of the water

585 molecules by the Y^{3+}. The improvement shown by $Y_{0.02}V_2O_5$ can be attributed

586 clearly to the pre-intercalated Y^{3+} stabilising the lattice structure and preventing

587 irreversible phase transitions that maar pristine V_2O_5. The pre-intercalation of

588 Al^{3+} is another popular method for stabilizing the V_2O_5 structure, forming

589 hydrogen aluminium vanadium oxide (HAVO). By altering the amount of Al^{3+}

590 in between the VO layers, Mai *et al.* demonstrated for aqueous ZIBs that there is

591 indeed a concentration dependent relationship for pre-intercalated ions [64].

592 When the mass ratio of Al:V was 1:16 or above 1:20, cycling performance and

593 capacity were reduced. However, at 1:18, excellent stability and capacity were

594 observed, retaining 252.9 mAh g^{-1} after 3000 cycles at 1 A g^{-1}. This was

595 supported by XRD analysis of the charge-discharge cycles, where minimal peak

596 shifts or new peaks were observed in either *ex-situ* or *in-situ* XRD. The (001)

597 peak shifted slightly to a higher 2θ angle, but the change was minimal. This is in

598 sharp contrast to other *in-situ* work on un-pre-intercalated work, that observed

599 both peak shifts, indicating lattice parameter shifts via intercalation, and new

600 peaks appearing, indicating phase changes [65]. This superb structural stability

601 and good capacity retention on cycling indicate that Al^{3+} can pillar effectively in

602 V_2O_5, but also that over pre-intercalating can have detrimental effects to both

31

capacity and cycling stability. It was posited that a high Al:V ratio blocked

channels in the structure, reducing diffusion more than the expansion of the

interlayer spacing helped diffusion, thus requiring a balance.

Tunnel-type manganese dioxides are well known to suffer from significant

capacity fading in ZIBs, due to phase transitions during Zn^{2+} insertion, collapsing

the structure and inactivation of the tunnels, in addition to the Jahn–Teller effect

of Mn^{3+} bringing additional structural distortion. To remain active, these tunnels

require stabilisation. Pre-intercalation is well suited for this, as the pre-

intercalating metal cations can stabilise the tunnels via the strong MO bonds that

they form, along with providing doping energy levels, enhancing electronic

conductivity. Yan *et al.* described Al^{3+} pre-intercalation to stabilise α-MnO_2 as a

cathode for ZIBs [37]. By observing a shift in the (211) plane to lower angles

after pre-intercalation, it was concluded that the Al^{3+} intercalated into the tunnels,

expanding them through multiple M–O bonds. DFT calculations suggested that

the pre-intercalated Al^{3+} resulted in Mn^{4+} reduction, lengthening the Mn–O bond,

resulting in a wider and thus more favourable channels for Zn^{2+} diffusion. This

was observed experimentally as Mn satellite peaks were present in the XPS

spectra. The Al^{3+} was also observed to prevent the dissolution of manganese into

the electrolyte, a common problem with manganese-based materials, as the

stronger Al–O–Mn bonds stabilised the structure [24]. The stabilisation of Al^{3+}

is further demonstrated by Lin *et al.* who synthesised V_2O_5 with a dual pre-

intercalation strategy using benzoquinone and Al^{3+} for ZIBs [27]. With the

32

625 benzoquinone alone, the stability was adequate, dropping by around 30% over

626 500 cycles. However, with the addition of electrochemically pre-intercalated

627 Al^{3+}, the retained capacity is nearly 100%, which was attributed to the Al^{3+}

628 insertion stabilising the V_2O_5 structure. In addition, the co-intercalation of Al^{3+}

629 was observed to suppress formation of $Zn_3(OH)_2V_2O_7 \cdot 2H_2O$, which appears as

630 rose-like nanosheets and is thought to reduced cyclability, so by supressing this

631 phase, improvements to cyclability were observed. The strong Al–O–M bonds

632 prevent local structural deformations, reducing phase transitions. As mentioned

633 previously, this effect is a valuable area of further study.

634 Overall, pre-intercalation is well proven within the literature to efficiently

635 improve cycling performance by limiting structural deformation and preventing

636 phase changes via the pillaring effect. By pre-intercalating a larger species than

637 the charge carriers, the lattice can be stabilised and its expansion and contraction

638 on intercalation/de-intercalation can be reduced, sometimes even eliminated.

639 However, restraint must be used when using pre-intercalation in this manner, as

640 commonly observed is that excessive pre-intercalation can have adverse effects

641 on both stability and capacity, either by occupying active sites that charge carriers

642 could occupy, or by blocking channels that they would use to diffuse through the

643 structure. In addition, to pillar effectively, the pre-intercalated species should be

644 as minimally labile in the structure as possible, as it can contaminate and poison

645 the electrolyte, increase side reactions or damaging the electrode structure when

de-intercalating. Pre-intercalation is an excellent strategy for improving the

cycling performance of materials.

3.3 Widening and Activation of Ionic Diffusion Channels

One of the most industrially important parameters is a materials rate performance. Fast charging has been deemed a key metric by the United States Advanced Battery Consortium (USABC), setting a 80% SOC within 15 mins goal for 2025 [66]. The largest roadblock to this target is the diffusion of ions within an active material in a short timeframe. The ionic conductivity of common carbonate electrolytes range from 3.1 to 36.7 mS cm^{-1}, whereas ion diffusion coefficients in materials is often $\sim$x10^{-12} m^2 s^{-1}, suggesting ionic diffusion in the material is the limiting factor [67]. Pre-intercalation can help alleviate this discrepancy, by increasing the distance between the layers, not only is more space provided to the charge carriers, but the coulombic interactions with the negatively charged layers is also reduced as the interaction decreases with the square of the distance, as per coulombs law. The improved ionic diffusion is commonly measured through two methods. Electrochemical impedance spectroscopy (EIS) allows for the direct measurement of the diffusion coefficient of ions through the analysis of the Warburg diffusion [68]. While less direct than EIS, rate performance is another valuable measurement method for ionic diffusion. As the ionic diffusion is the limiting factor, improvement to it will be most pronounced at higher rates. Titanium MXenes are an excellent candidate for high-rate electrode materials [69]. Their high electronic and ionic

668   conductivity compared to metal oxides allows for facile transport of ions and

669   electrons. They can be further improved via pre-intercalation, as molybdenum

670   has been pre-intercalated into titanium MXenes for LIBs, showing a significant

671   rate performance increase [70]. Wang *et al.* pre-intercalated K^+ into $Ti_3C_2T_x$ to

672   form K^+-$Ti_3C_2T_x$, as a high rate K-ion hybrid capacitor [71]. The rate

673   performance was significantly improved, retaining 40.3 mAh g^{-1} at 5 A g^{-1},

674   compared to the controls (Fig. 8d). This was attributed to the larger interlayer

675   distance, which from XRD was expanded from 12.9 Å to 13.2 Å (Fig. 8a–c),

676   which allowed for the faster diffusion of ions through the 3D structure. An

677   additional benefit was that the pillaring K^+ ions also prevented significant

678   restacking of the MXene sheets, a common issue with exfoliated layered

679   materials [72].

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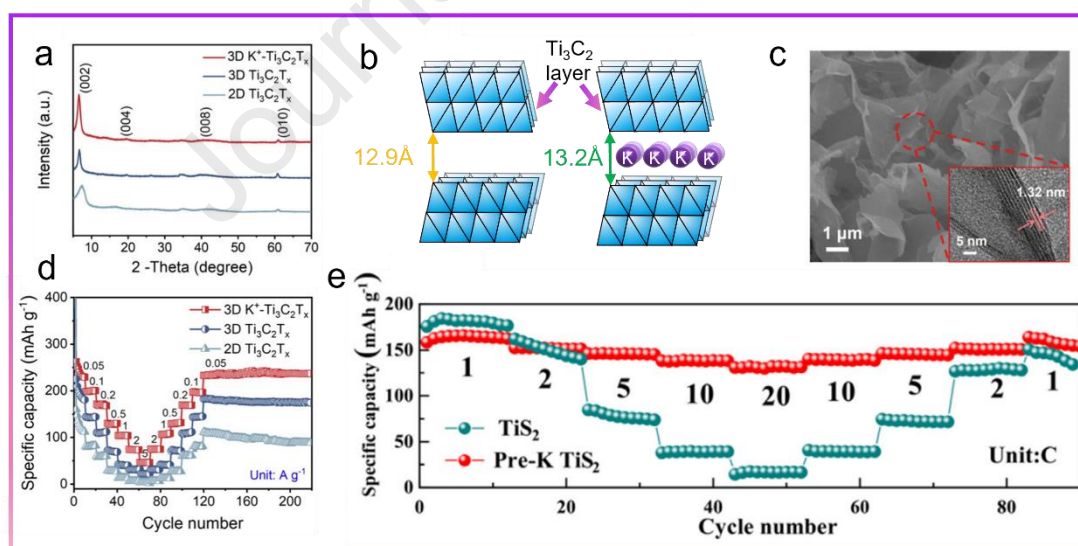
681 **Fig. 8.** (a) XRD patterns of $Ti_3C_2T_x$, crumpled $Ti_3C_2T_x$ and K^+-$Ti_3C_2T_x$. (b)
682 Schematic representing the effects of pre-intercalating K^+ in the interlayer
683 spacing. (c) TEM image displaying the (002) plane. (d) The rate performance of
684 $Ti_3C_2T_x$, crumpled $Ti_3C_2T_x$ and K^+-$Ti_3C_2T_x$ from 50 mA g^{-1} to 5 A g^{-1}.
685 Reproduced with permission from Ref. [71]. Copyright © 2021 Wiley-VCH
686 GmbH. (e) Rate performance of TiS_2 and pre-intercalated K-TiS_2 from 1C to
687 20C. Reproduced with permission from Ref. [73]. Copyright © 2022 Published

688 by Elsevier Ltd on behalf of the editorial office of Journal of Materials Science
689 & Technology.

690 In addition to improved capacity and cycling stability, vanadium oxides also

691 show improved rate performance with upon pre-intercalation. Shao *et al.*

692 reported carbon-coated calcium pre-intercalated V_2O_5 ($Ca_{0.34}V_2O_5$) nanoribbons

693 as an anode for NIBs [61]. The calcium ions were shown via XRD and Rietveld

694 refinement to be pillaring between the VO layers, expanding the interlayer

695 spacing to 10.68 Å and stabilising the crystalline water. The $Ca_{0.34}V_2O_5$ and

696 carbon coated variation showed improved rate performance over other reported

697 values for V_2O_5. Interestingly, there was observed to be a phase change during

698 the initial charge and discharge, with the Ca^{2+} stabilising a metastable

699 intermediary structure, resulting in final structure that can reversibly store Na^+

700 without reverting to its initial state. Without the calcium pillaring and stabilising

701 the intermediary phase, the structure would collapse and result in large

702 irreversible capacity. Another promising material for fast rate charging in NIBs

703 is TiS_2, but as before regarding the stability, its rate performance is also hampered

704 by the large ionic radii of the post-Li ions. To address this, Shu *et al.*

705 electrochemically pre-intercalated K^+ into commercial TiS_2, expanding the

706 interlayer spacing from 5.72 Å to 6.94 Å [73]. This expanded interlayer spacing

707 translated into a hugely improved rate performance in NIBs for the K-TiS_2,

708 achieving 132.1 mAh g^{-1} at 20 C, whereas the commercial TiS_2 only achieved

709 16.4 mAh g^{-1} (Fig. 8e). In addition, the diffusion coefficient was estimated via

710 galvanostatic intermittent titration technique (GITT) during charge and

36

discharge, showing that the D_{Na^+} for the K-TiS$_2$ was consistently higher than

TiS$_2$, 10^{-7}–10^{-12} for K-TiS$_2$ and 10^{-9}–10^{-13} for TiS$_2$. Although ICP-OES was said

to be performed, no quantification of K content was contained, most likely due

to the electrochemical synthesis method also intercalating K$^+$ into the

surrounding conductive carbon, making quantification challenging. However,

EDS was performed on samples after 500 cycles, with the result indicating that

the K$^+$ remained in the structure, pillaring effectively without deintercalating

during cycling. The effect of pre-intercalation on rate performance was also

demonstrated in ZIBs with a dual pre-intercalation of Cs$^+$ and Na$^+$ by Zhang *et

al.* into V$_2$O$_5$, forming monoclinic Na$_{0.33}$V$_2$O$_5$ and Na$_{0.33}$Cs$_{0.03}$V$_2$O$_5$ [74]. These

both display layered structures that have 1D tunnels for intercalation of charge

carriers, providing an interesting case of the effect of pre-intercalation on

tunnelled structures, rather than purely layered. The inclusion of Cs$^+$ in the

structure, was observed to expand the interlayer spacing of the (100) plane to

9.481 Å, from 9.342 Å with Na$_{0.33}$V$_2$O$_5$, increasing the size of the tunnels. This

was observed to improve rate performance, where the Na$_{0.33}$Cs$_{0.03}$V$_2$O$_5$

outperformed the Na$_{0.33}$V$_2$O$_5$ by retaining 46.1% of the capacity at 5 A g^{-1} that it

achieved at 0.1 A g^{-1} (376.5 mAh g^{-1}), vs only 21.8% for Na$_{0.33}$V$_2$O$_5$. Zhang *et

al.* also performed GITT to investigate the diffusion coefficient of Zn^{2+} within

the structures, which was observed to be superior with pre-intercalated Cs$^+$ at all

SOC, varying from ~5×10^{-10} to ~1×10^{-10} cm^2 s^{-1}. As the structure is not the

typical layered type, with instead channels for ion diffusion, it is interesting that

733   the pre-intercalation of the larger cation did not result in significant channel

734   blockages, which would significantly reduce capacity and rate performance,

735   particularly as larger cations are inherently less labile. Lastly, Mai *et al.*

736   demonstrated the performance of hydrated pre-magnesiated vanadium oxide,

737    $Mg_{0.3}V_2O_5 \cdot 1.1\,H_2O$ in MIBs, comparing it to the hydrated V_2O_5 and un-hydrated

738    $Mg_{0.3}V_2O_5$ [75]. Without interstitial H_2O, the $Mg_{0.3}V_2O_5$ exhibited the smallest

739   interlayer spacing and did not exhibit a bi-layered structure, leading to

740   significantly impaired capacity and rate performance. However, a synergistic

741   effect was observed with magnesium and water pre-intercalation, with it

742   exhibiting a rate performance of retaining 80% of the initial capacity at 2 A g^{-1},

743   85 mAh g^{-1}, compared to ~30 mAh g^{-1} for hydrated V_2O_5 and ~20 mAh g^{-1} for

744    $Mg_{0.3}V_2O_5$. The additional stabilisation of the pillaring Mg^{2+}, combined with the

745   water expanding the interlayer spacing to sufficiently accommodate the

746   intercalating Mg^{2+} was the hypothesised reason for the improved rate

747   performance. In summary, pre-intercalation is well suited to improve rate

748   performance, as by pre-intercalating pillaring species, the *d*-spacing can be

749   optimised to allow for the fastest diffusion of ions. By holding the layers apart at

750   most commonly a larger *d*-spacing, the interactions of the intercalation ions with

751   the lattice can be reduced, thus speeding up their diffusion throughout the

752   structure. Counter examples do exist, where a reduction in lattice spacing

753   increases the rate, but these are structures with already large absolute *d*-spacings,

754   indicating optimisation is more important than absolute distance.

755

3.4 Introduction of Dopants

The electronic conductivity of transition metal oxide electrode materials is often

poor, as the weakly held valence electrons that formed the conduction band of

the metal centres have now been covalently bonded with the oxygen groups,

preventing electron delocalisation and thus reduced conductivity [76].

Commonly, the conductivity of metal oxides in the energy storage literature is

improved extrinsically, specifically through carbon coating [77]. This can greatly

improve the rate performance and capacity of the material but results in a greater

percentage of carbon in the electrode, leading to a thick SEI formation and poor

cycling performance [78, 79]. By altering a material's inherent conductivity, rate

performance and potential capacity can be further improved. This can be

achieved via pre-intercalation, as by pre-intercalating charged species, some of

the metal centres are reduced, resulting in additional levels in the band-gap,

allowing for the promotion of electrons and the creation of charge carrying holes

or electrons in the valence band or conduction band respectively [80]. While this

process would occur eventually with the intercalation of charge carriers during

cycling, by tuning the pre-intercalation level, the number of additional doping

levels provided by the pre-intercalated species can also be increased. In addition,

the introduction of additional species in the interlayer spacing can result in n-

type doping, where the additional electrons from the pre-intercalated species can

be donated to the structure, resulting in enhanced electronic conductivity. Direct

777   measures of electronic conductivity are rare but can be estimated from a direct

778   relationship to the charge transfer resistance (R_{ct}) of EIS measurements [81].

779   Meng *et al.* reported Na^+ pre-intercalated Birnessite and monoclinic manganese

780   oxides for NIBs, which provided an excellent example of the level of pre-

781   intercalation effecting the conductivity of the material [82]. The measured R_{ct} of

782     $Na_{0.46}MnO_{2-y}(OH)_{2y} \cdot 0.61$ H_2O, $Na_{0.71}MnO_{2-y}(OH)_{2y} \cdot 0.32$ H_2O and $NaMnO_{2-}$

783     $_y(OH)_{2y} \cdot 0.10$ H_2O was improved with the increasing Na^+ pre-intercalation, from

784   ~ 225 Ω to ~ 150 Ω (Fig. 9a). This was then carried over into the performance,

785   with the monoclinic $NaMnO_{2-y}(OH)_{2y} \cdot 0.10$ H_2O, denoted as S3, outperforming

786   the both the other samples in both capacity and rate performance (Fig. 9b). The

787   final sample (S4) included oxygen vacancies, which was the ascribed reason for

788   the improved electronic conductivity. However, the other samples showed

789   increasing electronic conductivity without the vacancies, so much of the

790   improved electronic conductivity must have come from the level of pre-

791   intercalated Na^+, but requires further work and direct conductivity measurements

792   to confirm. Meng *et al.* continued utilising this effect to improve the electronic

793   conductivity of VS_4/ nitrogen doped tubular graphene (N-TG), by

794   electrochemically pre-intercalating K^+ into the layers [83]. Observed was a

795   significant reduction in the internal resistance compared to pristine VS_4/N-TG,

796   with an average resistance of 8 Ω vs 15 Ω (Fig. 9d). As the internal resistance

797   includes charge transfer resistance, it was concluded that pre-intercalated K^+

798   improved the electronic conductivity of the VS_4. The effect of increasing a pre-

40

799 intercalated species was further investigated by Cao *et al.* using the

800 aforementioned $Y_xV_2O_5$, where they investigated the R_{ct} of V_2O_5 with varying

801 degrees of Y pre-intercalation for NIBs (Fig. 9c) [30].

802

803
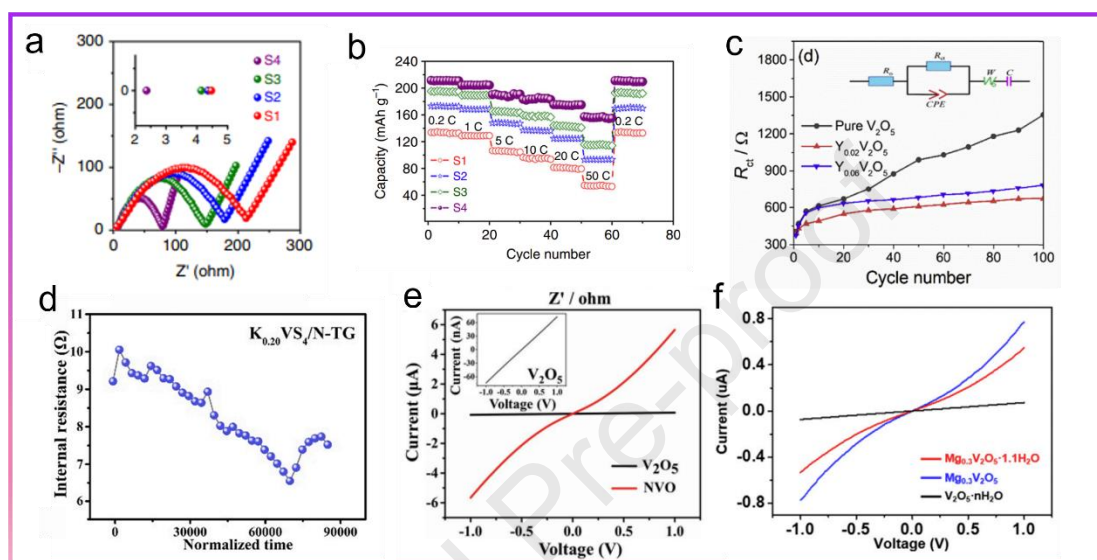
804 **Fig. 9.** (a) EIS measurement of $Na_{0.46}MnO_{2-y}(OH)_{2y}\cdot 0.61\ H_2O$ (S1), $Na_{0.71}MnO_{2-}$
805 $_y(OH)_{2y}\cdot 0.32\ H_2O$ (S2) and $NaMnO_{2-y}(OH)_{2y}\cdot 0.10\ H_2O$ (S3). (b) Rate
806 performance of $Na_{0.46}MnO_{2-y}(OH)_{2y}\cdot 0.61\ H_2O$ (S1), $Na_{0.71}MnO_{2-y}(OH)_{2y}\cdot 0.32$
807 H_2O (S2) and $NaMnO_{2-y}(OH)_{2y}\cdot 0.10\ H_2O$ (S3) from 0.2C to 50C. Reproduced
808 with permission from Ref. [82]. Copyright © 2018, Hui Xia *et al.* (c) Comparison
809 of R_{ct} over cycling for V_2O_5, $Y_{0.02}V_2O_5$ and $Y_{0.06}V_2O_5$. Reproduced with
810 permission from Ref. [30]. Copyright © 2018 Elsevier Ltd. All rights reserved.
811 (d) Calculated internal resistance of $K_{0.2}VS_4$/N-TG. Copyright © 2021 Elsevier
812 Ltd. All rights reserved. (e) I-V curves of V_2O_5 and $Na_{0.33}V_2O_5$. Reproduced with
813 permission from Ref. [84]. Copyright © 2018 WILEY-VCH Verlag GmbH &
814 Co. KGaA, Weinheim. (f) I-V curves of $Mg_{0.3}V_2O_5\cdot 1.1\ H_2O$, $Mg_{0.3}V_2O_5$ and
815 $V_2O_5\cdot n\ H_2O$. Reproduced with permission from Ref. [75]. Copyright © 2019
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817

818 What was observed contradicts the result from Meng *et al.* as when the yttrium

819 content was increased from x = 0.02 to x = 0.06, the R_{ct} increases to ∼ 700 Ω,

820 from ∼ 600 Ω. This indicates that increasing the pre-intercalated species may not

821 always be beneficial to conductivity, as generally a large number of dopants can

822   result in a more impeded path for the electrons, as in this case the yttrium ions

823   can pull charge density away from the lattice, reducing charge carriers and thus

824   creating a non-linear doping effect. While yttrium is a rather unique pre-

825   intercalated ion, Na^+ pre-intercalated vanadium oxide nanowires, $Na_{0.33}V_2O_5$ was

826   investigated by Mai *et al.* for ZIBs [84]. The Na^+ ions induced V^{4+} vacancies in

827   the V^{5+} lattice, resulting in a conductivity of 5.9×10^4 S m^{-1}, compared to pristine

828   V_2O_5 with a conductivity of 7.3 S m^{-1} (Fig. 9e). This was also confirmed in the

829   EIS, with $Na_{0.33}V_2O_5$ displaying an R_{ct} of 5.6 Ω after the first cycle, vs 8.7 Ω for

830   V_2O_5. This improved electronic conductivity translated to an improved rate

831   performance, with the $Na_{0.33}V_2O_5$ retaining 96.4 mAh g^{-1} at 2 A g^{-1}. As before,

832   this indicates that the pre-intercalation of charged ions inducing valances changes

833   in small numbers of redox active metal centers is beneficial to conductivity,

834   which in turn improves electrochemical performance. This is further evidenced

835   by another work by Mai *et al.*, as they investigated magnesium pre-intercalated

836   bi-layered vanadium oxide, $Mg_{0.3}V_2O_5 \cdot 1.1$ H_2O for MIBs [75]. When compared

837   to the bi-layered $V_2O_5 \cdot n$ H_2O control, the conductivity is significantly improved,

838   from 10.1 S m^{-1} to 5.0×10^3 S m^{-1} (Fig. 9f). The stabilising structural water was

839   also attempted to be removed to form $Mg_{0.3}V_2O_5$, but the structure collapsed and

840   while the electronic conductivity is improved, the structure was observed to not

841   be conducive for ionic diffusion and thus the performance is reduced to only 200

842   cycles before failing, with below 50 mAh g^{-1} for most of the cycles.

843 Overall, pre-intercalation is a valuable tool for improving the inherent electronic

844 conductivity of poorly conducting active materials. The combination of the

845 introduction of additional dopant levels from the pre-intercalated species and the

846 valance changes of the metal redox centres to provide additional levels within

847 the band gap of these insulators or semiconductors can dramatically improve the

848 initial conductivity the material. However, this process will inevitably happen

849 during the charge–discharge process, as to charge balance the incoming cations,

850 a metal centre must accept an electron, creating a valance doped structure.

851 However as discussed, even during different SOC, the pre-intercalated materials

852 are still more conductive, implying that pre-intercalation amplifies this effect.

853 Another cautionary aspect is that the pre-intercalation level should be

854 thoughtfully considered, as over pre-intercalating or the removal of stabilizing

855 species in favour of pre-intercalated species can have negative effects, despite

856 having an improved conductivity.

857 **4. Perspectives and Outlook**

858 Despite being one of the oldest techniques for altering the properties of

859 intercalation-type battery materials, pre-intercalation has seen a resurgence in

860 recent years and is rapidly proving to be a timely and impactful tool [42, 43].

861 By intelligently optimising the pre-intercalated species, namely its valance and

862 size, along with the degree of pre-intercalation, the key properties of d-spacing,

863 lattice stability with cycling and the level of doping by inducing valance changes

864 in the metal redox centres can be positively altered. These correspond to

865   improvements in capacity, ionic and electronic conductivity, and have been

866   proven repeatedly to be superior to the un-pre-intercalated materials. The benefits

867   to this approach are numerous. Firstly, the alternations to the material are

868   intrinsic, so any morphology optimisation and post-synthesis processing, such as

869   carbon coating, can also be applied to pre-intercalated materials in addition,

870   rather than in place of. Secondly, while many pre-intercalation syntheses can be

871   criticised for their cost, use of toxic and unsustainable reagents and lack of

872   control, equally as many are facile, cheap and sustainable, requiring only a small

873   amount of the pre-intercalated species to be included in the synthesis or a simple

874   aqueous ion-exchange post synthesis [30, 85, 86]. Thirdly, the level of pre-

875   intercalation can be highly tuneable, allowing for a large degree of control over

876   the final product, resulting in a highly specific product that can be directed for a

877   specific merit of the product, e.g. high rate or high stability.

878   However, as with all tools, there are some pitfalls. Firstly, the lability of the pre-

879   intercalated species must be cautiously considered, as during cycling, the partial

880   or total de-intercalation of the pre-intercalated species is highly likely, if not

881   certain. This can not only reduce the effect of the pre-intercalated species, but

882   also cause poisoning of the electrolyte and opposite electrode, along with

883   unwanted side reactions and destruction of the host lattice. Keeping this in mind,

884   very labile species should be avoided to minimise this effect. Secondly,

885   considerable restraint must also be employed with the degree of pre-intercalation,

886   as too many pre-intercalated species can start blocking diffusion paths of the

887   charge carriers and occupying active sites, along with increasing the electrostatic

888   interactions with the charge carriers, which increases electrostatic repulsions and

889   reducing the storage capacity of the material.

890   For the outlook of the field, there are some distinctly fruitful avenues that require

891   further investigation. Firstly, the pre-intercalation of redox active species could

892   be a novel avenue, as none of the species mentioned in this review were

893   demonstrated to be redox active, within their host structures. This could totally

894   off-set the energy density reduction associated with pre-intercalation, while

895   retaining the benefits of pre-intercalation, addressing a common criticism of pre-

896   intercalation. Secondly, multi-species pre-intercalation could be a promising

897   further development. Each species could be optimised to provide synergistic

898   benefits to the host material, further enhancing the electrochemical performance.

899   Thirdly, the relationship of d-spacing enlargement could be further investigated

900   by a staging of multiple rounds of pre-intercalation, activating the lattice to

901   further accommodate larger species. This would expand the d-spacing further,

902   potentially enhancing electrochemical performance further. Fourthly, in the

903   authors opinion, there is a significant research gap in investigating the structure

904   of the pre-intercalated materials. The occupation sites of the pre-intercalated

905   species and its local environment changes are almost never investigated, with

906   often the only evidence given being the increase in d-spacing via XRD. A

907   thorough investigation into the occupied sites and how these changes affect the

908   mechanism of intercalation is sorely needed.

45

909 Finally, the benefits of pre-intercalation have been proven almost exclusively in

910 a half-cell configuration, with no ion intercalation taking place at the metal

911 counter electrode. Given the "Rocking chair" nature of rechargeable ion

912 batteries, an investigation into the behaviour of the pre-intercalated species in a

913 full-cell configuration would be of great value. Of particular interest, is the de-

914 intercalation and re-intercalation of the pre-intercalated species from the working

915 electrode into an intercalation based counter electrode, for which intercalation

916 behaviour of the species and liability to full-cell performance are unclear. In the

917 authors' opinion, pre-intercalation research is an under-utilised aspect in the

918 energy storage field. If continued research finds that the lability of the pre-

919 intercalated species do not impose significant negatives, we believe that many

920 materials could strongly benefit from the positives pre-intercalation provides.

921 Also, the most convincing is the pillaring effect and its improvements to stability.

922 A material that retains its stability, at both high and low rates, is essential for

923 large-scale storage, which currently is a topical aspect of energy research. Pre-

924 intercalation has concretely demonstrated that through careful and insightful

925 choice of intercalation degree and species, the stability of materials can be

926 dramatically improved.

927
928 **Author contributions**

929 Conceptualisation, C.A.F.N.; Writing – Original Draft, C.A.F.N.; Writing – Review

930 & Editing, Y.X. and C.A.F.N.; Supervision and Funding Acquisition, Y.X. All authors

931 participated in manuscript discussion.

46

Competing financial interests

References

[1]K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, LixCoO$_2$ (0<x<-1): A new cathode material for batteries of high energy density, Mater. Res. Bull. 15 (1980) 783-789.

[2]G. Liu, Z. Zhao, A. Ghahreman, Novel approaches for lithium extraction from salt-lake brines: A review, Hydrometallurgy 187 (2019) 81-100.

[3]London Metals Exchange (Acessed Nov 2022).

[4]R. P. Ramasamy, Toward a least-effort principle for evaluating prices of elements as indicators of sustainability, MRS Energy Sustain. 8 (2021) 16–32.

[5]A. Konarov, H. J. Kim, H. Yashiro, S.-T. Myung, Passivation of aluminum current collectors in non-aqueous carbonate solutions containing sodium or potassium hexafluorophosphate salts, J. Mater. Chem. A 7 (2019) 13012-13018.

[6]R. C. Asher, A lamellar compound of sodium and graphite, J. Inorg. Nucl. Chem. 10 (1959) 238-249.

[7]S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, Potassium intercalation into graphite to realize high-voltage/high-power potassium-ion batteries and potassium-ion capacitors, Electrochem. Commun. 60 (2015) 172-175.

[8]Y. Marcus, Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 3 - Standard potentials of selected electrodes, Pure Appl. Chem. 57 (1985) 1129-1132.

[9]CRC Handbook of Chemistry and Physics. 97th ed 2016-2017.

[10]A. Eftekhari, Potassium secondary cell based on Prussian blue cathode, J. Power Sources. 126 (2004) 221-228.

[11]V. Gabaudan, L. Monconduit, L. Stievano, R. Berthelot, Snapshot on negative electrode materials for potassium-ion Batteries, Front. Energy Res. 7 (2019) 46.

[12]H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, Y. Wang, F. Kang, B. Li, C. Zhi, An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte, Energy Environ. Sci. 11 (2018) 941-951.

[13]Z. Zhao-Karger, M. Fichtner, Beyond intercalation chemistry for rechargeable Mg batteries: A short review and perspective, Front Chem. 6 (2018) 656.

[14]W. L. Worrell, Electrochemical investigations of novel electrode materials. Progress report, November 1, 1981-December 31, 1982. Office of Scientific and Technical Information (OSTI); 1982.

[15]M. B. Armand. Intercalation Electrodes. In: Murphy DW, Broadhead J, Steele BCH, editors. Materials for advanced batteries. Boston, MA: Springer US; 1980. p. 145-161.

[16]G. Demazeau, Solvothermal and hydrothermal processes: the main physico-chemical factors involved and new trends, Res. Chem. Intermed. 37 (2011) 107-123.

[17]D. Navas, S. Fuentes, A. Castro-Alvarez, E. Chavez-Angel, Review on sol-gel synthesis of perovskite and oxide nanomaterials, Gels 7 (2021) 275.

[18]M. Aykol, J. H. Montoya, J. Hummelshoj, Rational solid-state synthesis routes for inorganic materials, J Am Chem Soc. 143 (2021) 9244-9259.

[19]Y.-H. Luo, Q.-L. Pan, H.-X. Wei, Y.-D. Huang, L.-B. Tang, Z.-Y. Wang, C. Yan, J. Mao, K.-H. Dai, Q. Wu, X.-H. Zhang, J.-C. Zheng, Fundamentals of ion-exchange synthesis and its implications in layered oxide cathodes: Recent advances and perspective, Adv. Energy Mater. 13 (2023) 2300125.

[20]R. Uppuluri, A. Sen Gupta, A. S. Rosas, T. E. Mallouk, Soft chemistry of ion-exchangeable layered metal oxides, Chem. Soc. Rev. 47 (2018) 2401-2430.

[21]H. Chen, X. Qiu, W. Zhu, P. Hagenmuller, Synthesis and high rate properties of nanoparticled lithium cobalt oxides as the cathode material for lithium-ion battery, Electrochem. Commun. 4 (2002) 488-491.

[22]S. Park, J.-N. Chotard, D. Carlier, I. Moog, M. Duttine, F. Fauth, A. Iadecola, L. Croguennec, C. Masquelier, An asymmetric sodium extraction/insertion mechanism for the Fe/V-mixed NASICON $Na_4FeV(PO_4)_3$, Chem. Mater. 34 (2022) 4142-4152.

[23]S. Park, J.-N. Chotard, D. Carlier, I. Moog, M. Courty, M. Duttine, F. Fauth, A. Iadecola, L. Croguennec, C. Masquelier, Crystal structures and local environments of NASICON-Type $Na_3FeV(PO_4)_3$ and $Na_4FeV(PO_4)_3$ positive electrode materials for Na-ion batteries, Chem. Mater. 33 (2021) 5355-5367.

[24]K. Li, J. Lv, T. Cao, Y. Gong, D. L. Zhang, Anthraquinone-intercalated $V(2)O(5)$ with $Al(3+)$ for superior zinc-ion batteries: reversible transformation between disorder and order, Chem Commun. 58 (2022) 12365-12368.

[25]O. C. Gagne, F. C. Hawthorne, Bond-length distributions for ions bonded to oxygen: alkali and alkaline-earth metals, Acta Crystallogr. Sect. B: Struct. Sci. 72 (2016) 602-625.

[26]J. W. Steed, First- and second-sphere coordination chemistry of alkali metal crown ether complexes, Coord. Chem. Rev. 215 (2001) 171-221.

[27]K. Li, Y. Gong, J. H. Lin, Benzoquinone-intercalated vanadium oxide in the electrolyte with Al^{3+} for zinc-ion storage: dual-pillar effect and reversible disorder–order conversion, Chem. Eng. J. 452 (2023) 139621.

[28]K. W. Hipps, U. Mazur, Electron affinity states of metal supported phthalocyanines measured by tunneling spectroscopy, J. Porphyrins Phthalocyanines. 16 (2012) 273-281.

[29]P. Chomkhuntod, K. Hantanasirisakul, S. Duangdangchote, N. Phattharasupakun, M. Sawangphruk, The charge density of intercalants inside layered birnessite manganese oxide nanosheets determining Zn-ion storage capability towards rechargeable Zn-ion batteries, J. Mater. Chem. A 10 (2022) 5561-5568.

[30]C. Liu, J. Yao, Z. Zou, Y. Li, G. Cao, Boosting the cycling stability of hydrated vanadium pentoxide by Y3+ pillaring for sodium-ion batteries, Mater. Today Energy 11 (2019) 218-227.

[31]T. Jing, Y. Dai, X. Ma, W. Wei, B. Huang, Effects of intrinsic defects and extrinsic doping on the electronic and photocatalytic properties of Ta_3N_5, RSC Adv. 5 (2015) 59390-59397.

[32]K. Kanetani, K. Sugawara, T. Sato, R. Shimizu, K. Iwaya, T. Hitosugi, T. Takahashi, Ca intercalated bilayer graphene as a thinnest limit of superconducting C_6Ca, PNAS 109 (2012) 19610-19613.

[33]S. Tosoni, C. Di Valentin, G. Pacchioni, Effect of Alkali Metals Interstitial Doping on Structural and Electronic Properties of WO_3, J. Phys. Chem. C 118 (2014) 3000-3006.

[34]G. V. Gibbs, F. C. Hill, M. B. Boisen, R. T. Downs, Power law relationships between bond length, bond strength and electron density distributions, Phys. Chem. Miner. 25 (1998) 585-590.

[35]J. Zhang, L. Cheng, L. Ma, S. Sang, L. Xu, Y. Jiang, SiS_2 monolayer: An auspicious alkali-ion anode material with high specific capacity and ultrafast ion diffusion. Phys. E: Low-Dimens, Syst. Nanostructures. 144 (2022) 115474.

[36]J. L. Kaufman, J. Vinckevičiūtė, S. Krishna Kolli, J. Gabriel Goiri, A. Van der Ven, Understanding intercalation compounds for sodium-ion batteries and beyond, Philos. Trans. Royal Soc. A PHILOS T R SOC A. 377 (2019) 20190020.

[37]C. Chen, M. Shi, Y. Zhao, C. Yang, L. Zhao, C. Yan, Al-Intercalated MnO_2 cathode with reversible phase transition for aqueous Zn-ion batteries, Chem. Eng. J. 422 (2021) 130375.

[38]Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, C. Wang, Expanded graphite as superior anode for sodium-ion batteries, Nat. Commun. 5 (2014) 4033.

[39]M. Tian, C. Liu, J. Zheng, X. Jia, E. P. Jahrman, G. T. Seidler, D. Long, M. Atif, M. Alsalhi, G. Cao, Structural engineering of hydrated vanadium oxide cathode by K+ incorporation for high-capacity and long-cycling aqueous zinc ion batteries,. Energy Stor. Mater. 29 (2020) 9-16.

[40]X. Zhang, Z. Zhang, S. Yao, A. Chen, X. Zhao, Z. Zhou, An effective method to screen sodium-based layered materials for sodium ion batteries, Npj Comput. Mater. 4 (2018) 13.

[41]M. Feng, Q. Du, L. Su, G. Zhang, G. Wang, Z. Ma, W. Gao, X. Qin, G. Shao, Manganese oxide electrode with excellent electrochemical performance for

sodium ion batteries by pre-intercalation of K and Na ions, Sci Rep. 7 (2017) 2219.

[42] X. Yao, Y. Zhao, F. A. Castro, L. Mai, Rational Design of Preintercalated Electrodes for Rechargeable Batteries, ACS Energy Lett. 4 (2019) 771-778.

[43] Y. Liu, J. Xu, J. Li, Z. Yang, C. Huang, H. Yu, L. Zhang, J. Shu, Pre-intercalation chemistry of electrode materials in aqueous energy storage systems, Coord. Chem. Rev. 460 (2022) 214477.

[44] Q. Liu, F. Han, J. Zhou, Y. Li, L. Chen, F. Zhang, D. Zhou, C. Ye, J. Yang, X. Wu, J. Liu, Boosting the potassium-ion storage performance in soft carbon anodes by the synergistic effect of optimized molten salt medium and N/S dual-doping. ACS Appl. Mater. Interfaces 12 (2020) 20838-20848.

[45] C. Liu, N. Xiao, H. Li, Q. Dong, Y. Wang, H. Li, S. Wang, X. Zhang, J. Qiu, Nitrogen-doped soft carbon frameworks built of well-interconnected nanocapsules enabling a superior potassium-ion batteries anode, Chem. Eng. J. 382 (2020) 121759.

[46] K.-H. Nam, V. Ganesan, K. H. Chae, C.-M. Park, High-performance carbon by amorphization and prepotassiation for potassium-ion battery anodes, Carbon 181 (2021) 290-299.

[47] S. Tepavcevic, H. Xiong, V. R. Stamenkovic, X. Zuo, M. Balasubramanian, V. B. Prakapenka, C. S. Johnson, T. Rajh, Nanostructured Bilayered Vanadium Oxide Electrodes for Rechargeable Sodium-Ion Batteries, ACS Nano 6 (2012) 530-538.

[48] Q. Ren, N. Qin, B. Liu, Y. Yao, X. Zhao, Z. Deng, Y. Li, Y. Dong, D. Qian, B.-L. Su, W. Zhang, H.-E. Wang, An oxygen-deficient vanadium oxide@N-doped carbon heterostructure for sodium-ion batteries: insights into the charge storage mechanism and enhanced reaction kinetics, J. Mater. Chem. A 8 (2020) 3450-3458.

[49] J. Song, S. Park, S. Kim, V. Mathew, M. H. Alfaruqi, J. Jo, J. Kim, Uniform Carbon coated $Na_3V_2(PO_4)_2O_{2x}F_{3-2x}$ nanoparticles for sodium ion batteries as cathode, ACS Sustain. Chem. Eng. 7 (2019) 18826-18834.

[50] M. Clites, B. W. Byles, E. Pomerantseva, Effect of aging and hydrothermal treatment on electrochemical performance of chemically pre-intercalated Na–V–O nanowires for Na-ion batteries, J. Mater. Chem. A 4 (2016) 7754-7761.

[51] D. Su, G. Wang, Single-crystalline bilayered V_2O_5 nanobelts for high-capacity sodium-ion batteries. ACS Nano 7 (2013) 11218-11226.

[52] V. Raju, J. Rains, C. Gates, W. Luo, X. Wang, W. F. Stickle, G. D. Stucky, X. Ji, Superior cathode of sodium-ion batteries: orthorhombic V_2O_5 nanoparticles generated in nanoporous carbon by ambient hydrolysis deposition, Nano Lett. 14 (2014) 4119-4124.

[53] M. Clites, J. L. Hart, M. L. Taheri, E. Pomerantseva, Chemically preintercalated bilayered $K_xV_2O_5 \cdot nH_2O$ nanobelts as a high-performing cathode material for K-ion batteries, ACS Energy Lett. 3 (2018) 562-567.
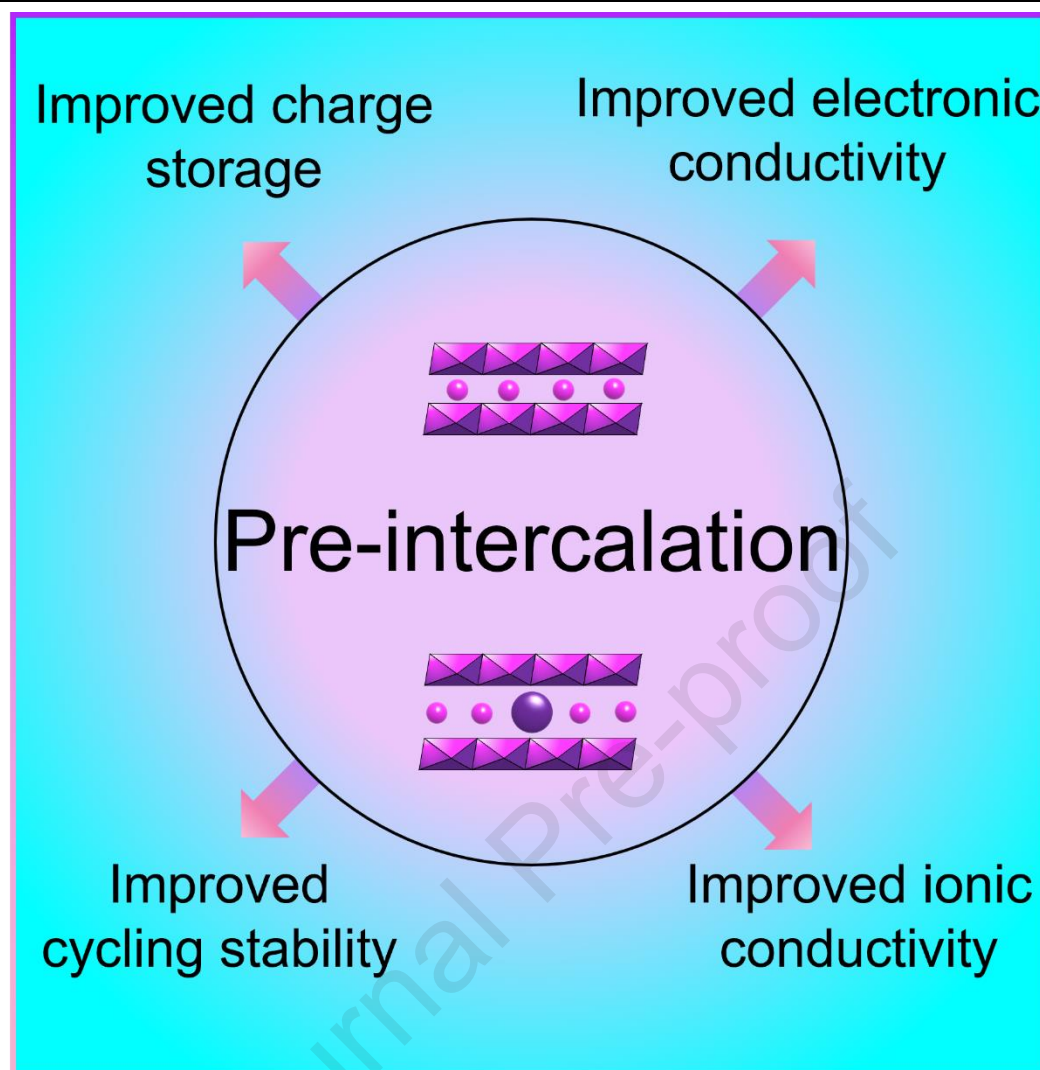
[54] D. S. Charles, M. Feygenson, K. Page, J. Neuefeind, W. Xu, X. Teng, Structural water engaged disordered vanadium oxide nanosheets for high capacity aqueous potassium-ion storage, Nat Commun. 8 (2017) 15520.

[55] Q. Xie, G. Cheng, T. Xue, L. Huang, S. Chen, Y. Sun, M. Sun, H. Wang, L. Yu, Alkali ions pre-intercalation of δ-MnO2 nanosheets for high-capacity and stable Zn-ion battery, Mater. Today Energy. 24 (2022) 100934.

[56] X. Wang, P. Hu, C. Niu, J. Meng, X. Xu, X. Wei, C. Tang, W. Luo, L. Zhou, Q. An, L. Mai, New-type $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ cathode with an expanded and stabilized interlayer structure for high-capacity sodium-ion batteries, Nano Energy 35 (2017) 71-78.

[57] Y. Zhao, C. Han, J. Yang, J. Su, X. Xu, S. Li, L. Xu, R. Fang, H. Jiang, X. Zou, B. Song, L. Mai, Q. Zhang, Stable alkali metal ion intercalation compounds as optimized metal oxide nanowire cathodes for lithium batteries, Nano Lett. 15 (2015) 2180-2185.

[58] M. S. Whittingham, Electrical energy storage and intercalation chemistry, Science 192 (1976) 1126-1127.

[59] G. L. Holleck, J. R. Driscoll, Transition metal sulfides as cathodes for secondary lithium batteries—II. titanium sulfides, Electrochim. Acta. 22 (1977) 647-655.

[60] B. Tian, W. Tang, K. Leng, Z. Chen, S. J. R. Tan, C. Peng, G.-H. Ning, W. Fu, C. Su, G. W. Zheng, K. P. Loh, Phase transformations in TiS2 during K intercalation, ACS Energy Lett. 2 (2017) 1835-1840.

[61] Y. Tang, H. Zhang, S. Zhang, L. Li, Z. Liu, Z. Li, J. Shen, H. Shao, High performance anode for sodium-ion batteries: Calcium pre-intercalated layered vanadium oxide/carbon composite, Chem. Eng. J. 424 (2021) 130378.

[62] Y. Fan, Z. Qu, W. Zhong, Z. Hu, H. A. Younus, C. Yang, X. Wang, S. Zhang, Understanding the effect of interplanar space and preintercalated cations of vanadate cathode materials on potassium-ion battery performance, ACS Appl. Mater. Interfaces 13 (2021) 7377-7388.

[63] B. Tian, W. Tang, C. Su, Y. Li, Reticular $V_2O_5 \cdot 0.6H_2O$ xerogel as cathode for rechargeable potassium ion batteries, ACS Appl. Mater. Interfaces 10 (2018) 642-650.

[64] L. Xing, C. Zhang, M. Li, P. Hu, X. Zhang, Y. Dai, X. Pan, W. Sun, S. Li, J. Xue, Q. An, L. Mai, Revealing excess Al^{3+} preinsertion on altering diffusion paths of aluminum vanadate for zinc-ion batteries, Energy Stor. Mater. 52 (2022) 291-298.

[65] P. Jing, W. Wei, W. Luo, X. Li, F. Xu, H. Li, M. Wei, D. Yu, Q. Zhu, G. Liu, In-situ XRD study of the structure and electrochemical performance of V_2O_5 nanosheets in aqueous zinc ion batteries, Inorg. Chem. Commun. 117 (2020) 107953.

[66] A. Masias, J. Marcicki, W. A. Paxton, Opportunities and challenges of lithium ion batteries in automotive applications, ACS Energy Lett. 6 (2021) 621-630.
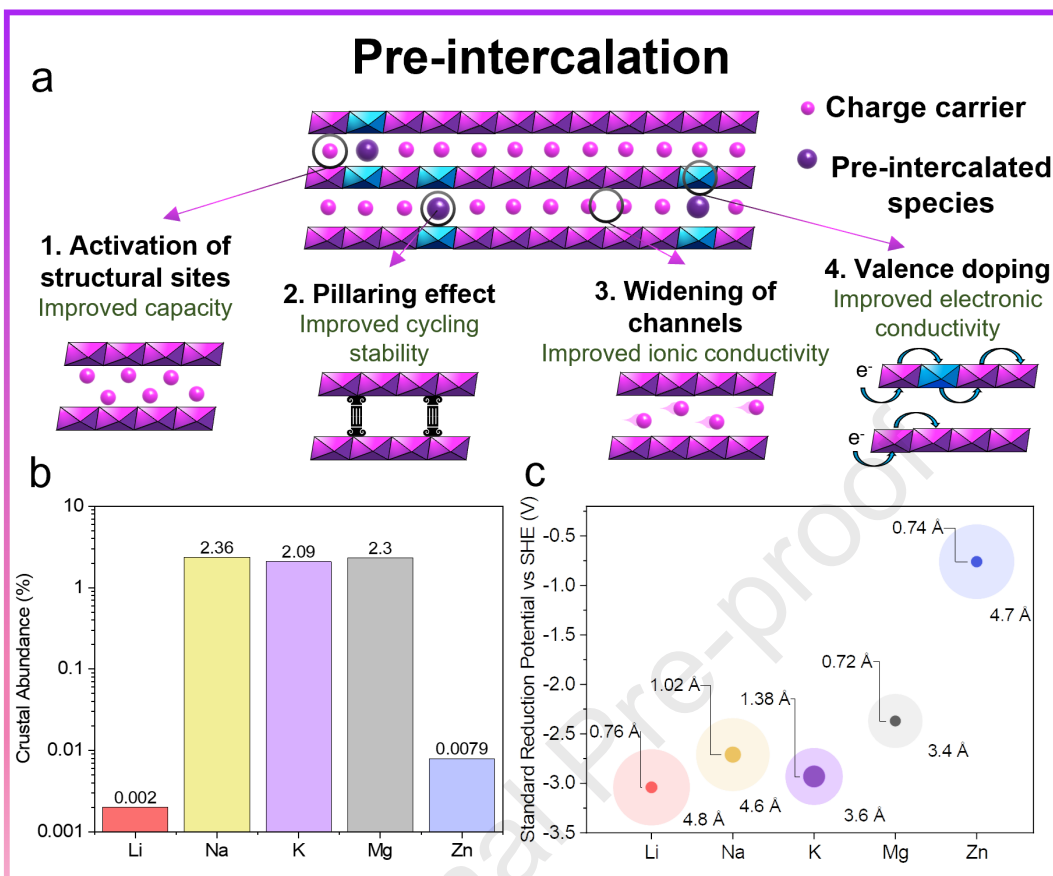
[67] M. Zhou, P. Bai, X. Ji, J. Yang, C. Wang, Y. Xu, Electrolytes and interphases in potassium ion batteries. Adv Mater. 33 (2021) e2003741.

[68] J. Huang, Diffusion impedance of electroactive materials, electrolytic solutions and porous electrodes: Warburg impedance and beyond, Electrochim. Acta. 281 (2018) 170-188.

[69] C.-H. Wang, N. Kurra, M. Alhabeb, J.-K. Chang, H. N. Alshareef, Y. Gogotsi, Titanium carbide (MXene) as a current collector for lithium-ion batteries, ACS Omega 3 (2018) 12489-12494.

[70] P. A. Maughan, L. Bouscarrat, V. R. Seymour, S. Shao, S. J. Haigh, R. Dawson, N. Tapia-Ruiz, N. Bimbo, Pillared Mo_2TiC_2 MXene for high-power and long-life lithium and sodium-ion batteries, Nanoscale Adv. 3 (2021) 3145-3158.

[71] S. Zhao, Z. Liu, G. Xie, X. Guo, Z. Guo, F. Song, G. Li, C. Chen, X. Xie, N. Zhang, B. Sun, S. Guo, G. Wang, Achieving high-performance 3D K(+) -pre-intercalated $Ti_3C_2T_x$ MXene for potassium-ion hybrid capacitors via regulating electrolyte solvation structure, Angew Chem. Int. Ed. 60 (2021) 26246-26253.

[72] G. Ma, H. Shao, J. Xu, Y. Liu, Q. Huang, P.-L. Taberna, P. Simon, Z. Lin, Li-ion storage properties of two-dimensional titanium-carbide synthesized via fast one-pot method in air atmosphere, Nat. Commun. 12 (2021) 5085.

[73] C. Huang, Y. Liu, R. Zheng, Z. Yang, Z. Miao, J. Zhang, X. Cai, H. Yu, L. Zhang, J. Shu, Interlayer gap widened TiS_2 for highly efficient sodium-ion storage, J. Mater. Sci. Technol. 107 (2022) 64-69.

[74] H. Tian, Y. He, L. Wang, Y. Lai, J. Wang, H. Xiang, W. Zhao, L. Zhang, Simultaneous pre-intercalation of caesium and sodium ions into vanadium oxide bronze nanowires for high-performance aqueous zinc-ion batteries, Mater. Chem. Front. 6 (2022) 1920-1928.

[75] Y. Xu, X. Deng, Q. Li, G. Zhang, F. Xiong, S. Tan, Q. Wei, J. Lu, J. Li, Q. An, L. Mai, Vanadium oxide pillared by interlayer Mg^{2+} ions and water as ultralong-life cathodes for magnesium-ion batteries, Chem. 5 (2019) 1194-1209.

[76] C. N. R. Rao, G. V. Subba Rao, Electrical conduction in metal oxides. physica status solidi (a) 1 (1970) 597-652.

[77] L. Ling, X. Wang, M. Zhou, K. Wu, C. Lin, H. A. Younus, M. Zhang, S. Zhang, F. Cheng, Y. Zhang, Carbon-coated flower-like TiO_2 nanosphere as an ultrastable anode material for potassium-ion batteries: Structure design and mechanism study, ACS Appl. Energy Mater. 5 (2022) 15586-15596.

[78] J. Collins, G. Gourdin, M. Foster, D. Qu, Carbon surface functionalities and SEI formation during Li intercalation, Carbon 92 (2015) 193-244.

[79] J. O. Besenhard, M. Winter, J. Yang, W. Biberacher, Filming mechanism of lithium-carbon anodes in organic and inorganic electrolytes, J. Power Sources. 54 (1995) 228-231.

[80] A. G. Milnes, Deep impurities in semiconductors: Wiley-Interscience; 1973.

[81] Y. P. Sánchez, A. Santos, P. R. Bueno, Quantum mechanical meaning of the charge transfer resistance, J. Phys. Chem. C 126 (2022) 3151-3162.
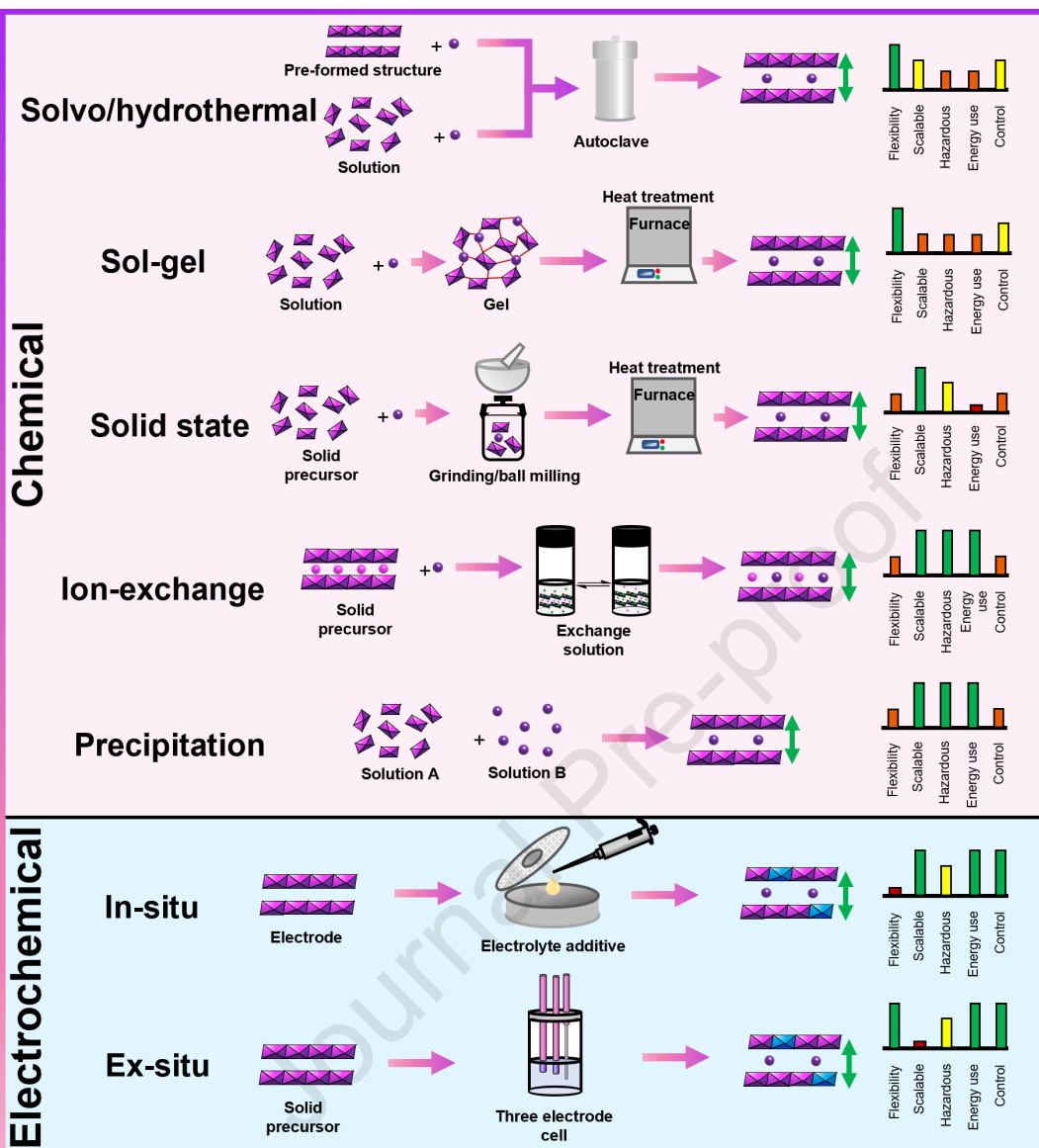
1185   [82]H. Xia, X. Zhu, J. Liu, Q. Liu, S. Lan, Q. Zhang, X. Liu, J. K. Seo, T. Chen,
1186   L. Gu, Y. S. Meng, A monoclinic polymorph of sodium birnessite for ultrafast
1187   and ultrastable sodium ion storage, Nat Commun. 9 (2018) 5100.
1188   [83]S. Ding, X. Dai, Y. Tian, B. Song, L. Wang, G. Li, S. Li, J. Huang, Z. Li, A.
1189   Meng, Insight into the coordinating mechanism of multi-electron reaction and
1190   structural stability induced by K+ pre-intercalation for magnesium ions batteries,
1191   Nano Energy 93 (2022) 106838.
1192   [84]P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu, L. Mai, Sodium ion
1193   stabilized vanadium oxide nanowire cathode for high-performance zinc-ion
1194   batteries, Adv. Energy Mater. 8 (2018) 1702463.
1195   [85]X. Zhao, L. Mao, Q. Cheng, F. Liao, G. Yang, L. Chen, A new sodium ion
1196   preintercalated and oxygen vacancy-enriched vanadyl phosphate cathode for
1197   aqueous zinc-ion batteries, J Colloid Interface Sci. 627 (2022) 1021-1029.
1198   [86]X. Zhao, L. Mao, Q. Cheng, F. Liao, G. Yang, L. Chen, Dual-cation
1199   preintercalated and amorphous carbon confined vanadium oxides as a superior
1200   cathode for aqueous zinc-ion batteries, Carbon 186 (2022) 160-170.

1201

1202

1203   **Graphical Abstract**

54

1204

Increasing species size

vs

Larger *d*-spacing

Less labile

Often heavier atomic mass

Occupies more space

Increasing charge density

vs

More effective pillaring

Occupies less volume

Increased repulsions with charge carriers

Doping of the bandgap

Conduction band

Donor level

ΔE_g

E

Valence band

Enhanced electronic conductivity

Added mass reducing specific energy density
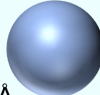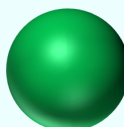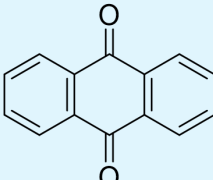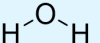
Monovalent

Li⁺
20 ppm
0.73 Å
52 C mm⁻³

Na⁺
23,600 ppm
1.16 Å
24 C mm⁻³

K⁺
20,900 ppm
1.43 Å
11 C mm⁻³

NH₄⁺
1.48 Å
11 C mm⁻³

Cs⁺
3 ppm
1.88 Å
6 C mm⁻³

Divalent

Mg²⁺
23,300 ppm
0.86 Å
52 C mm⁻³

Ca²⁺
41,500 ppm
1.14 Å
120 C mm⁻³

Trivalent

Al³⁺
82,300 ppm
0.67 Å
364 C mm⁻³

Y³⁺
33 ppm
1.15 Å
102 C mm⁻³

Uncharged

9.20 Å
5.36 Å
Anthraquinone

1.60 Å
0.58 Å
Water

4.41 Å
5.27 Å
Benzoquinone

- *d*-spacing too small
- Bonds too short
- Poor spatial fit
- Hampered performance
- Volume change on intercalation

- Optimised *d*-spacing
- Optimum bond length
- Good spatial fit
- Improved performance
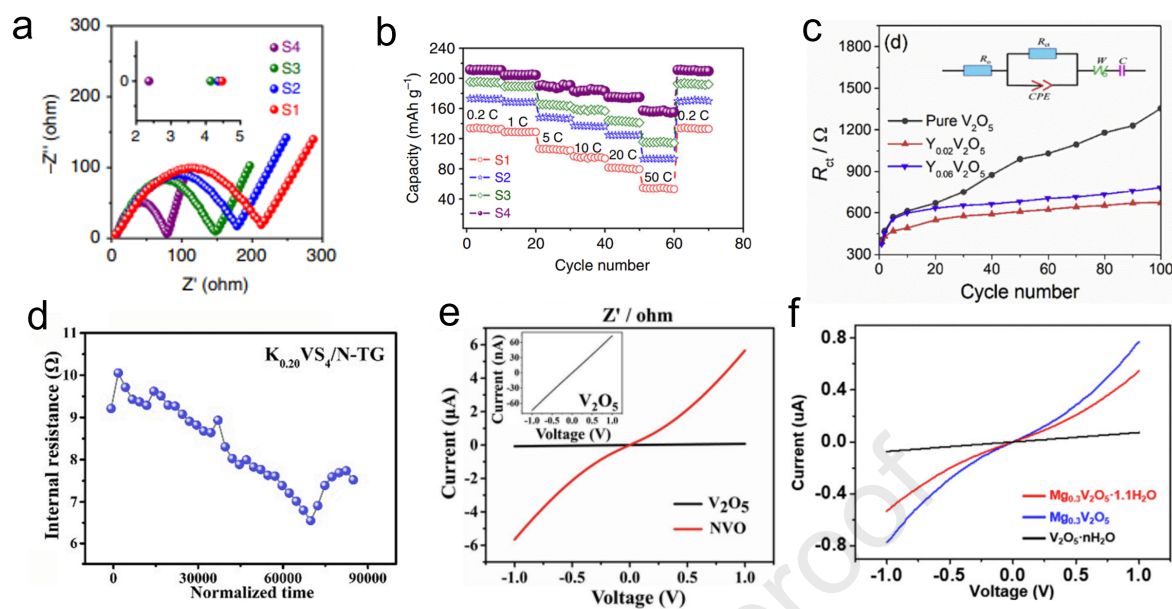- Reduced volume change on intercalation

Highlights for Manuscript ESCI-D-22-00058:

- The fundamentals, effects, advantages and pitfalls of pre-intercalation are covered.
- A wide range of materials are reviewed to illustrate and analyse pre-intercalation.
- Perspectives and opinions on the future work in the field are offered.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: