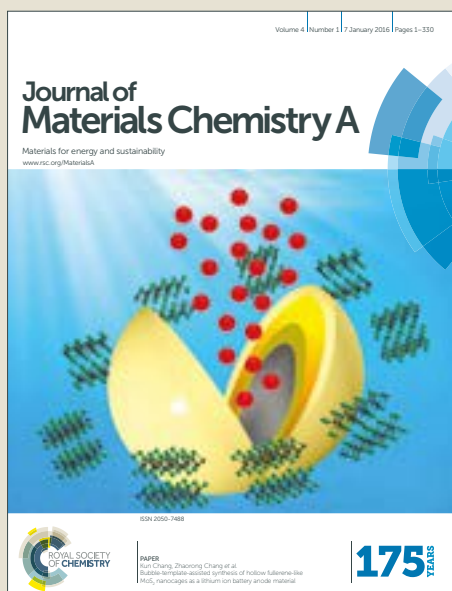


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1
2 **Cathode Materials for Rechargeable Aluminum Batteries: Current Status**
3 **and Progress**

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23

24 **Abstract**

25 Rechargeable aluminum batteries (RABs) are amongst the most promising of the post-
26 lithium energy storage systems (ESS) with substantially higher specific volumetric capacity
27 (8046 mAh cm^{-3}), higher safety and lower cost. The development of such efficient and low
28 cost ESS is of the essence in order to meet future energy storage demands of modern
29 society. In recent years, a number of research articles have been reported on the evolution
30 of cathode materials for RABs, which makes a critical review timely in order to provide
31 inspiration for future research. This article highlights the cathode materials developed
32 specifically for RABs, in detail, the development of the carbon-based cathode materials,
33 and then that of transition metal oxides (TMOs), sulfides and chloride based cathode
34 materials and then finally, a few other cathode materials are also discussed. Accordingly,
35 future perspectives and opportunities are highlighted.

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47 **1. Introduction**

48 In the past few decades, extensive research has been carried out on the development of
49 renewable energy generation and storage systems. Solar, wind and other renewable energy
50 generation technologies are now well developed but all of these technologies are
51 intermittent and require energy storage systems (ESS), such as batteries and supercapacitors
52 ¹⁻³ to buffer between periods of excess production and demand. Unfortunately, less than one
53 percent of the total energy produced from all renewable energy resources can be stored ^{3,4}.
54 The rocking-chair LIBs came into existence in the last decade of 20th century and have been
55 proven to be an efficient ESS due to its high energy density and operating voltage ⁵⁻⁷, which
56 are serving from smart portable devices to large energy grid applications. However, the
57 scarcity of lithium resources along with high cost and safety concerns have turned the
58 current research focus towards cost effective, safe, ultrahigh energy density, earth-abundant
59 and environment-friendly ESS ⁸⁻¹⁵.

60 RABs are proposed as the next generation ultrahigh volumetric capacity batteries. As a
61 trivalent metal, Al exchanges three electrons during the redox reaction, hence provides
62 approximately four and two fold volumetric capacity (8046 mAh cm^{-3}) ¹⁶⁻¹⁸ than the
63 monovalent LIBs (2062 mAh cm^{-3}) ¹⁰ and the divalent magnesium-ion batteries (3833 mAh
64 cm^{-3}) ¹⁹⁻²², respectively. Furthermore, Al is the third most abundant element in the earth's
65 crust ²³⁻²⁵ and less reactive and easier handled than Li ¹⁸. A detailed comparison of the
66 characteristics of Al with other metals is summarised in **Table 1**.

67 Conventionally, RABs work on the principal of intercalation/deintercalation chemistry.
68 More specifically, two interfacial processes take place in the chloroaluminated ionic liquid

69 (IL) electrolyte based systems. One is between Al metal and the electrolyte where
70 electrochemical deposition and dissolution of Al metal occur at the anode side, the other is
71 between the electrolyte and cathode materials where chloroaluminate anions (AlCl_4^-) and
72 trivalent Al^{3+} ions intercalate and deintercalate during the charge/discharge process^{26, 27}.
73 However, the development of trivalent RABs is still hindered by the lack of practical and
74 high specific capacity cathode materials. The design principles of cathode materials for
75 RABs have not yet been determined. The current cathode materials reported for RABs are
76 not satisfactory and have suffered many intrinsic problems, such as (a) capacitive behavior
77 without stable discharge voltage plateaus²⁷⁻²⁹, (b) very low (less than 0.55 volts) discharge
78 voltages,^{27, 30, 31} (c) poor reversibility leading to low coulombic efficiencies^{27, 28}, (d) low
79 and unstable discharge capacities with sharp decay after few cycles^{32, 33}, limited cycle life
80 (~100 cycles)^{18, 28, 34}, structural disintegration and volume expansions due to the
81 intercalation of large sized intercalation products^{26, 35, 36}. All of these issues result in the
82 poor electrochemical performance of the current cathode materials and limit the
83 practicability and commercialisation of high energy density RABs.

84 Very recently, a topical review has been reported by Elia et al.³⁷ on rechargeable
85 aluminum batteries. In their review, they have summarized the development of several
86 electrochemical aluminum energy storage systems based on aqueous and non-aqueous
87 electrolytes, specifically the attention was paid to the most recent evolution of the
88 electrolytic media characterized by low reactivity towards other cell components. In
89 addition, they have also focused on electrode materials for different aluminum battery
90 systems involving intercalation-deintercalation processes and Al-Sulfur batteries. However,
91 the recent progress on the cathode materials for RABs requires an immediate and

92 comprehensive review. Thus, this review article has been prepared with a special focus on
93 the current status and progress of the cathode materials for RABs, in order to provide
94 readers with a better understanding of the practical issues and challenges associated with
95 the current cathode materials. The main body of the review is divided into four sub-
96 sections. The first two sections cover the evolution of carbon and transition metal oxide
97 (TMOs) based cathode materials. Later section describes the sulfide and chloride based
98 cathode materials and the last highlights a few other cathode materials which have been
99 reported for RABs. Accordingly, future prospects of cathode materials are suggested in
100 order to address current problems and roadblocks in the commercialisation of low cost, safe
101 and high energy density next generation RAB systems.

102 **2. Current Cathode materials for Rechargeable Aluminum batteries**

103 The role of Al metal in ESS dates back to the 19th century^{19, 38-40}, but the first secondary
104 aluminum battery was reported in 1973 by Holleck and Giner⁴¹, who demonstrated the use
105 of a chlorine cathode against an Al metal anode in a eutectic molten salt electrolyte
106 composed of AlCl₃, KCl and NaCl. However, the further development of cathode materials
107 for RABs was prompted in the last decade, therein different types of materials have been
108 appraised to obtain a practical and low cost post-lithium ESS. All of the reported cathode
109 materials are categorized and discussed in the following sub-sections.

110 **2.1 Carbon based cathode materials**

111 Carbon as energy storage material is being implemented in ESS, due to its exceptional
112 electrochemical properties, high conductivity, low cost and abundance in nature^{24, 42, 43}.
113 Porous carbons, activated carbons, graphitic and amorphous carbons have contributed
114 greatly to the development of LIBs, Li-S batteries and other ESS⁴⁴⁻⁴⁷. However, in RABs,

115 the first carbon based cathode was reported in 1988 by Gifford and Palmisani³⁶, who
116 presented an Al/Graphite battery using a room-temperature ionic liquid (RTIL) electrolyte
117 composed of AlCl₃ and 1,2-dimethyl-3-propylimidazolium-chloride (DMPIC) with a molar
118 ratio of 1.5:1. The average operating voltage was 1.7 volts with discharge capacities in the
119 range of 35 to 40 mAh g⁻¹_(Graphite) at the current densities of 1-10 mA g⁻¹_(Graphite). The battery
120 was run for more than 150 cycles at 100% depth of discharge (DOD). However, the
121 evolution of Cl₂ gas limited further development of this system.

122 Aside from pure graphite, Rani et al.²⁸ reported an electrochemically fluorinated natural
123 graphite (FG) as a cathode in a RTIL electrolyte, composed of AlCl₃ and 1,3-di-n-
124 butylimidazolium bromide ([bim] [Br]) with a molar ratio of 0.5:1. The as-prepared cathode
125 was made up of semi-ionic C-F bonds and showed a high discharge capacity of 225 mAh
126 g⁻¹ for up to 40 cycles. However, the coulombic efficiency was only 75%. Furthermore,
127 there were no obvious charge/discharge plateaus in the charging and discharging curves.
128 Previously, FG has also been reported by Levitin et al.⁴⁸ as a cathode material in an
129 organic electrolyte and found that the high degree of fluorination (63%) significantly
130 improved the discharged capacity.

131 More recently, Jiao's research group³⁵ developed a low cost and safer RABs by
132 applying a commercial carbon paper as cathode material in a RTIL electrolyte utilizing
133 AlCl₃ and 1-ethyl-3-methylimidazolium chloride [EMIm]Cl (AlCl₃/[EMIm]Cl=1.3 by
134 mole). The intermediate voltage plateau was calculated at around 1.8 volts which made this
135 system more practical and viable. Moreover, the stainless steel current collector was
136 replaced by molybdenum to avoid potential corrosion reactions of stainless steel in the
137 acidic RTIL electrolyte. The most important finding was the confirmation of the

138 intercalation/deintercalation of two types of ions, Al^{3+} and chloroaluminate $[\text{Al}_x\text{Cl}_y]^-$ during
139 the charge/discharge process, which introduced the theory of “multi-coordination ion/single
140 ion intercalation and deintercalation”. On account of intercalation of comparatively large
141 $[\text{Al}_x\text{Cl}_y]^-$ anions, the volume of the carbon paper was expanded evidently after just 20
142 cycles, as observable in the TEM and HRTEM images taken before and after the charging
143 **(Fig. 1 a-b)**. The Al/graphite paper based battery showed good discharge capacity of 84.55
144 mAh g^{-1} at the current density of 50 mA g^{-1} up to 50 cycles however, at high current density
145 of 100 mA g^{-1} the obtained capacity was only 70 mAh g^{-1} **(Fig. 1 c-d)**. Although the
146 discharge capacity for the reported battery was low, the cheap carbon paper showed
147 promising aspects in the commercial applications of the RABs. Hence, the first
148 industrialized prototype of Ah-level RABs was demonstrated by the same research group
149 ⁴⁹, based on the identical cathode material to the earlier report ³⁵. The battery with stable
150 discharge capacity as high as 1.3 Ah at a current density of 10 mA g^{-1} and discharge
151 voltage plateau in the range of 2 to 1.44 V was able to illuminate a LED lamp for 14 h.
152 Moreover, a series of prototype RABs drove a super mini kart steadily. The interesting
153 feature of this battery is that the waste cycled graphitic cathode material was recycled and
154 converted into few-layer graphene by a facile and eco-friendly electrochemical exfoliation.
155 However, the self-discharge was observed about 7.28 and 5.89% per day for the 1st and 10th
156 day, respectively, which was carried out by charging the battery to 2.3 V followed by
157 resting for 24 h and draining to 0.3 V at 10 mA g^{-1} . In the subsequent cycles, a self-
158 discharge of nearly 6% per day was recorded which is still very high. Furthermore the
159 energy density (36 Wh/kg) was also low in comparison with lead-acid batteries and
160 aqueous LIBs ⁵⁰. In addition, the consumption of high cost RTIL electrolyte was quite high

161 (142.8 mL per Ah), which puts into question the feasibility and industrialization of the
162 proposed RAB prototype. In order to avoid the use of expensive and extremely moisture
163 sensitive RTIL electrolyte, Jiao et al.⁵¹ demonstrated a low cost alkali chloroaluminate
164 (NaCl-AlCl₃) electrolyte for long life rechargeable aluminum battery working at 120°C.
165 This reflects remarkable progress, because the operating temperature for similar batteries
166 using melt salts as electrolyte was impracticably high (~200°C) in the past^{52, 53}. The high
167 discharge capacity of 190 mAh g⁻¹ was delivered at a current density of 100 mA g⁻¹.
168 Meanwhile, a good cycling performance was obtained at extremely high current density of
169 4000 mA g⁻¹ with a discharged capacity of 60 mAh g⁻¹, maintained up to 5000 cycles and
170 finally, 43 mAh g⁻¹ was recorded after 9000 cycles with a coulombic efficiency constantly
171 above 99% (**Fig. 2 a-c**). In addition, the alkali chloroaluminate based RAB also exhibited
172 good shelf-life, as only 20% of potential was lost after 3 months of resting. However, the
173 high temperature operation makes this system impracticable and less appealing.

174 Graphene has been established as a viable choice for energy storage and conversion
175 devices along with biosensors and catalysts⁵⁴⁻⁶³, owing to its good physical, mechanical
176 and electrochemical properties including high specific surface area and excellent thermal
177 and electrical conductivity⁶⁴⁻⁶⁶. In particular, 3D-graphene based materials have appeared
178 as a practical cathode and anode materials for ESS^{63, 67-70}. Recently a RAB employing 3D-
179 Graphene foam (3D-GF) as a cathode with stable and high voltage, ultra-high cycle life and
180 ultrafast charging/discharging was discovered by Dai's group²⁶, representing a major
181 breakthrough in the field of RABs with unprecedented results. The RAB utilizing RTIL
182 electrolyte showed a relatively high specific capacity of 70 mAh g⁻¹ with a coulombic
183 efficiency of over 98%. This was the first RAB with high and well-defined discharge

184 plateau of 2 volts. The 3D-GF material with a flexible structure showed very stable cycle
185 life of more than 7500 cycles without reducing capacity and providing an excellent rate
186 capability even at a very high current density of 6000 mA g^{-1} . Significantly, the battery
187 showed a very fast charging time of nearly 1 minute at an extremely high current density of
188 4000 mA g^{-1} (**Fig. 3 a-d**). Dai's work contributed greatly in the development of RABs as
189 many key factors were discussed. For instance, (i) the optimized molar ratio of AlCl_3 to
190 $[\text{EMim}]\text{Cl}$ was determined as 1.3; (ii) the high water content (>7500 to 10000 ppm) results
191 in a low coulombic efficiency and H_2 evolution, so a controlled level of water was found to
192 be 500 to 700 ppm in a RTIL electrolyte, and (iii) the charge cut-off voltage was dictated to
193 be 2.45V or less due to electrolyte side reactions at high voltage.

194 More recently, Dai's group also reported a monolithic 3D graphitic foam (3D-GrF)⁷¹
195 containing aligned few-layered graphene sheets and low density of defects or oxygen
196 groups as a follow on to their previous work²⁶. A new strategy was implemented by the
197 research team in order to reduce the diffusion path for the $[\text{Al}_x\text{Cl}_y]^-$ to obtain high rate
198 capability. The graphene sheets of 3D-GrF were tailored perpendicular to the current
199 collector so that the electrolyte can readily diffuse into the sheets and ultrafast
200 intercalation/deintercalation of $[\text{Al}_x\text{Cl}_y]^-$ could be achieved. The RABs with this
201 configuration resulted in very promising electrochemical performance, exhibiting a high
202 discharge voltage plateau of 1.8 V, a discharge capacity of 60 mAh g^{-1} at an extremely high
203 current density of 12000 mA g^{-1} and a coulombic efficiency of almost 100% with about
204 100% capacity retention over 4000 cycles.

205 Inspired by Dai's work²⁶, Yang et al.⁷² applied a unique approach to develop
206 interconnected 3D graphene mesh network (3D-GMN) using folded Ni mesh-assisted CVD

207 method. The structural parameters of 3D-GMN were optimized by tuning the Ni mesh
208 period and electroplating time. It was found that by increasing the density of 3D-GMN, the
209 electrical conductivity was improved compared to 3D-GF. Furthermore, when 3D-GMN
210 was applied as a cathode in a RAB, it exhibited a fairly high capacity of 57 mAh g^{-1} at an
211 high C-rate of 40 (3000 mA g^{-1}) and excellent capacity retention of 97.5% up to 200
212 cycles.

213 It should be noted that all 3D-Graphene based materials reported for RABs have shown
214 excellent electrochemical performances. However, they demonstrated rather limited
215 discharge capacities in the range of 60 to 66 mAh g^{-1} , which are not satisfactory for
216 practical applications. In order to improve the specific discharge capacities, a novel strategy
217 was introduced by Yu et al.⁷³, who prepared graphene nanoribbons on highly porous 3D-
218 graphene (GNHPG) foam by plasma-etching, which provided extra spaces and short
219 diffusion paths for the intercalation/deintercalation of AlCl_4^- anions throughout the 3D-
220 graphene foam. The as-prepared GNHPG material showed exceptionally high
221 electrochemical performance for RABs. The discharge capacity was doubled (123 mAh g^{-1})
222 compared to the 3D-graphene foams ($\sim 60 \text{ mAh g}^{-1}$) at high current density of 5000 mA g^{-1}
223 while maintaining a high coulombic efficiency of 98%. Furthermore, the GNHPG not only
224 enhanced the discharged capacity but an unprecedentedly high cycle life of 10000 cycles
225 was also obtained without any capacity decay (**Fig. 4 a**). The Al/GNHPG battery as well
226 demonstrated high rate capability at different current densities from 2000 to 8000 mA g^{-1} .
227 Another important feature of GNHPG based rechargeable aluminum battery was its

228 excellent electrochemical performance at different temperature ranges from 0 to 80°C (Fig.
229 4 b-c).

230 The carbon based cathode materials have contributed greatly by showing excellent
231 electrochemical performances in terms of better cycle stability, high rate capability and
232 high cell voltage for the RABs. FG has shown good capacity but short cycle life with low
233 average voltage plateau. The commercial carbon paper has proved to be a high working
234 voltage cathode material in RTIL electrolyte but suffered from structural disintegration,
235 volume expansion and high self-discharge rates. Whereas, in alkali chloroaluminate melt
236 electrolyte it has demonstrated good electrochemical performance but high operating
237 temperature curbed its practicability. In contrast to these, 3D carbons (3D-GF, 3D-GrF, 3D-
238 GMN and GNHPG) exhibited excellent cycling, ultrafast charging/discharging and high
239 rate-capability along with high voltage. The superior electrochemical performance of these
240 materials is enlightened by Lee et al.⁷⁴ and Jung et al.⁷⁵, who elucidated that the open
241 structured 3D configurations of graphitic foam plays a vital role in the ultrafast charging
242 and discharging. In addition, Wu et al.⁷⁶ confirmed the geometry and fast diffusion of
243 $[Al_xCl_y]^-$ anions in the graphite by first principle calculations. However, the capacity was
244 limited to 60 mAh g⁻¹ in these carbon based cathode materials except for GNHPF which
245 showed relatively high and stable discharge capacity of 123 mAh g⁻¹. The electrochemical
246 performance of these carbon based cathode materials is mainly due to the
247 intercalation/deintercalation of monovalent chloroaluminate anions rather than trivalent
248 Al³⁺ cations⁷⁷. The monovalent chemistry has placed limitations in the achievement of high
249 capacity RABs, so in order to improve the capacity without reducing the electrochemical

250 performance, a carbon-based cathode material which encourages trivalent reaction is highly
251 requisite.

252 **2.2 Transition metal oxide (TMOs) based cathode materials**

253 Transition metal oxides (TMOs), in contrast to carbon based materials, have also been
254 used as cathode materials for rechargeable batteries because they provide enough space for
255 intercalation/deintercalation during cycling^{78, 79}. Apart from batteries, these materials have
256 performed efficiently in photocatalysis, dye-sensitized solar cells and
257 photoelectrochemistry, owing to the various materials advantages such as surface area and
258 short solid state diffusion paths⁸⁰⁻⁸². Since RABs are multivalent-ion batteries, TMOs
259 could be good candidates for cathode materials, as they can accommodate more electrons
260 because of their multivalent nature.

261 The first report on the use of TMOs in RABs was presented by Paranthaman et al.⁸³.
262 They applied λ -Mn₂O₄ as a cathode material in AlCl₃/[EMIm]Cl electrolyte with a molar
263 ratio of 2:1. The Al/ λ -Mn₂O₄ battery system showed high discharge capacity of 400 mAh
264 g⁻¹ and energy density of 1060 Wh/kg compared to LiC₆-Mn₂O₄ system with discharge
265 capacity and energy density of only 106 mAh g⁻¹ and 424 Wh/kg, respectively. The RAB
266 retained 50% of its initial capacity after 50 cycles.

267 V₂O₅ has been widely employed in rechargeable batteries^{84, 85}. However, the slow
268 diffusion and rigid fixing of Al³⁺ ions between the V₂O₅ interlayers are key concerns of its
269 use in multivalent aluminum batteries. To overcome this issue, Jayaprakash et al.²⁷
270 synthesized uniform V₂O₅ nanowires by a facile hydrothermal method (**Fig. 5 a**), and
271 implemented it as a cathode in a RTIL electrolyte with the molar ratio of 1.1:1. A high
272 discharge capacity (305 mAh g⁻¹) was obtained on its first cycle (**Fig. 5 b**), and retained up

273 to 273 mAh g⁻¹ after 20 cycles. However, the coulombic efficiency was poor, in addition a
274 practical working voltage could not be maintained. The root cause of the poor performance
275 of this battery was investigated by Reed et al.⁸⁶. They found that the V₂O₅ cathode was
276 electrochemically inactive and the battery-like performance was principally associated with
277 the chromium and iron presented in the stainless steel current collector. These metals were
278 gradually deposited on the anode side of the separator followed by dendrite formation,
279 which consequently failed the battery after 20 cycles. To further elucidate the reactivity of
280 V₂O₅ towards Al in RTIL electrolyte, Wang et al.³⁰ developed a Ni foam supported binder-
281 free Ni-V₂O₅ cathode and proved that the V₂O₅ was reactive towards Al metal in acidic
282 RTIL electrolyte. They also compared the electrochemical performance of the binder-free
283 Ni-V₂O₅ cathode with PVDF and PTFE binder supported V₂O₅ cathodes and found that the
284 binder-free cathode showed much higher capacity than the binder-assisted cathodes.
285 Moreover, the direct synthesis of the V₂O₅ particles on the Ni foam improved the electrical
286 contact and also provided fast diffusion pathways for Al ions.

287 Recently, Gu et al.⁷⁷ demonstrated the reversible storage of Al³⁺ cations in the V₂O₅
288 nanowires. The electrochemical activity of V₂O₅ nanowires was observed against the Al
289 metal and two-phase transition reactions were suggested. It was concluded that Al³⁺ cations
290 could be intercalated reversibly into the metal oxide by the intercalation and phase-
291 transition reactions. In addition, formation of amorphous layers on the edges of nanowires
292 was observed due to the intercalation of Al³⁺ which reduced the V⁵⁺ state. Further, the
293 composite of carbon and amorphous V₂O₅ was studied by Chiku et al.¹⁸. The maximum
294 discharge capacity of over 200 mAh g⁻¹ was obtained for the first cycle. XPS analyses after
295 discharging and the subsequent charging showed the evidence for the occurrence of the

296 redox changes of the vanadium ion in the V_2O_5/C active material during discharging and
297 charging. Recently, González et al.⁸⁷ studied the reversible intercalation of Al ions into
298 orthorhombic V_2O_5 xerogel in 1 M $AlCl_3$ aqueous electrolyte instead of RTIL electrolyte.
299 When tested in a three electrode configuration cell, the as-prepared materials showed good
300 reversible capacity of 120 mAh g^{-1} at a current density of 60 mA g^{-1} . However, the water
301 and protons were also intercalated into V_2O_5 by means of chemical reactions or ion
302 exchange besides the electrochemical intercalation of Al ions. The use of aqueous
303 electrolytes for the multivalent Al batteries is very promising, but the reported battery
304 system here exhibited poor coulombic efficiency and limited cycle life.

305 The tunneled-structured VO_2 nanorods, which is considered to be a highly reversible and
306 stable cathode material for LIBs⁸⁸⁻⁹⁰, was investigated by Wang et al.²⁹ as potential
307 cathode material for RABs. The as-synthesized VO_2 nanorods (**Fig. 5 c**), with dimensions
308 of 60-100 nm in width and 1 micrometer in length and SSA of $37 \text{ m}^2 \text{ g}^{-1}$, exhibited a very
309 stable electrochemical performance in the RTIL electrolyte composed of $AlCl_3$ and 1-butyl-
310 3-methylimidazolium chloride ($[BMIm]Cl$) in a 1:1 molar ratio. The benzyl sulfoxide (0.5
311 wt%) was added to assist corrosion resistance because RTIL electrolytes have a corrosive
312 nature and could affect the battery performance by corroding the stainless steel current
313 collector and coin cell shells. The initial capacity was 165 mAh g^{-1} at the current density of
314 50 mA g^{-1} and retained up to 116 mAh g^{-1} after 100 cycles (**Fig. 5 d**). However, the
315 trapping of intercalation products inside the VO_2 tunnels might occur as suggested by the
316 over coulombic efficiency.

317 Anatase TiO_2 nanotube-arrays (TiO_2 -NTAs) were reported as a cathode material for
318 RABs in an aqueous $AlCl_3$ electrolyte by Liu et al.³⁴. The obtained results confirmed the

319 reversible intercalation/deintercalation of Al^{3+} cations into TiO_2 -NTAs due to the small
320 ionic radius of Al^{3+} (53.5 pm). The unique structure of the as-prepared TiO_2 -NTAs was
321 supportive for both the fast transport of electrons and the short ion diffusion paths.
322 However, the electrochemical performance of anatase TiO_2 -NTAs might suffer from the
323 formation of Al oxidative layers on Al anode, other corrosion products and parasitic
324 hydrogen evolution in aqueous systems that hinder redox reactions and lower the cell
325 potential^{48, 91}. Subsequently, Liu et al.⁸² found that Cl^- ions takes part in the
326 electrochemical insertion/extraction process of Al^{3+} in TiO_2 -NTAs. Sang et al.⁹² further
327 reported that in aqueous RABs, both H^+ and Al^{3+} have electrochemical activity towards
328 TiO_2 -NTAs. However, H^+ takes part in the surface hydroxylation of TiO_2 -NTAs and thus a
329 suitable pH value (~ 3) for AlCl_3 based aqueous electrolyte is requisite to minimize the
330 effect of H^+ .

331 TMOs are suggested as practical cathode materials for multivalent ion batteries due to the
332 variable valence and good stability of transition metals. The reported TMOs (V_2O_5 , V_2O
333 and TiO_2) in RABs, have presented high capacity than the carbon based cathode materials
334 but the cycle life, coulombic efficiency and cell voltage were compromised. Unlike
335 monovalent lithium, the strong coulombic effect induced by the trivalent Al cations makes
336 its electrochemical intercalation into a host crystal structure very challenging. Therefore,
337 the transition metal oxides, i.e., oxide anionic frameworks, may not be the ideal hosts for
338 RABs⁹³.

339 **2.3 Sulfide and Chloride based cathode materials**

340 Sulfide and chloride based materials have been utilized successfully in LIBs and
341 supercapacitors, due to their high theoretical capacities and good conductivity^{94, 95}. For

342 RABs, they were proposed as potentially high capacity cathode materials ¹⁹. Donahue et al.
343 ⁹⁶ introduced an iron(III) chloride (FeCl_3) based RAB utilizing a low-temperature molten
344 salt IL electrolyte induced by mixing AlCl_3 and $[\text{EMIm}]\text{Cl}$. However, the low utilization of
345 active material (FeCl_3) in the IL electrolyte limited the discharged capacities. Furthermore,
346 the self-discharge was also encountered inside the Al/AlCl_3 system due to the dissolution of
347 FeCl_3 into the IL electrolyte, its transfer towards the Al anode and the subsequent reaction
348 with it.

349 Vanadium chloride (VCl_3) was investigated by Suto et al. ³³ in molten RTIL electrolyte.
350 However, the monovalent reaction was found to take place after a few cycles in the Al/VCl_3
351 cell, instead of the multivalent reaction between V^{3+} and V^0 . It was also found that the
352 dissolution of VCl_3 in the RTIL electrolyte was greatly reduced by the addition of the
353 fluorobenzene (FB), although it did not change the VCl_3 reaction process but improved the
354 capacity retention with cycling. This study demonstrated a way of improving the discharge
355 capacity during charge/discharge cycles by controlling the dissolution of the cathode
356 materials using an electrolyte additive.

357 Besides iron chloride, iron sulfide (FeS_2) was also reported by Koura ⁵². Later on, Mori
358 et al. ³¹ reported FeS_2 in a RTIL electrolyte as a conversion cathode material for RABs and
359 investigated its reaction mechanism at 55°C . The pristine FeS_2 converted into poorly
360 crystalline FeS and amorphous Al_2S_3 and transformed back to FeS_2 during the
361 charging/discharging process (**Fig. 6 a**), which is different from the reaction observed in
362 monovalent LIBs. For practical applications, the battery suffered from the low cell voltage
363 and the poor cycle stability due to the dissolution of the sulfides into the chloroaluminate
364 RTIL, as suggested previously ¹⁹.

365 Recently, Wang et al.⁹⁷ reported a novel nickel sulfide and graphene microflake
366 ($\text{Ni}_3\text{S}_2/\text{Graphene}$) composite cathode material in a RTIL. The tantalum metal was selected
367 as a current collector because of its stability under the potential range of 0 to 2V against
368 $\text{Al}^{3+}/\text{AlCl}_4^-$. The RABs was constructed in a pouch cell assembly and showed a
369 comparatively high voltage plateau of nearly 1 V vs. $\text{Al}^{3+}/\text{AlCl}_4^-$. The cell discharge
370 capacity was as high as ca. 300 mAh g^{-1} for the first few cycles at the current density of
371 100 mA g^{-1} . However, after a few cycles, it was dropped to 60 mAh g^{-1} and then remained
372 constant till 100 cycles with a coulombic efficiency of 99% (**Fig. 6 b-c**). It was proposed
373 that the Al^{3+} cations were the main intercalating/deintercalating species in the small tunnels
374 (3 Å) of Ni_3S_2 rather than the larger chloroaluminate anions (5.28 Å³⁴). The abrupt drop in
375 capacity could be caused by the destruction of the lattice during the Al^{3+}
376 intercalation/deintercalation process. Furthermore, the phenomenon of self-discharge was
377 also examined by charging the battery to 2 and 1.5 V against the $\text{Al}^{3+}/\text{AlCl}_4^-$ followed by 12
378 h at rest position. In both cases the open circuit voltage (OCV) dropped to nearly 1.2 V. It
379 is elucidated that at high voltages some side reactions occurred which caused the self-
380 discharge in the reported RAB utilizing graphene-based hybrid cathode material.

381 More recently, hexagonal nickel sulfide nanobelts (NiS-nanobelts) were utilized as
382 cathode material for RABs based on $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$ RTIL electrolyte by Yu et al.⁹⁸. The
383 special nano-banded structure facilitated the electrolyte immersion and enhanced the Al^{3+}
384 diffusion. The Al/NiS battery showed stable electrochemical performance with the OCV of
385 1.17 V, the coulombic efficiency of 97.66% for the 100th cycle at a current density of 200
386 mA g^{-1} and charging /discharging capacities of 106.9 and 104.4 mAh g^{-1} , respectively.

387 However, the cell voltage plateau was low (1.15 V vs. Al^{3+}/Al) and the cycle life (~100
388 cycles) was also not satisfactory for practical RABs (**Fig. 6 d-e**). In addition, the NiS
389 showed the same behavior of self-discharge as graphene supported Ni_3S_2 when charged to
390 high cut-off voltages of 2 and 1.7 V and rested for 12 h, as the OCV descended rapidly to
391 approximately 1.2 V after the charging process completed.

392 In terms of sulfide other than nickel and ferric, very recently, Want et al.⁹⁹ reported 3D-
393 hierarchical copper sulfide (CuS) as a cathode material in RTIL electrolyte for RABs. In
394 the initial charge/discharge cycle a high discharge capacity of nearly 240 mAh g⁻¹ was
395 obtained at the current density of 20 mA g⁻¹. However, it descended shortly after few cycles
396 and then a stable discharge capacity of 90 mA g⁻¹ was retained up to 100 cycles. It is worth
397 noticing that the coulombic efficiency remained constantly as high as 100%. Still, the
398 reason behind the rapid decay of capacity in CuS microspheres has not been addressed.

399 Sulfides and chlorides have presented promising results as cathode materials for RABs,
400 but their dissolution into the electrolyte hampers the development of such materials as
401 practical cathodes. Even though additives were introduced into the electrolyte to control
402 dissolution process, this issue has still not been completely resolved. In order to avoid the
403 dissolution of the sulfides and chlorides into the electrolyte, a detailed investigation of the
404 electrochemical reaction mechanisms and extensive optimization of the cathode materials
405 are required. In particular, the optimization of the cathode morphology and further coating
406 with some conductive polymers or carbon materials may restrict the dissolution of the
407 sulfides and chlorides into the electrolyte and enhance the electrochemical performance of
408 the RABs as practiced in Li-S batteries^{100, 101}.

409 **2.4 Other types of cathode materials**

410 In addition to carbon, TMOs, sulfide and chloride based cathode materials, other types of
411 cathode materials are also reported for use in RABs. Hudak¹⁰² presented chloroaluminate-
412 doped conducting polymers, polypyrrole and polythiophene as cathode materials in a RTIL
413 electrolyte (AlCl_3 :[EMIm]Cl molar ratio 2:1). The reported conducting polymers
414 demonstrated discharge capacities between 30 and 100 mAh g^{-1} . In detail, polypyrrole
415 showed an initial discharge capacity of 71 mAh g^{-1} at 0.2C (20 mA g^{-1}) and retained 49
416 mAh g^{-1} after 100 cycles, whereas polythiophene exhibited more promising results with
417 discharge capacity of nearly 90 mAh g^{-1} with a capacity retention of 80% after 100 cycles
418 at 0.2C (16 mA g^{-1}). It was noted that a remarkable coulombic efficiency of 100% was
419 attained for both polymer based cathodes. However, the dissolution of active materials into
420 the electrolyte reduced the capacities. Furthermore, the discharge voltage profiles for both
421 conducting polymers sharply declined and showed average low discharge voltage, which
422 hindered the future development of conducting polymer based cathodes.

423 The Chevrel phase is worthy of mention in the development of RABs, which can be
424 envisaged as the pillaring of Mo_6S_8 blocks, where six molybdenum atoms form an
425 octahedron inside a cube of eight sulfur atoms¹⁰³. They possess superconductive, high
426 magnetic, thermoelectric and catalytic properties¹⁰⁴. The unique crystal structure ensures
427 an exceptionally high mobility of mono and multivalent cations (Li^+ , Ni^{2+} , Zn^{2+} , Ca^{2+} ,
428 Mg^{2+}) in the host Mo_6S_8 lattice, especially in the presence of the Mo_6 clusters that can
429 easily hold up to four electrons. Furthermore, two types of sites are presented between
430 sulfur cubes to accommodate metal cations^{103, 105-107}. The Chevrel phase was firstly
431 reported as cathode material for RABs by Geng et al.⁹³, who tested aluminum batteries in a
432 mixture of AlCl_3 and [BMIm]Cl with a molar ratio of 1.5:1 both at room temperature and at

433 50°C. At room temperature, the reaction rate was found to be sluggish because of the
434 coarse Mo₆S₈ particles, which resulted in poor coulombic efficiency. On the contrary, at
435 50°C, the coulombic efficiency was slightly more than 100% however, discharge capacity
436 remained at nearly 75 mAh g⁻¹ after 50 cycles (**Fig. 7 a**). Moreover, good reversibility was
437 observed at different current densities. The SEM image of Mo₆S₈ after 50 cycles showed
438 many cracks in the particle surfaces providing evidence of significant mechanical stress
439 during the intercalation/deintercalation process (**Fig. 7 b**). The greater than 100%
440 coulombic efficiency suggested that Al ions were slowly trapped in Mo₆S₈ crystals
441 (Intercalation/deintercaation>1). The estimated specific energy was roughly 90 Wh/kg with
442 a nominal cell voltage of 0.5 V.

443 The open-framework Prussian blue analogues (PBAs) are also very promising cathode
444 materials for interaction/deintercalation of monovalent and multivalent ions because they
445 possess large channels and interstitial A sites (**Fig. 7 c**)^{108, 109}. Based on this knowledge,
446 Reed et al.³² synthesized copper hexacyanoferrate (CuHCF) by a precipitation method. In
447 an organic electrolyte, aluminum trifluoromethane sulfonate (Al triflate) dissolved in
448 diethylene glycol dimethyl ether (diglyme) with a molar ratio of 1:5, CuHCF showed the
449 first discharge capacity of 60 mAh g⁻¹. However, the battery barely accomplished 10 to 15
450 cycles due to deformation of the crystal structure of CuHCF and anode passivation. The
451 Gaussian calculations suggested that the Al/Diglyme complex was the primary intercalating
452 species rather than free Al³⁺ ions, which kinetically hindered the insertion reaction and
453 probably lowered the electrochemical performance of the system.

454 Previously, PBAs were shown to present good electrochemical performance and long
455 cycle life with high rate capability for many monovalent and divalent ions (Li⁺, Na⁺, Mg²⁺)

456 in aqueous systems ¹⁰⁸⁻¹¹¹. The residual zeolitic water within the framework plays a
457 shielding role on the charge of multivalent ions and helps insertions of ions ¹¹⁰. Based on
458 this assumption, Liu et al. ¹¹² demonstrated PBA-CuHCF in an aqueous electrolyte and
459 obtained improved results compared to previously reported in an organic electrolyte. The
460 electrochemical performance was evaluated in a three electrode cell rather than a two
461 electrode battery system. In detail, CuHCF was applied as the working electrode, graphite
462 as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in
463 0.5 M Al₂(SO₄)₃ aqueous electrolyte. A high specific capacity of 62.9 mAh g⁻¹ was
464 obtained at a low current density of 50 mA g⁻¹. However, 46.5 mAh g⁻¹ was achieved at a
465 high current density of 400 mA g⁻¹ and retained up to 22.5 mAh g⁻¹ after 1000 cycles with
466 100% coulombic efficiency (**Fig. 7 d**). The gradual capacity fading was attributed to the
467 dissolution of the cathode material into the acidic aqueous medium.

468 The cathode materials other than carbons, TMOs, chlorides or sulfides have also shown
469 electrochemical performances for RABs. Those based on polymers and cheverel phase
470 Mo₆S₈ demonstrated high average capacities in the range of 30 to 100 mAh g⁻¹ and
471 coulombic efficiencies of 100%. The open framework PBA-CuHCF has proved to be a
472 promising cathode material for aqueous aluminum batteries with high cycle life and
473 excellent coulombic efficiency. However, none of these could be confirmed as high
474 capacity cathode materials for RABs and mostly suffered from low capacities and low
475 average cell voltages, which calls for further development and optimization of the cathode
476 materials and design principals of the cathode materials to achieve practical, high capacity
477 and high energy density RABs.

478 All of the above-quoted cathode materials for RABs are summarized in **Table. 2**.

479 **Conclusions and future outlook**

480 In this review, the cathode materials implemented in RABs to date have been summarised,
481 in a manner aimed at highlighting the successes and remaining issues which require
482 attention by current and future researchers and scientists intending to work on RABs.

483 The key characteristics of all reported cathode materials are described comprehensively
484 along with their electrochemical performances. Those based on carbons (FG, 3D-GF, 3D-
485 GMN and 3D-GrF, transition metal oxides, sulfides and chlorides, and other types of
486 cathode materials, including conducting polymers, open framework PBA-CuHCF and
487 Chevrel phase Mo_6O_8 , are reported. Besides these, composite cathode materials such as
488 carbon- V_2O_5 and hazelwoodite Ni_3S_2 /graphene are also considered. Among these, graphite-
489 based materials have shown the most promising results for RABs, while others have
490 suffered from numerous problems. For instance, (1) capacitive behavior without stable
491 discharge voltage plateaus, (2) very low discharge voltages, below 0.55 volts, (3) poor
492 reversibility and consequently low coulombic efficiencies, (4) low and unstable discharge
493 capacities with sharp decay after few cycles, (5) limited cycle life (~100 cycles), and (6)
494 structural disintegration and volume expansions due to the intercalation of large sized
495 intercalation products. All of these factors lead to the poor electrochemical performance
496 and hamper the commercialization of high energy density RABs.

497 In order to achieve practical, low cost and high energy density RABs for EVs and grid
498 storage applications, a potential cathode material should not be subject to any side reactions
499 with electrolytes and other battery components. Moreover, it should be mechanically strong
500 enough to retain its morphology and structure during the intercalation and deintercalation of
501 largely sized $[\text{Al}_x\text{Cl}_y]^-$ anions. Three-dimensional graphene foam (3D-GF & 3D-GrF and

502 GNHPG) and graphene mesh network 3D-GMN were shown to be the most feasible and
503 stable cathodes, since they demonstrated long cycle life and ultrafast diffusion of $[Al_xCl_y]^-$
504 anions between the graphene layers during cycling. In particular, 3D-GF and GNHPG
505 showed very excellent cycling and rate-capability performances up to 7500 and 10000
506 cycles at ultrahigh current densities of 4000 and 5000 mAh g^{-1} , respectively without
507 capacity fading. The open structured 3D configurations of graphitic foam and the fast
508 diffusion of $[Al_xCl_y]^-$ anions played a vital role in the ultrafast charging and discharging in
509 3D-graphene foams. These reports provide a positive outlook on the future prospects of 3D
510 structured graphitic materials, which could be a viable choice as cathode materials for
511 RABs. Most likely, 3D graphene or 3D graphene-based hybrid materials (GBHMs) could
512 address the previously highlighted limitations of these systems in the near future.

513 It is hoped this paper will provide readers with a better understanding of issues and
514 challenges faced by present cathode materials for RABs. It is believed that this review can
515 urge more researchers and scientists to seek out novel cathode materials and open up new
516 avenues in the development and commercialization of low cost, safer and high energy
517 density next generation RABs.

518

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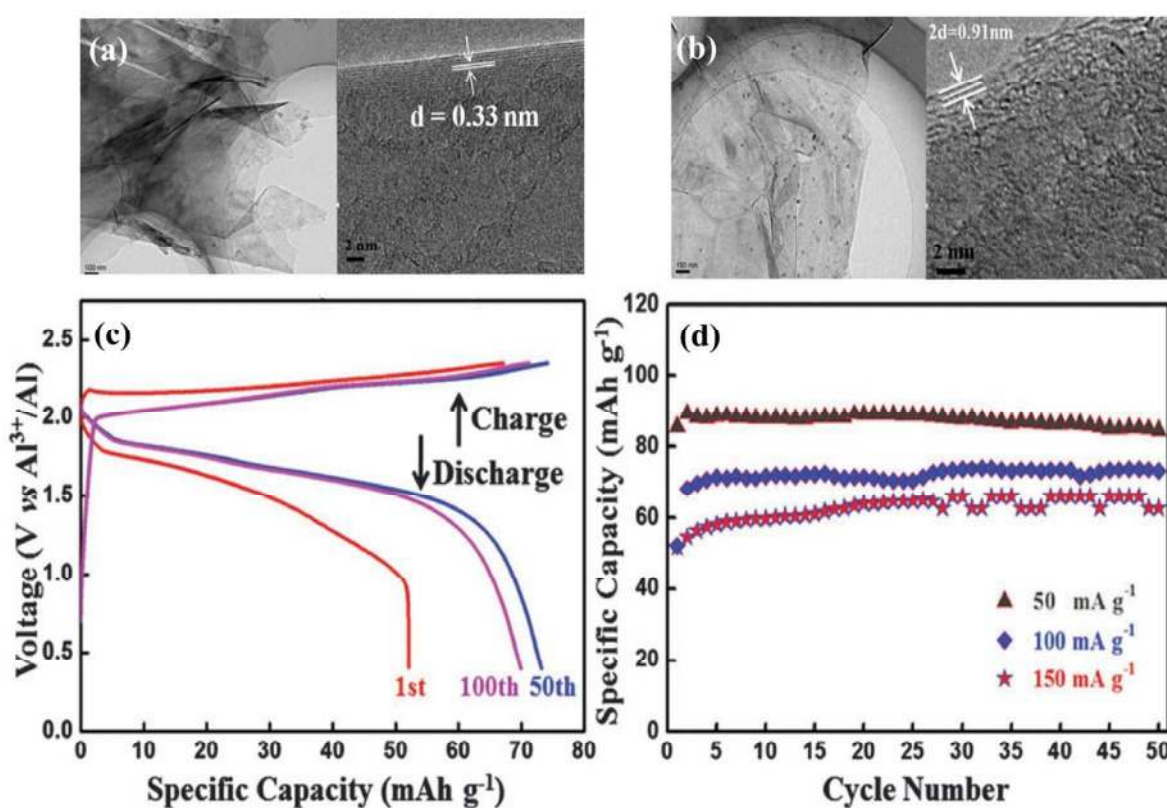
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735 **Figure 1**

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738 **Figure 1** (a) TEM (left) and HRTEM (right) images of Carbon-paper before, and (b) after739 charging, (c) Al/Carbon-paper battery charge–discharge curves at 100 mA g^{-1} for the 1st,740 50th and 100th cycles, and (d) Cycling performances at different current densities over 50

741 cycles. Reprinted with permission from Ref. ³⁵, Copyright 2015, Royal Society of
742 Chemistry.

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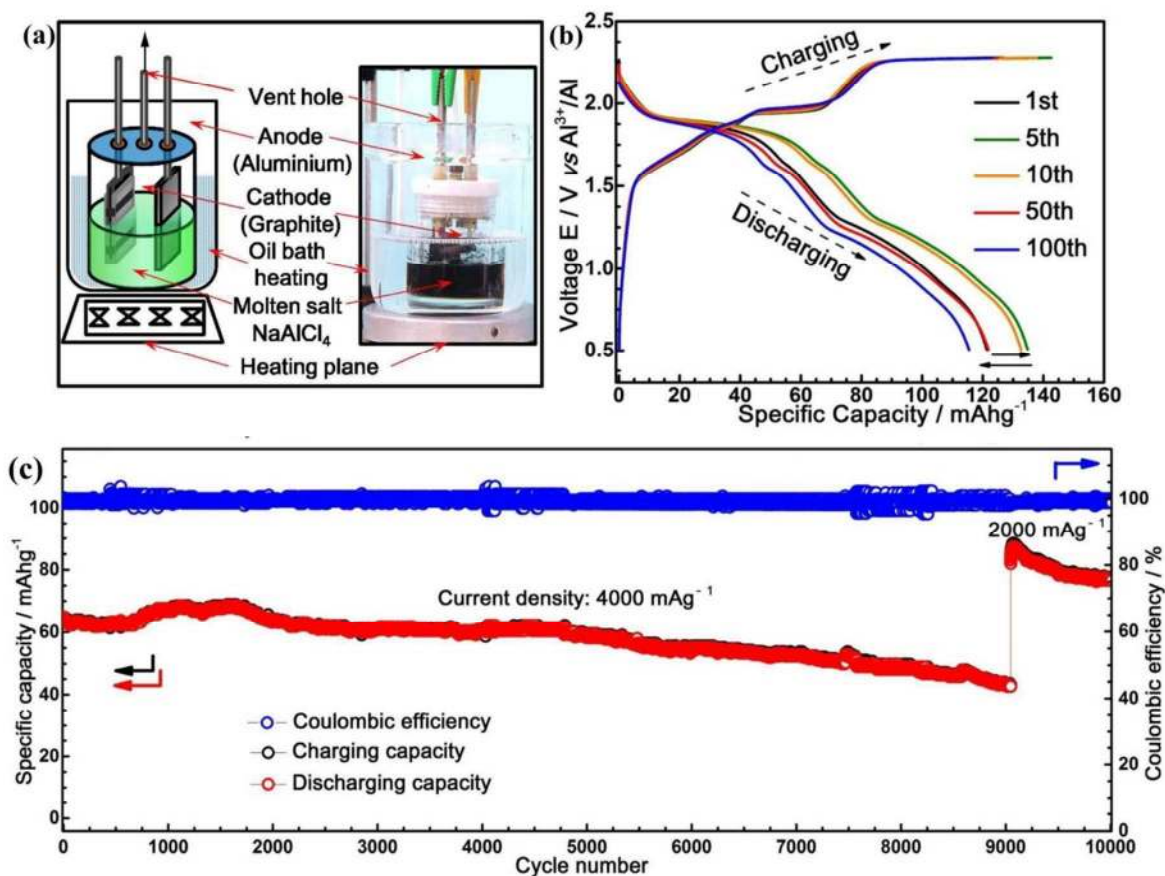
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748 **Figure 2**



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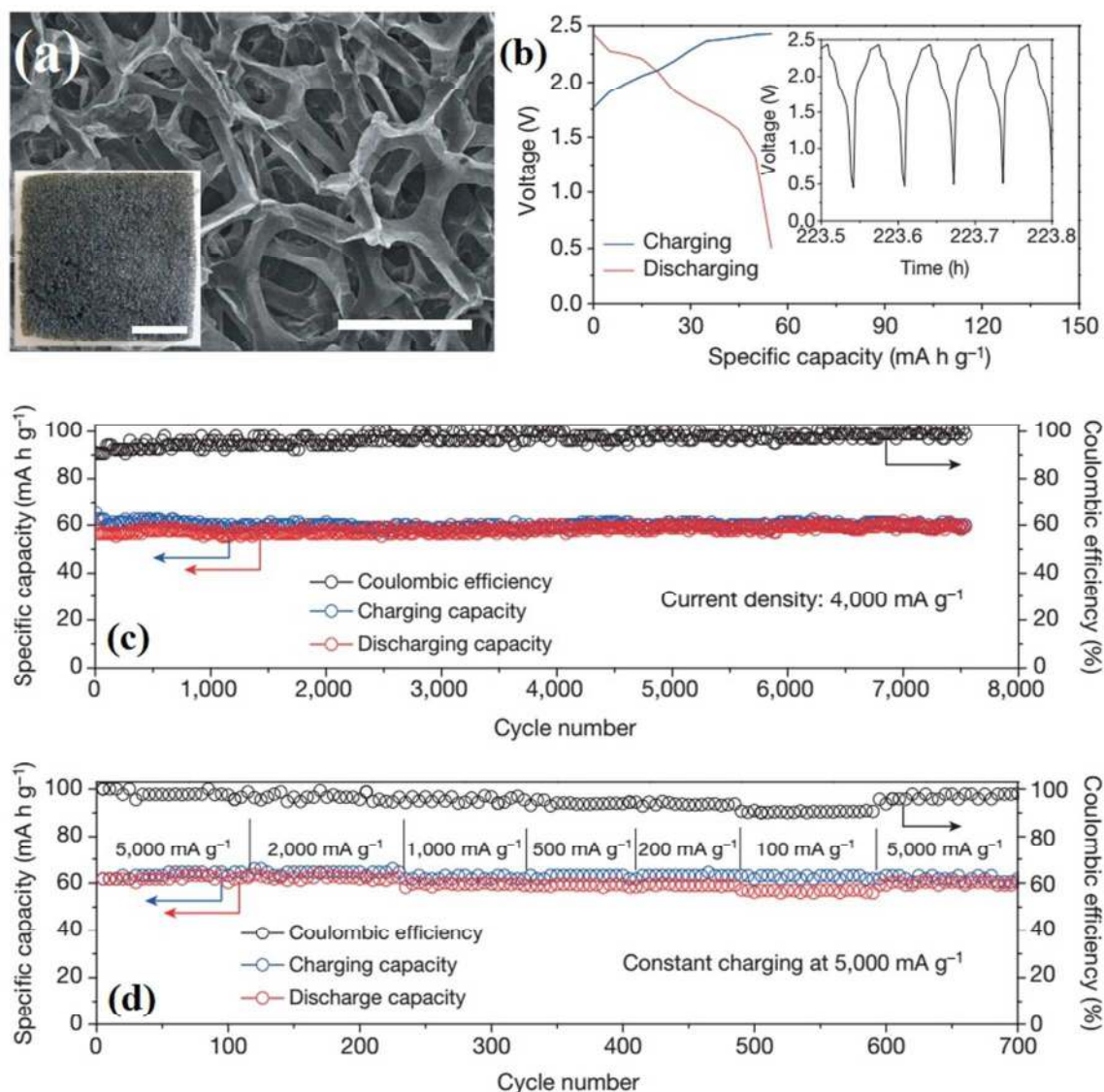
751 **Figure. 2** (a) Depiction of the rechargeable Al/graphite cell, (b) Charge–discharge curves
752 of 1st, 5th, 10th, 50th and 100th cycles at 500mA g⁻¹, and (c) The cycling performance of
753 the Al/carbon paper battery over 9000 cycles at a current density of 4000mA g⁻¹ and the
754 extra 1000 cycles at a current density of 2000mA g⁻¹. Reprinted with permission from Ref.
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759 **Figure 3**

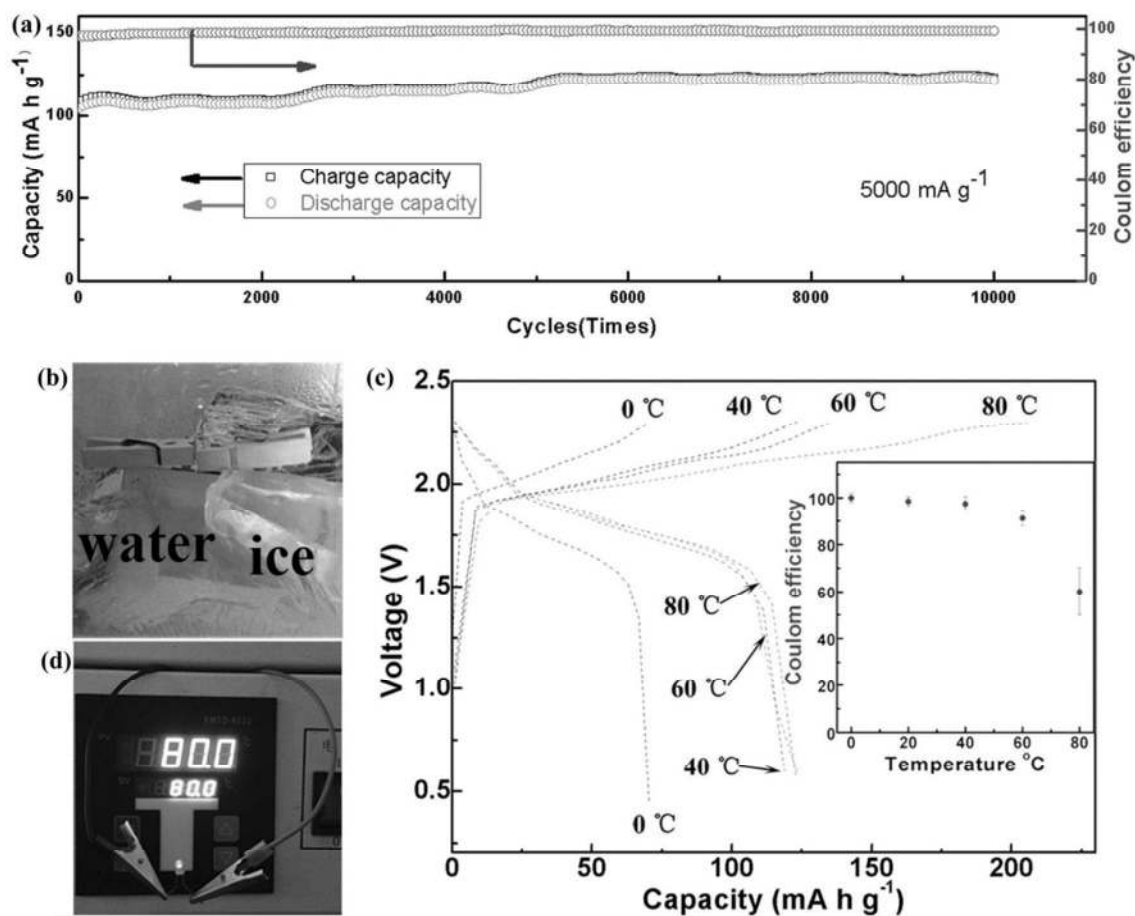


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761 **Figure 3** (a) SEM image of a 3D-GF with an open frame structure; scale bar, 300mm.

762 Inset, photograph of 3D-GF; scale bar, 1 cm. (b) Galvanostatic charge and discharge curves

763 of an Al/3D-GF pouch cell at a current density of 4,000 mA g⁻¹. (c) Cycle stability test of764 an Al/3D-GF pouch cell over 7,500 cycles at a current density of 4,000 mA g⁻¹ (d) An765 Al/3D-GF pouch cell charging at 5,000 mA g⁻¹ and discharging at different current766 densities. Reprinted with permission from Ref. ²⁶, Copyright 2015, Macmillan Publishers.767 **Figure 4**



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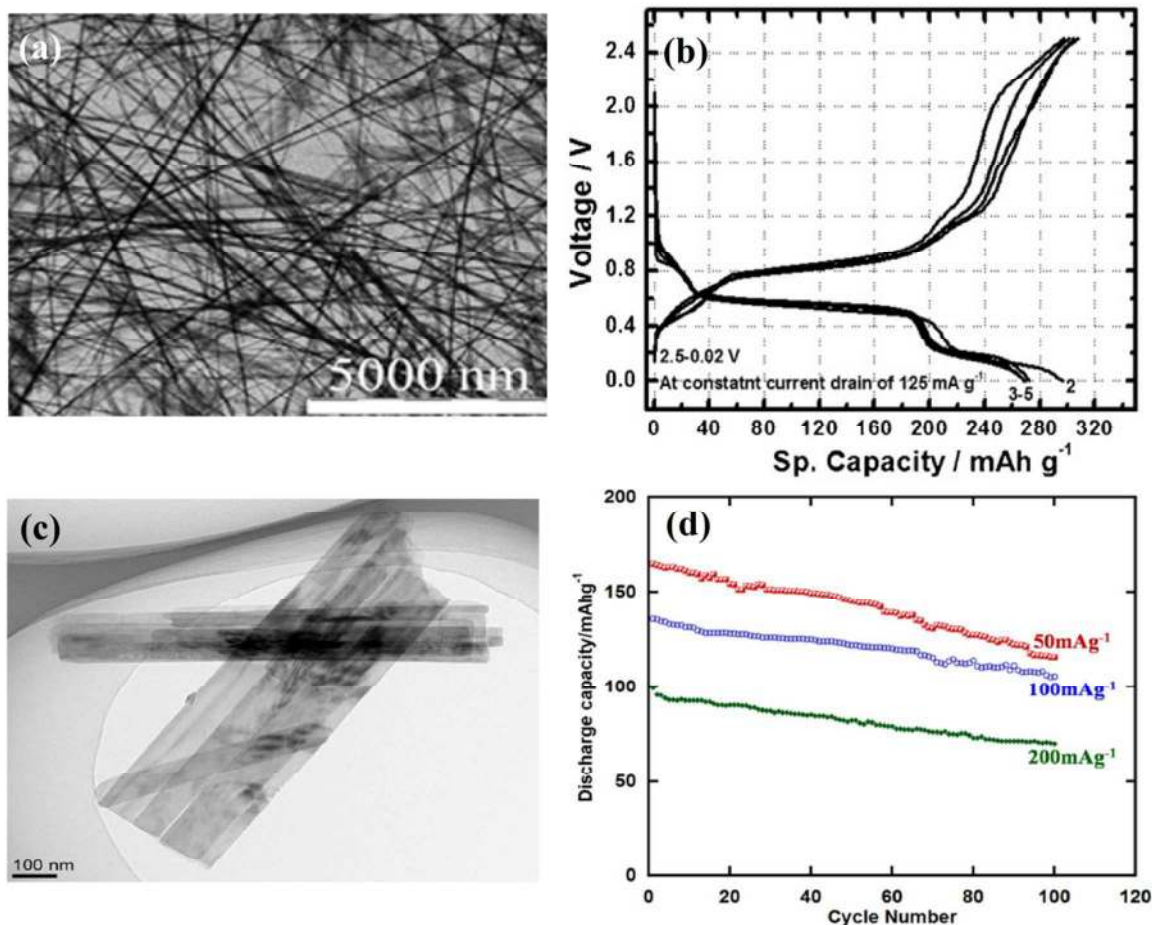
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770 **Figure 4** (a) Cycling performance of Al/GNHPG pouch cell at a current density of 5000 mA g^{-1} , (b)
 771 and c) Al/GNHPG pouch cell working at 0 and 80C, respectively as showing by illumined LED
 772 indicator (d) Charge and discharge curves at different temperatures of an Al/GNHPG pouch cell at a
 773 current density of 5000 mA g^{-1} . Reprinted with permission from Ref.⁷³, Copyright 2016,
 774 John Wiley and Sons.

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777 **Figure 5**



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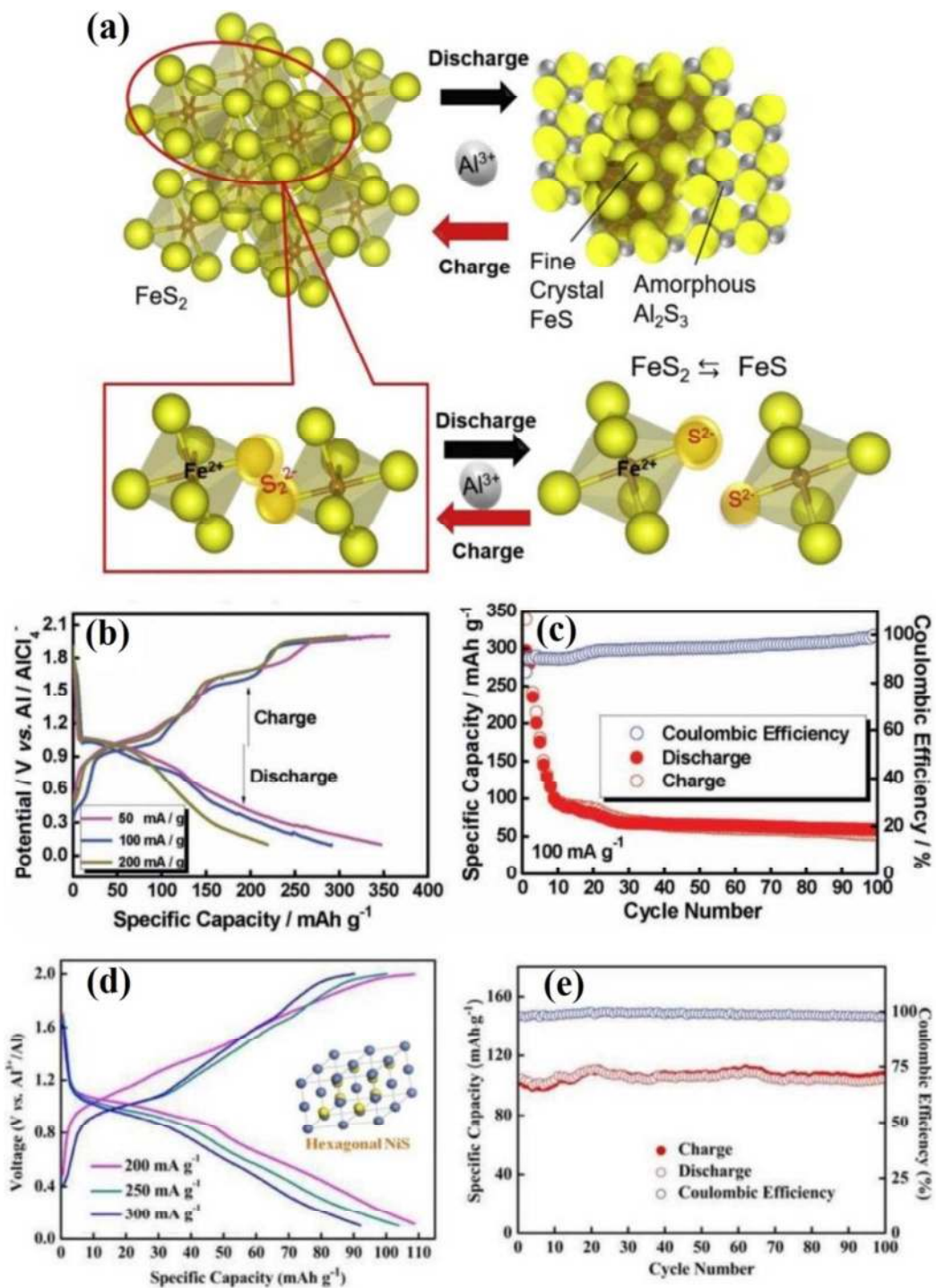
779 **Figure 5** (a) TEM image of V₂O₅-nanowires (b) V₂O₅-nanowires based rechargeable Al
780 battery charge/discharge curves for the first few cycles at constant current drain of 125 mA
781 g⁻¹. Reprinted with permission from Ref.²⁷ Copyright 2011, Royal Society of Chemistry.

782 (c) TEM image of VO₂ and, (d) Cycling performances of VO₂/Al battery under different
783 current densities over 100 cycles. Reprinted with permission from Ref.²⁹, Copyright 2013,
784 Macmillan Publishers.

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787 **Figure 6**



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789 **Figure 6** (a) Schematic charge-discharge reaction model of FeS_2 with aluminum ions at 55

790 °C, Reprinted with permission from Ref. [31], Copyright 2016, Elsevier Publishers (b) The

791 charge/discharge curves of $\text{Ni}_3\text{S}_2/\text{Graphene}$ cell for the second cycle at the current densities

792 of 50, 100, and 200 mA g⁻¹, respectively and (c) Its cycling performance and the coulombic
793 efficiency at a current density of 100 mA g⁻¹. Reprinted with permission from Ref.⁹⁷,
794 Copyright 2016, John Wiley and Sons. (d) The cycling performance and the Coulombic
795 efficiency of Al/NiS battery at a current density of 200 mA g⁻¹, inset, Hexagonal structure
796 of NiS and (e) The 10th charge and discharge curves under different current densities.
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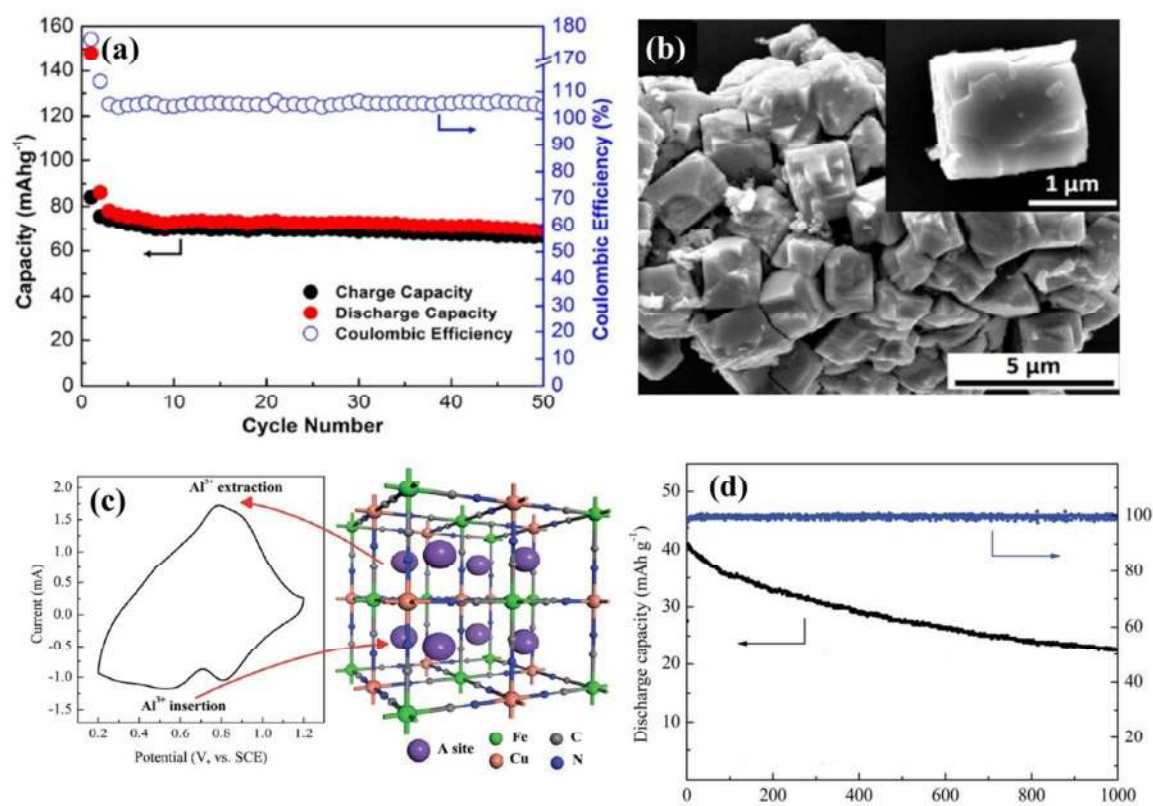
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814 **Figure 7**



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816 **Figure 7** (a) Cycle stability of Al/Mo₆S₈ battery, and (b) SEM image of Chevrel Phase
 817 Mo₆S₈, Reprinted with permission from Ref. ⁹³, Copyright 2015, American Chemical
 818 Society. (c) Typical CV curve of the CuHCF electrode in aqueous Al₂(SO₄)₃ (left) and the
 819 schematic positions of Al³⁺ in the interstitial A sites of CuHCF framework (right), (d) The
 820 cycle performance of Al/CuHCF based rechargeable Al battery at 400 mA g⁻¹ in 0.5 M
 821 Al₂(SO₄)₃ aqueous solution, inset, the schematic positions of Al³⁺ in CuHCF framework.
 822 Reprinted with permission from Ref. ¹¹², Copyright 2015, Royal Society of Chemistry.

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824 **Table 1.** A comparison of characteristics of aluminum metal with other metals

Category	Na	Ca	Mg	Li	Al	Ref.
Cation radius (Å)	1.02	0.99	0.72	0.76	0.535	¹¹³
Atomic weight (g mol ⁻¹)	22.99	40.07	24.30	6.94	26.98	¹¹⁴
E° (vs. SHE)	-2.71	-2.84	-2.35	-3.05	-1.67	¹¹⁵
Abundance in Earth's crust (wt%)	2.56	2.94	1.35	0.0022	7.74	²⁵
Capacity (mAh g ⁻¹), metal	1165	1337	2205	3861	2980	¹⁰
Energy density (mAh ml ⁻¹)	1128	2073	3833	2262	8046	¹⁰
Electrochemical Equivalent (g Ah ⁻¹)	0.8577	0.7477	0.4534	0.259	0.3355	¹¹³

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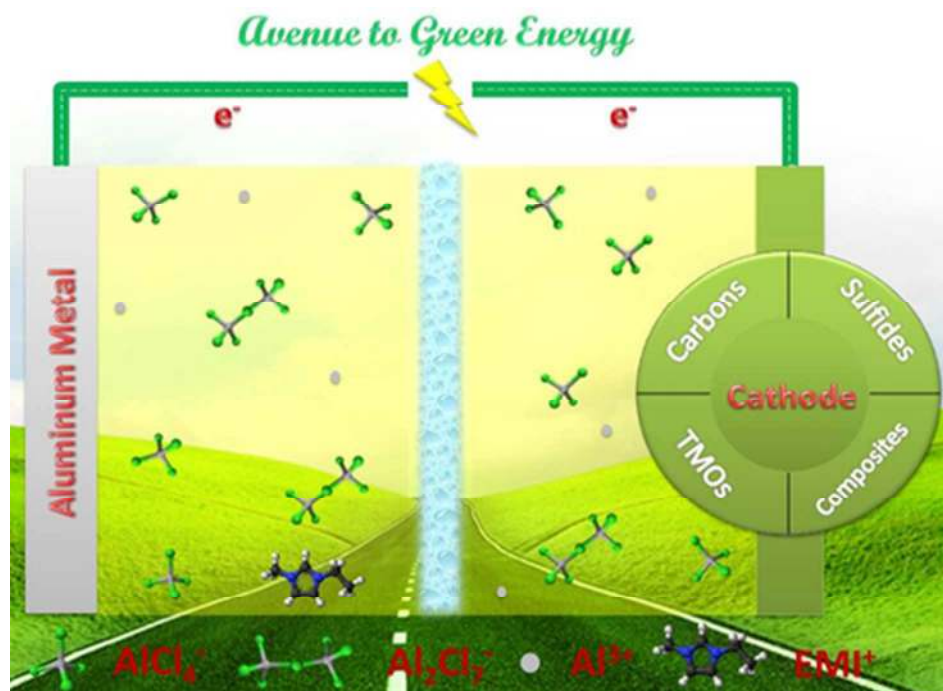
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838 Table 2. Summary of all cathode materials for RABs.

Cathode Material	Publication Year	Initial capacity* (mAh g ⁻¹)	Capacity retention (mAh g ⁻¹)	Current density (mA g ⁻¹)	Mean cell voltage (Volts)	Cycle life	Coulombic efficiency (%)	Electrolyte (Molar ratio)	Ref.
V ₂ O ₅ nano-wires	2011	305	273	125	0.5	20	~88	1.1:1 AlCl ₃ : [EMIm]Cl	27
Anatase TiO ₂ -NTAs	2012	50	75	4 mAcm ⁻²	0.98	13	N/A	1M AlCl ₃ aqueous solution	34
FG	2013	208	225	60	0.65	40	75	0.5:1 AlCl ₃ : [BIm]Br	28
Polypyrrole	2014	71	49	20	1.42	100	100	1.5:1 AlCl ₃ : [EMIm]Cl	102
Polythiophene	2014	89	71.5	16	1.47	100	100	1.5:1 AlCl ₃ : [EMIm]Cl	102
V ₂ O ₅ /C	2015	150	~75	0.05C	<1.0	30	N/A	1:10:5 AlCl ₃ :Dipropylsulfone:Toluene	18
Mo ₆ S ₈ [#]	2015	148	70	6	0.50	50	>100	1:1 AlCl ₃ : [BMIm]Cl	93
PG	2015	60	66	66	~2.0	>200	98.1	1.3:1 AlCl ₃ : [EMIm]Cl	26
3D-GF	2015	~60	60	4000	~2.0	7500	98	1.3:1 AlCl ₃ : [EMIm]Cl	26
CuHCF	2015	41	22.5	400	0.54	1000	100	0.5M Al ₂ (SO ₄) ₃ aqueous solution	112
Ni-V ₂ O ₅	2015	239	N/A	44.2	0.6	N/A	N/A	1:1 AlCl ₃ : [BMIm]Cl	30
Ni ₃ S ₂ @Graphene	2016	235	50	200	~1.0	300	99	1.3:1 AlCl ₃ : [EMIm]Cl	97
3D-GMN	2016	57	57	3000	N/A	200	97.5	1.3:1 AlCl ₃ : [EMIm]Cl	72
NiS	2016	104.7	104.4	200	1.17	100	97.66	1.3:1 AlCl ₃ : [EMIm]Cl	98
CuS	2016	240	90	20	~1	100	100	1.3:1 AlCl ₃ : [EMIm]Cl	99
3D-GrF	2016	60	60	12000	1.8	4000	100	1.3:1 AlCl ₃ : [EMIm]Cl	71
Carbon Paper ^{\$}	2016	60	43	4000	~1.8-1.2	9000	99	1.63:1 AlCl ₃ : NaCl	51
GNHPG	2016	123	123	5000	~2.0	10000	98	1.3:1 AlCl ₃ : [EMIm]Cl	73

839 #: Electrochemical performance at 50 °C

840 \$: Electrochemical performance at 120 °C



39x29mm (300 x 300 DPI)