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George Zheng Chen



**University of
Nottingham**

UK | CHINA | MALAYSIA

University of Nottingham Ningbo China, 199 Taikang East Road, Ningbo, 315100, Zhejiang, China.

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Supercapattery: Merit-merge of capacitive and Nernstian charge storage mechanisms

George Zheng Chen^{1,2}

¹ Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

² Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo China, University Park, Ningbo 315100, China

Email: george.chen@nottingham.ac.uk

Abstract

Supercapattery is the generic name for hybrids of supercapacitor and rechargeable battery. Batteries store charge via Faradaic processes, involving reversible transfer of localised or zone-delocalised valence electrons. The former is governed by the Nernst equation. The latter leads to pseudocapacitance (or Faradaic capacitance) which may be differentiated from electric double layer capacitance with spectroscopic assistance such as electron spin resonance. Since capacitive storage is the basis of supercapacitors, the combination of capacitive and Nernstian mechanisms has dominated supercapattery research since 2018, covering nanostructured and compounded metal oxides and sulfides, water-in-salt and redox active electrolytes and bipolar stacks of multi-cells. The technical achievements so far, such as specific energy of 270 Wh/kg in aqueous electrolyte, and charging-discharging for over 5000 cycles, benchmark a challenging but promising future of supercapattery.

Keywords

Supercapattery, Nernstian storage, delocalised valence electrons, pseudocapacitance, bipolar electrode, water-in-salt electrolytes, redox active electrolytes

1. Challenges to conventional electrochemical energy storage

Replacing fossil fuels by renewables requires energy storage, for which electrochemical energy storage (EES) devices are a desirable fit because of their modular nature, commercial choices and potentially fossil-comparable energy capacity. On the last point, oxidation of lithium in electrochemical cells causes a Gibbs energy change ($\Delta G_{\text{Li}}^{\circ} = 8.56 \text{ kWh/kg}$ at 1000 °C) that is comparable to that of coal combustion (9.16 kWh/kg) in internal combust engines (ICEs) [1]. Representative commercial EES devices include rechargeable batteries (RBs) and supercapacitors (SCs), whilst flow batteries are suitable for stationary and large scale storage [2-4]. Although far better in energy efficiency than ICEs (ca. 20%), EES devices have neither performed to expectations. Laboratory-tested lithium-air battery (LAB) and commercial lithium-ion battery (LIB) can only store energy up to 1.0 and 0.3 kWh/kg, respectively, pending further improvement in rate and durability.

Performance wise, RBs offer higher storage capacity than SCs which are however better in power capability, energy efficiency, and cycle life. These complementary merits have encouraged development of several hybrid devices, including lithium-ion capacitors, redox

capacitors, and pseudocapacitors [5]. These hybrids store charge differently from a capacitor, but the word capacitor in these names has led to misuse of capacitance as a performance indicator [6]. For unambiguous classification and comparison, the generic name supercapattery (= **supercapacitor** + **battery**) was proposed in 2007, followed by laboratory demonstration later [7,8]. In fact, combination of capacitive and lithium storage electrodes was reported in earlier literatures, although the term “lithium-ion capacitor” (LIC) first appeared also in 2007 [9-12]. Because of their close relation with LIBs, research and development of LICs have progressed fast, along with other ion capacitors [13-15]. On the contrary, supercapattery rarely appeared in the literature before 2015. The recent growing interests are partly driven by curiosity and exploration of new and improved EES mechanisms, materials and devices beyond SCs and RBs [16-18]. The other and more fundamental reason is related to pseudocapacitance that has been, unfortunately, misused to account for the behaviour of many new transition metal compounds that are capable of Nernstian storage.

2. Pseudocapacitance explained

All rechargeable EES devices work following one or a combination of electric double layer (EDL) capacitive, pseudocapacitive and battery-like mechanisms [4]. EDL storage is physical at the electrode/electrolyte interface, whilst the latter two involve charge transfer reactions on electrode and hence are both Faradaic in nature. Battery-like or Nernstian storage is widely known to result from reversible electrode reactions that are broadly governed by the Nernst equation. It is featured by peak-shaped cyclic voltammograms (CVs) and by potential plateaux on galvanostatic charging-discharging plots (GCDs). Pseudocapacitance (or Faradaic capacitance) presents features same as those of EDL capacitance, namely rectangular CVs and linear GCDs. A hypothesis explains such differences by the transfer of localised and partially or zone-delocalised valence electrons, leading to Nernstian and pseudocapacitive responses, respectively [19]. It agrees with density functional theory modelling of oxygen doped graphenes [20,21]. According to the band model [22], localised valence electrons have a fixed electronic energy level, corresponding to a fixed potential for their transfer. This in turn leads to peak-shaped CVs, and plateau-featured GCDs for Nernstian storage. For zone-delocalised valence electrons as in semiconductors (instead of full delocalisation as in metals and perfect monolayer graphene), their very close electronic energy levels are merged to a sufficiently wide band, into or from which electron transfer occurs in a continuous range of potentials. This hypothesis reflects well the rectangular CVs and linear GCDs for pseudocapacitive storage.

Although electrochemical characteristics of pseudocapacitance and EDL capacitance are recognised to be the same [4,6,23-25], some authors claimed differentiation between the two based on simulation against equation (11) or (12) below [26-28],

$$i = av + bv^{1/2} \quad (11)$$

$$i = mv^n \quad (12)$$

where i and v are the current and potential scan rate of the CV, respectively, and a , b , m and n are constants. For surface confined processes, $b = 0$, $n = 1$, but under diffusion control, $a = 0$, $n = 1/2$. Otherwise, the electrode reaction is under mixed control. It was assumed, but incorrectly, that the EDL currents resulted from surface confined changes and hence were

proportional to v , whilst Faradaic contributions were diffusion controlled, showing a linearity of i on $v^{1/2}$. Obviously, these assumptions contradict the basic knowledge that surface confined processes, either capacitive or Nernstian, dominate the behaviour of relatively thin electrode coatings. Also, diffusion control could happen in relatively thick electrode coatings, into or from which transport of ions are necessary to maintain charge neutrality, for both capacitive and Nernstian processes.

In fact, a Faradic process, either Nernstian or capacitive, always unpairs or pairs electrons in the atomic or molecular orbits, which in turn generates or demolishes spins that can be monitored by electron spin resonance (ESR) spectroscopy [29,30]. Fig. 1a shows the CVs of polyaniline (PAn). Whilst the three peak couples (A1/C1, A2/C2 and A3/C3) are well explained elsewhere [33,34], the capacitive responses are evident between 0.1 and 0.5 V. For comparison, Fig. 1b presents a typical cyclic esrogram of PAn between -0.2 and 0.5 V [30]. It can be seen that the ESR signal varied similarly as the currents on the CVs between 0.1 and 0.5 V, which is strong evidence of Faradaic dis-/charging with insignificant EDL contribution, if any. Note that A1 on the esrogram is at a more positive potential than A1 on the CVs. This difference is due to the ESR signal being proportional to the amount of charge passed, instead of the charge flow rate, i.e. the current.

Ironically, pseudocapacitance is responsible for the synthesis and test of a large number of nanostructured transition metal compounds, specially nickel and cobalt based oxides. These materials typically showed Nernstian features with appreciable power capability and cycling durability, but were unfortunately interpreted by pseudocapacitance with misleadingly high capacitance values [31,32]. Following several criticisms [4-6, 24,35], such Nernstian materials have been coupled with EDL materials in supercapatteries [36-45].

3. Basics of supercapattery and early development

Aiming at merging the merits of SC and RB [4,5,18,24], supercapattery engages with both capacitive and Faradaic mechanisms [18,46]. Because capacitive storage can be EDL or pseudocapacitive, and Faradaic storage can be pseudocapacitive or Nernstian, there is a large number of combination options.

Supercapattery behaviour can result from materials, such as heat treated nickel hydroxide films which exhibited fairly rectangular CVs from 0 to 0.35 V vs. SCE, but presented large current peaks at more positive potentials in aqueous KOH [47]. Composites of manganese oxides (MnO_x , $1.5 < x \leq 2$) with carbon nanotubes (CNTs) or graphenes can also store charges in mixed mechanisms [48-50]. Further, engaging electron transfer reactions of soluble species, such as iodide ions, with EDL capacitance of a porous carbon electrode is another effective way to combine capacitive and Nernstian mechanisms [24,52-54].

The device approach to supercapattery considers the relations between the two electrodes. Firstly, the charges passing through the capacitive (Q_{cap}) and Nernstian (Q_{bat}) electrodes must be equal as expressed by equation (13) [4] where Q_{sp} is the specific charge, and C_{sp} the specific capacitance.

$$Q_{bat} = m_{bat} Q_{sp} = m_{cap} C_{sp} \Delta E_{cap} = Q_{cap} \quad (13)$$

$$\Delta E_{cap} = \frac{Q_{sp} m_{bat}}{C_{sp} m_{cap}} \quad (14)$$

Equation (14) is useful for designing supercapattery, disregarding whether the capacitive or Nernstian electrode is the positrode or negatrode.

Secondly, equal currents occur on both electrodes at any time. For reversible storage in thin films, equation (15) governs the relation, linking with the Nernst equation (16) for reduction (charging on positrode, or discharging on negatrode) [4]:

$$i_{cap} = m_{cap} C_{sp} \frac{dE_{cap}}{dt} = \frac{nF\Gamma_{redox}}{t} = i_{bat} \quad (15)$$

$$E_{bat} = E_{bat}^o + \frac{RT}{nF} \ln\left(\frac{1-x}{x}\right), \quad x = \frac{\Gamma_{redox}}{\Gamma_{total}} = \frac{it}{nF\Gamma_{total}} \quad (16)$$

where Γ is the amount of the relevant or all redox species in the thin film. Equations (15) and (16) were used to calculate the GCD plots in Fig. 2a to 2c [4]. In practical cases, charging capacitive electrodes, either EDL or Faradaic, is highly reversible and hence fast. Thus, in the calculations, the charging rates of the cell are assumed to be such that the Nernstian electrode could respond in accordance with the Nernst equation (16). These are indeed achievable as shown by the experimentally recorded GCDs in Fig. 2d to 2f [38,55,56].

4. Selected progresses between 2018 and 2019

4.1. Electrode materials

Since 2018, supercapattery research, excluding ion capacitors which are reviewed elsewhere [13-15], has focused on novel nanostructured and compounded Nernstian materials [16,17,37-45]. For example, hydrothermal doping 40% sulfur into FeCo_2O_4 produced nanocaterpillars, and increased the capacitance to 1801 F/g from 779 F/g without doping at 2 A/g. The CVs and GCDs were fairly capacitive, but the capacitive potentials ranged only from 0 to 0.5 V vs. Ag/AgCl. Supercapatteries made from an undoped FeCo_2O_4 negatrode and the sulfur-doped positrode performed very well in aqueous 3 mol/L KOH. The cell voltage was 1.45 V, achieving specific energy and power of 140 Wh/kg and 1434 W/kg, respectively, and over 5000 dis-/charging cycles [16]. However, CVs and GCDs of the supercapattery showed clear resistive distortion, indicating higher resistance of the undoped negatrode. Also, energy efficiency estimated from the GCD at 2 A/g was lower than 60%.

Nanosheets of MoS_2 were hydrothermally grown in the pores of a carbon nitride template [17]. In aqueous 1 mol/L KOH, the composite showed Nernstian CVs and GCDs from 0.0 V to 0.5 V. The specific charge capacity reached over 500 C/g. Surprisingly, a symmetrical supercapattery was built from this material, leading to unreasonable tests and results.

An interesting Nernstian positrode was made from nanosheets of carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [45]. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ offers three valence states of V (III, IV and V), corresponding to storage of three Li^+ ions per formula at high positive potentials, > 3.8 V vs Li/Li^+ . With an activated carbon negatrode in mixed organic carbonates, the supercapattery was tested to 2.7 V to ensure reversible lithium storage in $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. The cell GCDs presented two shoulders, reflecting two steps of lithium storage. Reported specific energy and power were 53 Wh/kg and 3 kW/kg, respectively. However, after 2000 cycles, capacity loss reached 35%, apparently because repeated lithium-ion insertion and removal caused microscopic fatigue damage in the positrode.

Carbon negatodes are often chosen for aqueous electrolytes, imposing high overpotentials for hydrogen evolution. Further, nano-pores of activated carbon permit proton or water reduction to adsorbed hydrogen atoms or molecules, but restrict their nucleation and growth into bubbles. These adsorbed hydrogen species can also be re-oxidised and hence increase charge storage capacity [57,58].

More desirable negatodes are based on active metals because of their very negative redox potentials and reversible electrode reactions [13-15,55,56]. The concern on dendritic deposition upon cycling are addressed by several approaches, such as pulsed charging for both zinc and lithium deposition [59,60] and using 3D structured (porous) current collectors (e.g. copper foam) for lithium deposition [61,62].

Transition metal oxides are usually used on positrode, but iron or tungsten oxide undergoes reversible changes at negative potentials [63-65]. The crystalline/amorphous core/shell structured iron oxide with oxygen vacancies exhibited both capacitive and Nernstian features in 1 mol/L LiOH as shown in Fig. 3a and 3b. Specific capacitance of 701 F/g was claimed as averaged from the GCD plot. However, the reported GCD at 0.5 mA/cm² was non-linear, whilst the equation used for capacitance calculation, $C_s = \frac{I\Delta t}{m\Delta E}$, actually gives results for the inserted triangular dashed line in Fig. 3b. Thus, the performance should be better represented by specific charge. Further, the GCD is asymmetrical along the time axis, showing longer times for charging than discharging, suggesting a Columbic efficiency much lower than that for a true capacitive electrode.

Fig. 3c and 3d compare the CVs and GCDs of WO₃ and W₅O₁₄. Clearly, the oxygen deficient W₅O₁₄ performed better. In addition, the crystalline W₅O₁₄ contained more ion channels than WO₃. Consequently, the specific capacitance increased from 371 F/g for WO₃ to 524 F/g for W₅O₁₄ as derived from fairly linear GCDs. Note that, against convention, the GCDs in Fig. 3d start from discharging and then charging.

4.2. Electrolytes

Aqueous electrolytes match well with many redox materials [16-18, 37-44], and support cells to work at high voltages (>12.4 V) without water decomposition. For example, lead-acid batteries use sulfuric acid as electrolyte and work at >2.0 V.

An advanced approach to avoiding water decomposition is to use the so called water in salt (WIS) electrolytes in which all water molecules are bounded to, or surrounded closely by salt ions, water decomposition may not occur up to 3.0 V [66-69]. However, because of the minimum separation by a few layers of coordination and solvation water molecules, and hence strong attractions between cations and anions, WIS electrolytes show high viscosity and low conductivity. Addition of co-solvents could improve the performance, but also narrow the potential window [67,70].

Non-aqueous electrolytes, including ionic liquids, offer wider potential windows for utilising the very negative potentials of, for instance, lithium metal or lithiated carbon [9-11,13-15,45,71-73]. In such cases, the electrolyte not only conduct ions, but also participate in redox reaction, e.g. lithium-ion reduction or intercalation, which contributes directly to dis-/charging of the cell.

Similarly, redox electrolytes also help enhance storage in supercapacitors via both capacitive and Nernstian mechanisms [51-54,74]. Comparing with making new electrode materials, dissolved redox species (DRS) in electrolyte offer a simpler and cheaper approach to enhanced storage. A key issue is the cycling of electro-reacted DRS between the positive and negative electrodes via diffusion. For example, halide ions (X^-) are the early DRS [51,74] with a reversible electro-reaction of $3X^- = X_3^- + 2e^-$. Because both X^- and X_3^- are anions, they should be electrostatically attracted to, and trapped inside the pores of the activated carbon positive electrode. However, oxidation of I^- occurs near the equal potential of the positive and negative electrodes at full discharge, causing insufficient electrostatic attraction and hence redox cycling [52]. This understanding explains the current peaks near 0 V on the cell CV in Fig. 4a, and agrees with the absence of any current peaks on the CVs in Fig. 4b for the cell containing Br^- whose oxidation potential is about 500 mV more positive than that of I^- . Fig. 4c shows that simply discharging the cell to 0.1 V (not 0 V) also eliminated redox cycling [53]. By doing so, the cell repeated dis-/charging at 0.5 A/g to 4000 cycles with only 4 % capacitance loss.

4.3. Emerging merit-merging innovations

A particular recent progress is the combination of more than two storage mechanisms into supercapattery. A zinc-bromine supercapattery was studied, combining EDL capacitive, pseudocapacitive and Nernstian storage [54], although the claimed pseudocapacitive storage was in fact Nernstian with Br^- oxidation. This supercapattery was tested to 270 Wh/kg at 9300 W/kg with 81% capacity retention after 5000 cycles.

The combination of a positive electrode of the polyaniline/nano carbon fibres (NCF) composite, a NCF negative electrode for lithium intercalation, and a polymer gel electrolyte had led to a flexible supercapattery that offered specific energy of 106.5 Wh/kg, and 70.3% capacity retention after 9000 cycles [75].

Last but not the least, the sandwich configuration of supercapattery (and supercapacitor) permits to use bipolar electrodes to serially stack multi-cells [76]. A basic advantage is that if n cells are to be serially connected, the number of electrodes is $2n$ for external connection, but $n+1$ for bipolar stacking [76]. This will reduce significantly the mass and volume of the stack, and benefit to all gravimetric and volumetric properties. Importantly, the bipolar plates must be both liquid and gas proof. While the initial effort used titanium foils as the bipolar plates, it was shown that 50 μm thick carbon black/polyethylene composite films could be sufficiently conductive (through the film plane) and non-permeable, which also helped the fabrication of pouch cells for stacking [77]. The stack of bipolarly connected Zn- Br_2 cells performed satisfactorily, reaching 50 Wh/L and 500 W/L with less than 1 % loss over 500 dis-/charging cycles. Graphite plates with vertically grown CNTs on both sides were also used to stack EDL cells that retained 96.7% of the initial capacity after 50000 cycles [78].

5. End remarks

Supercapattery is being developed amongst questions on what should be defined for battery and supercapacitor, particularly in relation with the confusion on pseudocapacitance. It is identified that electrode reactions can involve the transfer of either localised valence electrons governed by the Nernst equation which is the basis of batteries, or zone-delocalised valence electrons leading to pseudocapacitive behaviour. Aiming at merging the merits of Faradaic Nernstian and capacitive storage mechanisms, supercapattery research has progressed steadily since 2018, utilising nanostructured and compounded metal oxides and sulfides capable of Nernstian storage, salt-in-water and redox active electrolytes, and bipolar stacks. There are undoubtedly further improvements but, thanks to the knowledge and technology advancements in batteries and supercapacitors, supercapattery will become more competitive and promising in the near future.

6. Conflict of interest statement

The author has no conflict of interest to declare.

7. Acknowledgements

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This review article is a useful reference for energy storage research, highlighting EES in the context of all currently available and predictable major energy storage technologies. Particularly, very useful 15 data tables and 60 illustrative figures and data plots are provided for easy understanding, comparison and analysis.

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The authors have made a good effort to clarify some typical misuses of scientific and technical terms, and conceptual misunderstanding and confusions in the EES literature, such as anode and cathode versus negatrode and positrode in terms of electrode reactions and electrical polarity, and pseudocapacitance and battery-like storage in terms of Faradaic processes.

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This is a good review article on lithium ion and other ion capacitors, highlighting the motivation and principle of hybridisation of rechargeable battery with supercapacitor. Note that anode and cathode used in this literature are replaced by negatrode and positrode in this article.

[14]* Chen JT, Yang BJ, Liu B, Lang JW, Yan XB: **Recent advances in anode materials for sodium- and potassium-ion hybrid capacitors.** *Curr Opin Electrochem* 2019, 18:1-8.

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This article reviews a relatively rare collection of literatures on sodium and potassium ion capacitors, focusing on the anode (= negatrode) materials. This article is worth reading if one considers the sustainability of energy storage technologies in terms of the wide and cheap availability of sodium and potassium resources compared with the highly geographically limited lithium resources.

[15]* Zou KY, Cai P, Cao XY, Zou GQ, Hou HS, Ji XB: **Carbon materials for high-performance lithium ion capacitor.** *Curr Opin Electrochem* 2020, 21:31-39.

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In the context of LICs, the authors have focused on the preparation, characterisation and application of various carbon materials for making the cathode (= positrode) and anode (= negatrode), highlighting the ways for, and effects of nanoengineering, doping, graphitisation, porous structuring and surface modification.

[16]* Lalwani S, Joshi A, Singh G, Sharma RK: **Sulphur doped iron cobalt oxide nanocaterpillars: An electrode for supercapattery with ultrahigh energy density and oxygen evolution reaction**, *Electrochim. Acta* 2019, **328**: 135076.

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The authors report a novel study on the positive contribution of doping Fe₂CoO₄ with sulfur to increasing the specific capacitance. The hydrothermal process for sulfur doping is likely also effective on other transition metal oxides.

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The authors report a rare work on doping Se into Ni-Co sulfide in the form of nanotubes or nanofibrils grown vertically on individual fibres of carbon cloth, forming a free standing positrode. Interesting SEM images of the nanotubes on single fibre are presented. CVs and GCDs were systematically applied to study the composite, revealing a positive contribution from Se doping to Nernstian storage capacity.

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This is a systematic study of the interesting electrochemistry of V(I, II, III) in the title mentioned composite for lithium storage at high positive potentials (3.0 to 4.3 V vs. Li⁺/Li) in mixed organic carbonate electrolyte. The specific energy of a supercapattery of the composite negatrode and an activated carbon positrode was measured to be 53 Wh/kg at a cell voltage of 2.7 V. The mass ratio of negatrode-to-positrode was 2:1, but no explanation was given how this ratio was selected, implying further improvement may be achievable

upon optimisation of the negatrode-to-positrode mass ratio, and also the cell voltage according to equations (15) and (16).

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A very simple approach is proposed and tested successfully to avoid redox cycling of iodide and tri-iodide ions between the positrode and negatrode of the same carbon material by limiting the discharging cell voltage to 0.1 V, instead of 0 V. This approach should also be applicable to avoid redox cycling in other supercapatteries with capacitive electrodes and redox active electrolytes.

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<https://doi.org/10.1039/c9mh01353a>

The authors report an effective research effort to combine three different charge storage mechanisms into a unique aqueous supercapattery. The claimed specific energy of 270 Wh/kg (without considering the mass of added KBr in the electrolyte) is amongst the top range of all reported EES devices with aqueous electrolytes.

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A simple but effective pulsed dis-/charging protocol is proposed and demonstrated to avoid dendritic deposition of lithium metal in LIBs, which should be equally applicable in, for example, the supercapattery of “Li | LiClO₄ in ionic liquid | activated carbon” [56].

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Effective suppression of dendritic deposition of lithium is reported on a copper plate covered with a porous membrane of submicron-wires of silicon nitride. The principle of this approach could be valid for deposition of other metals such as zinc and magnesium.

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Iron oxide is one of the few metal compounds that are redox active at negative potentials. Combining crystalline and amorphous iron oxide into a core/shell structure increases significantly the negative dis-/charging capacity in an alkaline LiOH electrolyte. The CVs and GCDs show clear supercapattery feature as represented by Fig. 2a and 2b.

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The authors grew nanowires of vanadium nitride on carbon cloth and coupled the composite with electro-deposited manganese oxide on carbon cloth to form an asymmetrical supercapacitor (actually a supercapattery). The materials and cell were analysed by electrochemical means in a typical “water in salt” electrolyte, i.e. 21 m aqueous solution lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) which allowed a cell voltage of 3.0 V. Note that this work is on using, but not studying “water-in-electrolyte”.

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The work reported is a conductive and non-permeable polymer-carbon composite membrane as thin as 40 μm . The conductivity of the composite is actually not very high in comparison with conventional conducting materials, but because of the thinness of the membrane, the through plane resistance of the membrane is sufficiently small. The challenging task is then to make such a thin membrane non-permeable to ions in aqueous solution, which seems to be successfully achieved. The work represents an important progress in development of affordable and corrosion resistant bipolar plate materials to serially stack multiple EES cells.

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9. Figures and captions

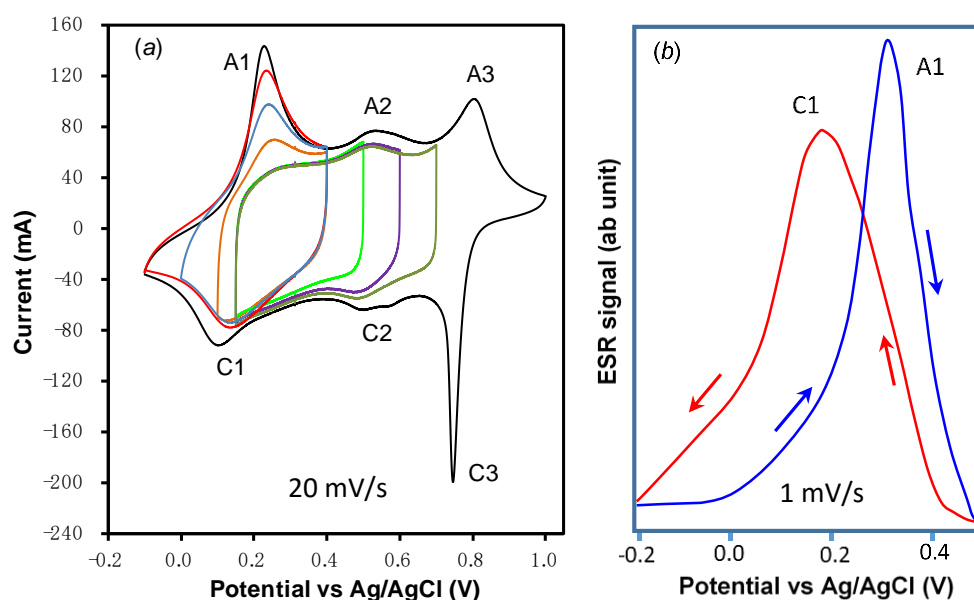


Fig. 1. (a) CVs in different potential ranges, and (b) a cyclic esrogram of electro-deposited polyaniline in acidic aqueous electrolytes. Redrawn from refs [34] and [30].

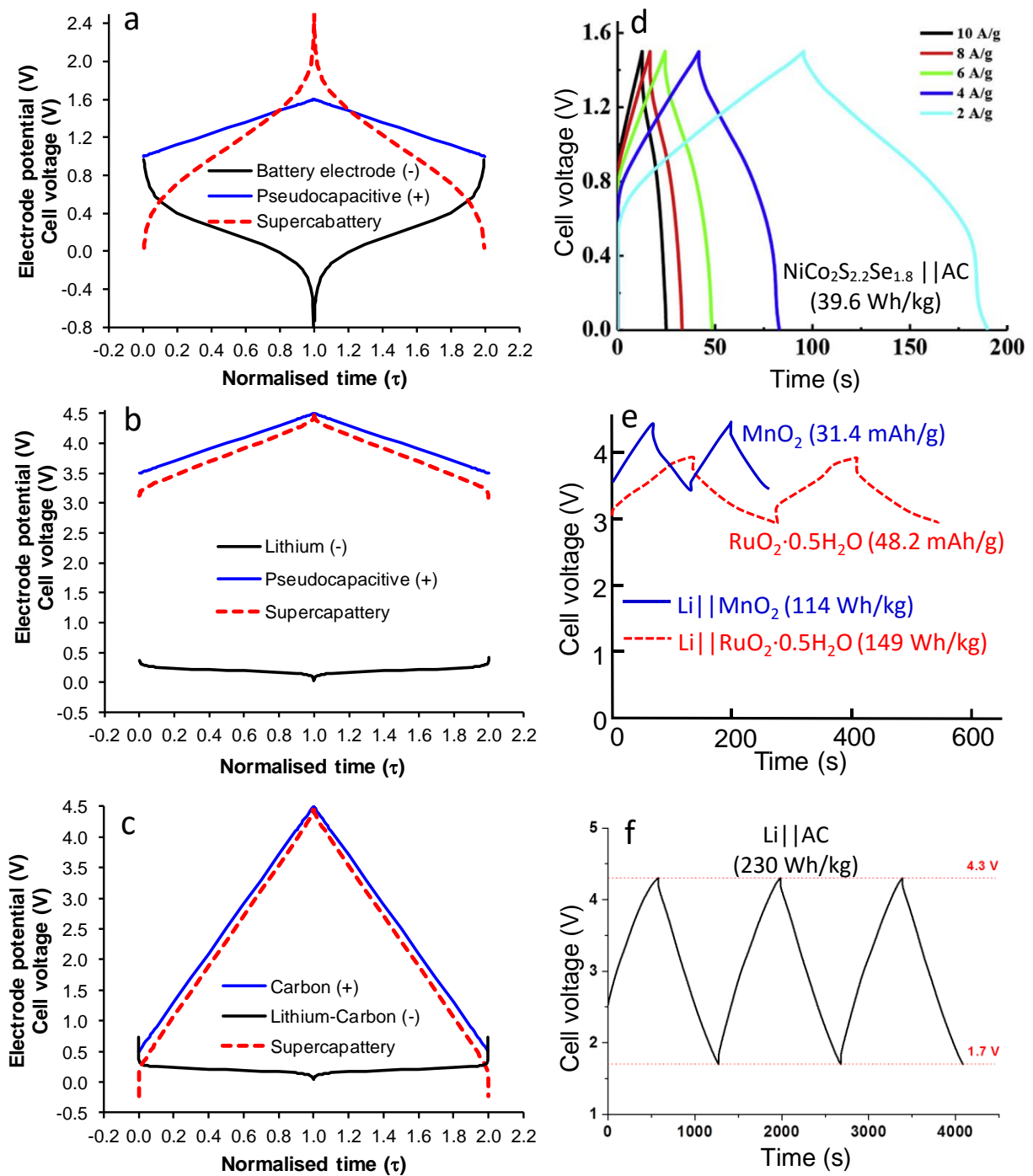


Fig. 2. (a-c) Calculated GCD plots of potentials of the positive (blue line) and negative (black line), and the cell voltage (red dashed lines) as a function of normalised time for three supercapatteries combining a pseudocapacitive positive electrode of narrow potential window with a Nernstian negative electrode of quasi-reversibility (a), and a lithium metal or lithiated carbon negative electrode (b), and an activated carbon positive electrode of wide potential window, and a lithiated carbon negative electrode (c). (d-f) Experimentally recorded GCD plots of the cell voltage against time for supercapatteries with aqueous (d), ionic liquid (e), and aqueous + solid electrolytes. Redrawn from [4,38,55,56].

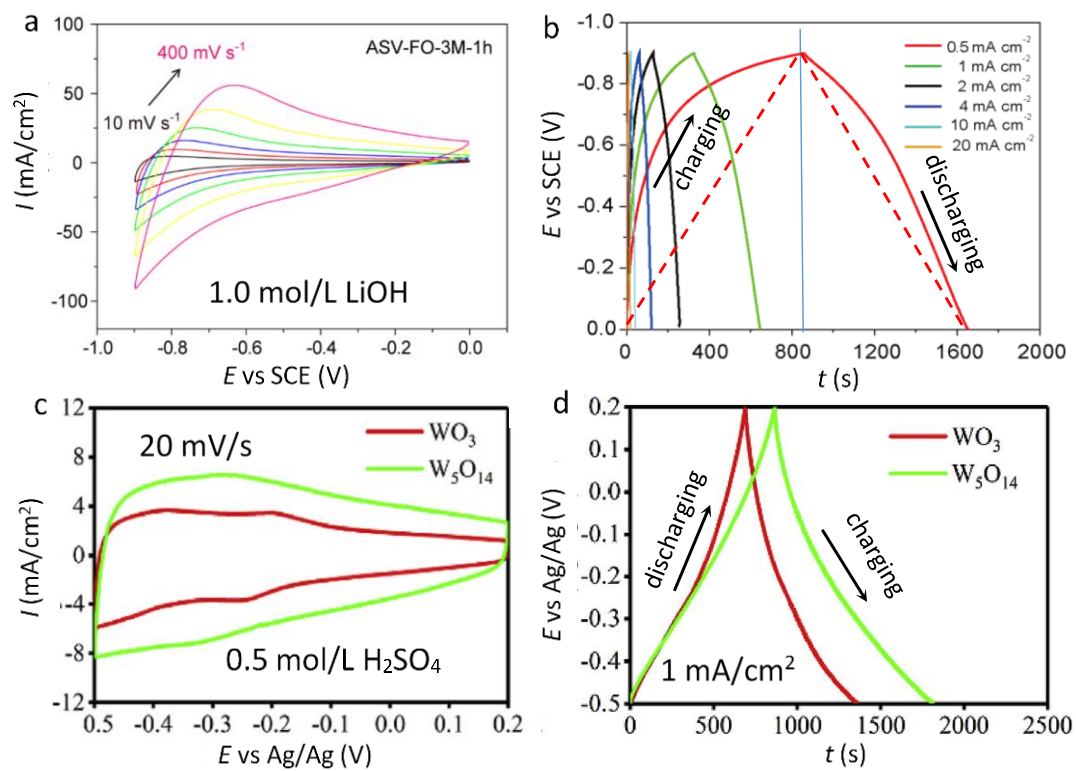


Fig. 3. (a,c) CVs and (b,d) GCDs of nanostructured and oxygen deficient (a,b) iron oxide, and (c,d) tungsten oxides. Redrawn from refs. [63,65].

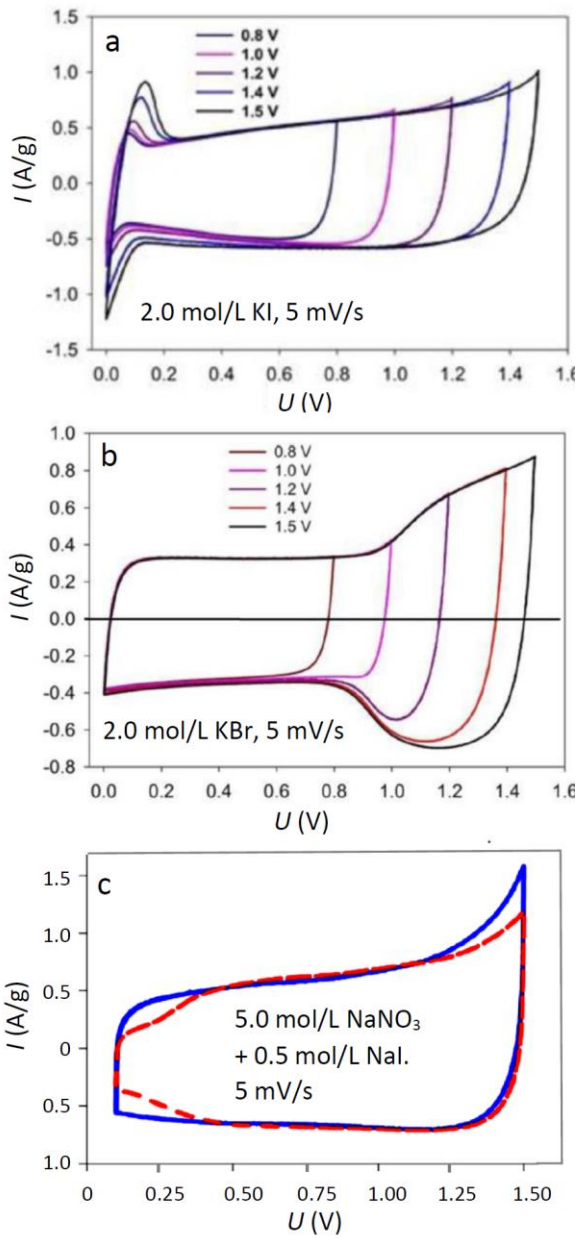


Fig. 4. CVs of supercapattery with activated carbon positrode and negatrode containing indicated electrolytes. Note that the potential window is from 0 to 1.5 V in (a) and (b) but from 0.1 to 1.5 V in (c) where the black line and red dashed line CVs were recorded before and after 100 charging-discharging cycles. Redrawn from refs. [52, 53]