Conducting polymer nanocomposites for energy storage applications: recent progress and future challenges

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These days, the requirement of developing new energy storage devices to store large amount of energy in high-rate applications is increasing. Thus, the cconducting polymers (CPs) hold a good future in energy storage field. This is related to their flexibility, light weight, high conductivity ($>10^3$ S cm^{-1}), cost effectiveness, controlled resistance over a wide range and excellent electrochemical properties. In particular, these materials can be used as an active material in rechargeable batteries and supercapacitors. CPs-based pseudocapacitors are capable to deliver large amount of energy that can last millions of cycles. Therefore, the current review summarizes how the choice of monomers and physical characteristics of dopants affect the electrical behavior of polymers and their widespread applications. The possible challenges to be overcome for their futuristic developments are also identified.

Keywords: Conducting polymer, Pseudocapacitance, Polyaniline, Polypyrole, Polythiopene, Supercapacitance.

INTRODUCTION

In today's scenario utilization of renewable and clean source of energy is very much needed. To use energy, it needs to be produced and stored. Since last few decades the field of energy generation and storage in an eco-friendly manner has evolved as a matter of huge significance. Hence, it is an area of intense research focus. It is also a fact that world population is growing at an alarming rate and so is the energy demand. Thus, it comes as no surprise that there is a continuously increasing gap between the demand and supply of energy. This is why efficient storage of energy is even more needed today than yesterday. In energy storage technologies initially, energy is stored in different forms such as chemical, mechanical, thermal, electromagnetic, electrochemical and electrical energy. This is done by different storage mechanisms i.e., direct storage and indirect storage (Fig. 1).

This stored energy is further used in electric form later on. There exist many forms of energy storage devices: (1) chemical energy storage (e.g. biofuels, hydrogen storage system), (2) mechanical energy storage (e.g. flywheel or hydropower), (3) thermal energy storage (e.g., steam accumulator), (4) electromagnetic energy storage (e.g. superconducting magnetic energy storage or SMES), (5) electrochemical energy storage (e.g. rechargeable batteries and supercapacitors), (6) electrical energy storage (e.g., a capacitor).

Supercapacitors or electrochemical capacitors are electrochemical devices based on the same principle as conventional capacitors (i.e. two electrodes separated by an electrolyte medium). But in the case of supercapacitors the distance between the electrodes is of atomic dimension which leads to significantly higher energy density in comparison to conventional capacitors [1]. Henceforth, electrochemical capacitors are supposed to serve as option capacitors and lithium ion-based devices [2, 3].

Due to their superior features [4-10], the applications of supercapacitors are increasing in portable, automotive systems and energy storage devices in comparison to the applications of the lithium ion batteries. Electric double layer capacitors (EDLCs) consist of carbon material-based electrodes [11, 12]. However, in pseudocapacitors the electrodes are made up of oxides of transition metals [13] or electroactive polymers [14, 15].

Power capability of electric double layer capacitors is generally high due to fast ionic adsorption and desorption of the electrolyte, however, their specific capacitance (Cs) is not up to the mark. On the other hand, pseudocapacitors can give rise to higher Cs values but cycling performance is not so good [16, 17]. In comparison to the relatively expensive transition metal oxides, the CPs are considered as the low-cost potential candidate electrode material for the pseudocapacitors.

If the electrode material is prepared from the combination carbon material/ CPs or metal oxide/ CPs then both the electric double layer formation and faradaic reactions add to the capacitance value and comparatively high Cs value is obtained (Fig. 2). The data displayed in Fig. 2 presents a comparative account of average specific values for electric double layer capacitors, pseudocapacitors and hybrid materials. The performance of the electrodes is influenced by the individual active constituents, as well as the interfacial characteristics and morphology of materials [1]. Charge storage mechanism of both EDLCs and pseudocapacitors is different due to the different charge-storing property of the electrode materials. In EDLCs charge is stored by the accumulation of the charge (due to double layers) on the electrode/electrolyte interface, whereas in pseudocapacitors (Fig. 3) [12] electric charges are confined in as electric double layers sandwiched between the carbon electrode and
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ionically conducting electrolyte. These layers are separated by atomic distances (~10 Å). Different models such as Helmholtz model, Gouy and Chapman diffuse model, and Stern model have been proposed for the explanation of double layer formation in EDLCs. The behavior of electrolyte ions, microstructure of electrode material, and the compatibility of the electrolyte ions by electrode material affects the performance of EDLCs. On the other hand, in pseudocapacitors whether the electrode material is transition metal oxides [13] or CPs [16] charge is stored by the reversible and fast redox faradaic reactions occurring in the electrode material (Fig. 4) [12]. Calation and intercalation of the electrolyte ions plays an important role in determining the pseudocapacitance performance. In comparison to other pseudocapacitive materials, the CPs possess high redox contributions, good flexibility and intrinsic conductivity
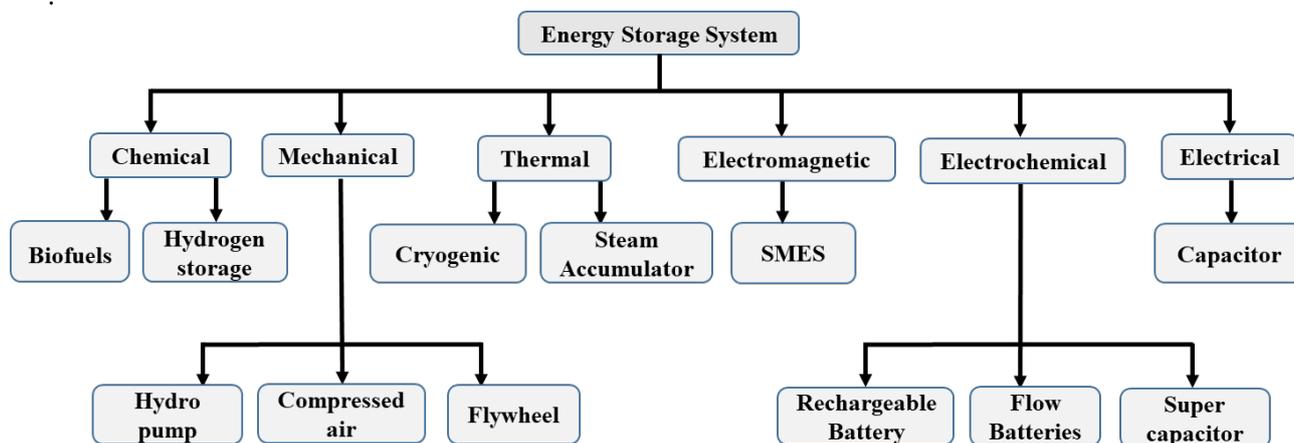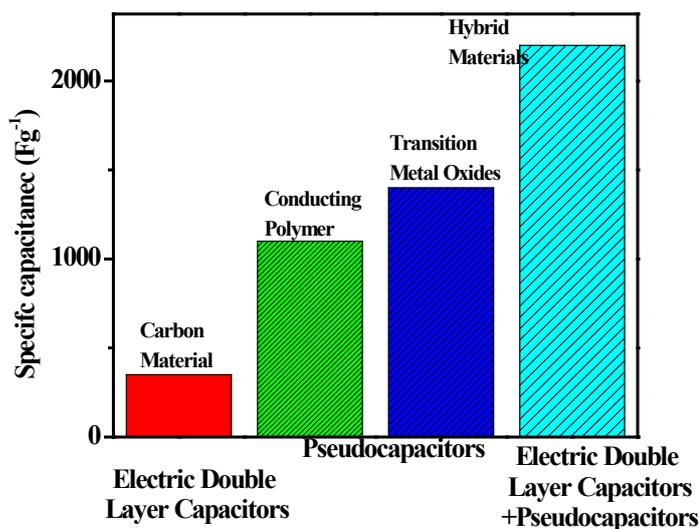

Fig. 1. Energy storage classifications

Fig. 2. Comparison of Cs values for different kinds of supercapacitor electrode materials
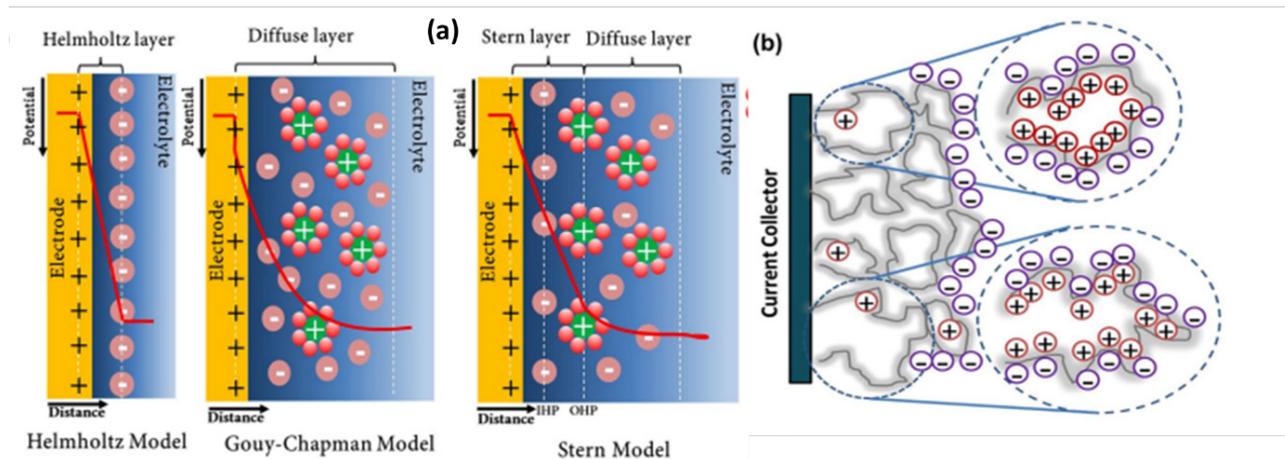
Fig. 3. (a) Different models (Helmholtz model, Gouy–Chapman model and Gouy-Chapman–Stern model) for the charge storage mechanism, and (b) Schematic illustration of charge storage mechanism of EDLC [12].
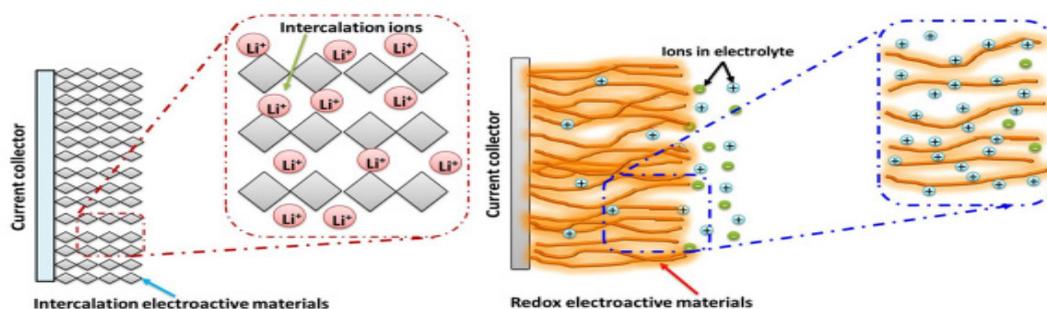

Fig. 4. (a) Pictorial illustration of the calation and intercalation of electrolyte ions in pseudocapacitors. (b) Redox mechanism of charge storage mechanisms in pseudocapacitors. [12]

The current review is mainly focused on the CPs-based pseudocapacitors. Different type of CP-based supercapacitors, their designing concepts and fabrication methods are discussed. It outlines the recent developments, finally point towards the future challenges for the route of flexible CP-based electrode materials and relevant device fabrications.

Properties of Conducting Polymers and Composites

Polyphenylene vinylene or PPV (10^{-3}–100 S cm^{-1}), polyacetylene or PA (3–1000 S cm^{-1}) polypyrole (PPy, 0.3–100 S cm^{-1}), polythiopene (PTh, 2–150 S cm^{-1}), polyaniline (PANI, 0.01–5 S cm^{-1}), and polyphenylene are few examples of conducting polymers (CPs) [21, 22]. Since discovery, the CPs have been praised by industry and academia for their applications in sensors [23, 24], and electrochromic devices [25].

CPs are obtained by vapor phase synthesis, electrochemical polymerization, solvothermal, hydrothermal, electrospinning, inclusion, template assisted, and plasma polymerization methods [26-29]. Though CPs offer good electrical conductivity and it can be tuned by the synthesis methods, their mechanical properties are not good. The CPs consist of sp^2 hybridized carbon atoms and one electron of these carbon atoms is present in a p$_z$ orbital and is orthogonal to the other 3 sigma bonds. All the p$_z$ orbitals of a molecule combine together and form a wide delocalized set. The electrons from these delocalized orbitals give rise to high mobility if the material is doped by oxidation. So, undoped or neutral conjugate polymers are found to have typically low electrical conductivity (10^{-10} to 10^{-8} S/cm) and it is found that even a small amount of doping can cause an increase of several orders of magnitude in electrical conductivity. The conductivity of the doped CPs depends on both the type and amount of the dopant. Doping in the CPs is a reversible process (Fig. 5). The CPs consist of long chains of Π conjugate polymers. The Π conjugate polymers are polymers consisting of alternating single and double or triple bonds. There can be also covalent bonds. Their charge transport phenomena are independent of their charge transport characteristics and intrinsic conductivity.

The application of CPs in energy storage devices such as grid scale storage, electrical vehicles, and portable electronic devices is attracting technological and scientific interest and it will

increase in future. Energy stored per unit weight or volume, power density, Cs, rate capability, cycle life, environment safety and cost are the few parameters which affect the overall performance of the CPs-based electrochemical energy storage devices or pseudocapacitors. Lithium-ion batteries are the main energy storage device. Although they have high energy density, cycle life and charge discharge rate are comparatively low. In comparison, the supercapacitors (both electric double layer and pseudocapacitors) possess high power density but at the cost of low energy density.

To enhance the performance of these novel electrical energy storage devices, the exploration of novel resources and methods to optimize the properties is therefore an area of major, emerging global research focus. For instance, the usage of nanomaterial for pseudocapacitors offers shortened pathways for mass or charge transport and new reaction pathways which are not possible to become available for the bulk material. Also, nanomaterial-based electrodes may lead to other potential advantages, e.g., (a) better accommodation of strain value induced by the electrochemical reactions, (b) high surface area, (c) flexibility, and (d) excellent mechanical properties [30].
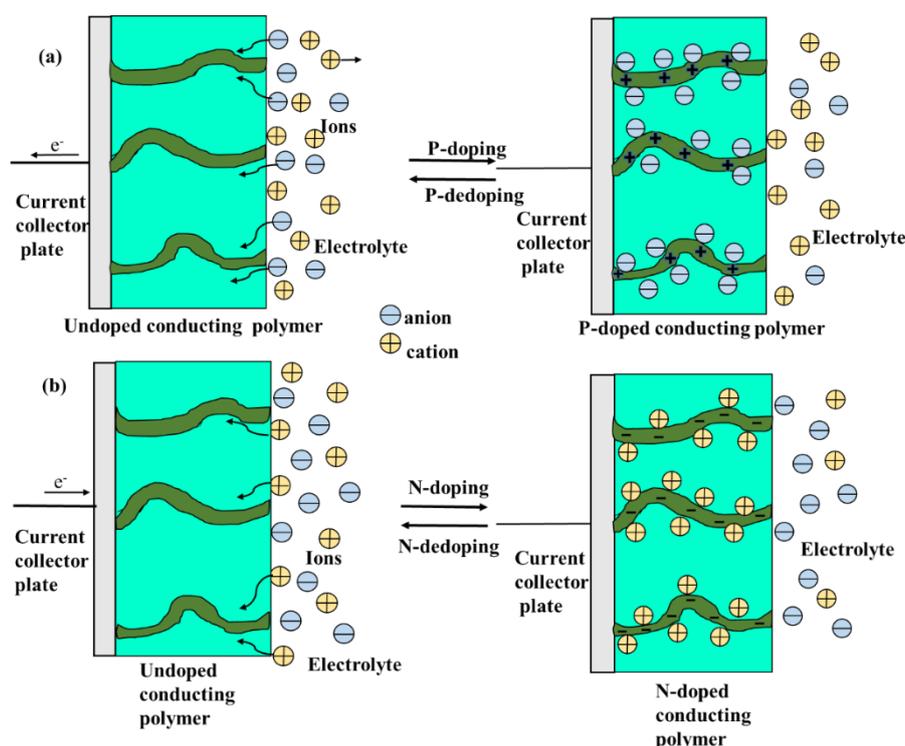

Fig. 5. Schematic representation of charging and discharging over CPs-derived electrodes associated with (a) p-doping and (b) n-doping.

Conductive polymers and composites for energy storage applications

Although a very high value of Cs value can be obtained from the CP based pseudocapacitors but some CP such as PPy and PANI lack in cycling stability [31]. During the charging and discharging process the CPs suffers from swelling and shrinkage problem which leads to cyclic instability. The CPs exhibit the greatest electrochemical performance in acidic electrolytes. PANI is the most studied CPs for the electrochemical performance. Research reported by others [32-34] confirm that it shows poor mechanical instability, volumetric shrinking and swelling during doping-dedoping process. This process leads to crack formation. Crack formation leads to breaking. The breaking ultimately leads to fast capacitance decay [32-34]. The

eelectrochemical performance of polypyrrole and polyindole (PIn) have been also studied in various applications including sensors, organic light emitting diodes and energy storing devices [35-38]. Owing to their excellent mechanical strength, optical properties, and chemical activity, these CPs find applications in other fields such as chemical sensors [39], biosensors [40], and also electromagnetic shielding [41].

Combination of CPs and carbon material

Superior electrochemical properties can be obtained if composite materials are made from CPs and carbon material. Carbon material not only provides substrate backbone but also gives highly conductive pathways. Therefore, the carbon materials of all dimensions i.e., 1D, 2D, and 3D such

as activated carbon, graphene nanoribbons (GNRs), carbon nanofibers (CNFs), and carbon nano tubes (CNTs) have been combined with CPs to be used as an electrode material [42]. These composites provide electrochemical performance much superior than that of the CPs. This performance enhancement happens due to a synergistic effect between the electrostatic ions from the electric double layers and faradaic reactions of the of the CPs [43, 44].

The Cs (F g^{-1}) are calculated by the following equation (1).

$$C_s = \frac{i\Delta t}{m\,\Delta V} \qquad (1)$$

where i (Amp) is the discharge current, m (g) is the mass of one working electrode, Δt (sec) is the discharge time in seconds and the ΔV (V) represents the voltage change (exclusive of the IR drop for the duration of the discharge process) in volt.

The Cs can also be calculated from the area of the CV cycle by the following equation (2),

$$Cs = \int IdV/(s\,m\,\Delta V) \qquad (2)$$

The term ∫Idv is the integral area of the CV cycle, s is the scan rate, m is the mass of materials, and ΔV is the potential range.

The energy density E (Wh g^{-1}) of the electrode materials can be calculated using the equation (3):

$$E = \frac{C_s \times \Delta V^2}{2 \times 3.6} \qquad (3)$$

where C_s (F g^{-1}) represents the specific capacitance and ΔV (V) is the potential window.

The power density P (W kg^{-1}) of the electrode material can also be evaluated from the energy density by the equation (4):

$$P = \frac{3600 \times E}{\Delta t} \qquad (4)$$

Here E represents the energy density and Δt corresponds to the discharge time.

The Coulombic efficiency (η) can be calculated from the results of galvanostatic charge-discharge experiment and can be expressed as:

$$\eta = \frac{t_D}{t_C} \times 100 \qquad (5)$$

The hydrothermal carbon coating on the PANI nanowire improves the cycling stability (95% retention) after 10000 cycles by the three-electrode system [45]. Deposition of carbonmaterial on CPs including enhances the cycling stability. Liu and Co workers deposited cloth shell on PANI and PPy pseudocapacitive material (i.e, PANI@C and PPy@C) and reported a cycling retention value of 95% and and 85 %, respectively, after 10000 cycles as shown in Fig. 6. Fig. 6 represents the variation of the areal capacitance of PANI, PANI@C, PPy, and PPy@C at varying current densities. In comparison to bare CPs (PANI and PPy) core shell structures display higher areal capacitance values but it decreases rapidly at higher current densities.

At higher current densities the presence of carbon shell on the polymer surface decreases the movement of electrolyte ions towards the polymer surface which leads to the increase of *iR* drop. But the presence of the carbon shell increases the cycling performance of the bare polynomial, where PANI@C shows 95% cycling retention value which is very high in comparison to 20% capacitance retention for PANI. PPy@C also shows enhancement in cycling retention value (85%) in comparison to bare PPy (25%) (Fig. 7).
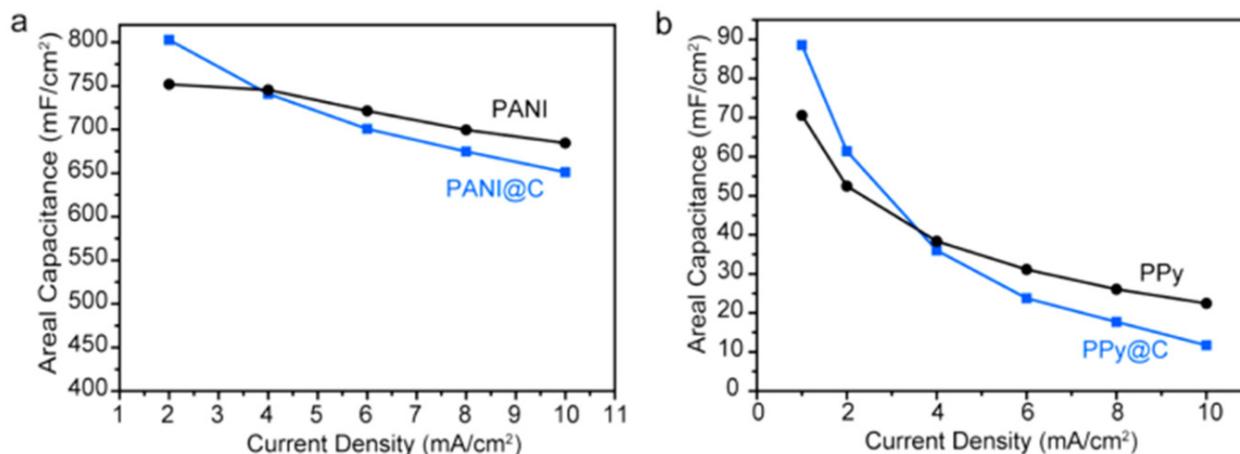

Fig. 6. Areal capacitance of (a) PANI, PANI@C and (b) PPy, PPy @C electrodes collected at different current densities [46].
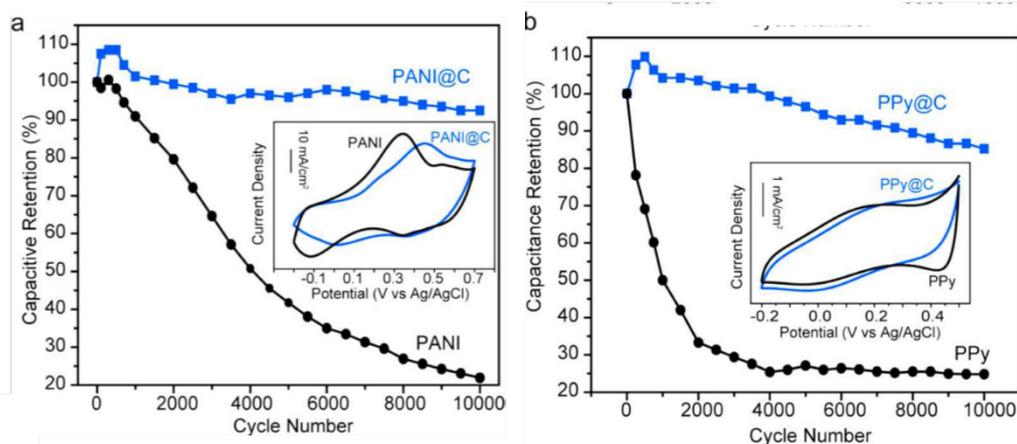
Fig. 7. Cycling performance of (a) PANI and PANI@C and (b) PPy and Ppy@C electrodes [46].
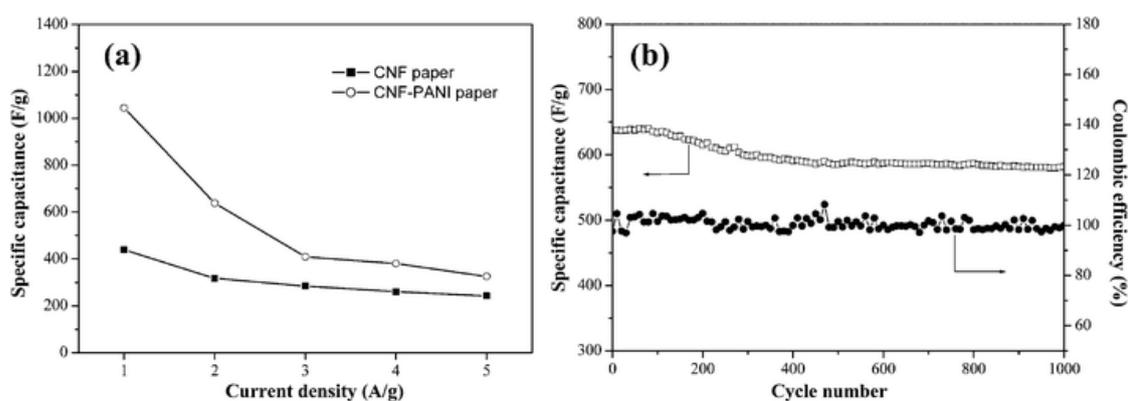

Fig. 8. (a) Variation of Cs of CNF and CNF/PANI with current density. (b) Variation of Cs and Coulomb efficiency of CNF/PANi at a current density of 2 A g^{-1} [51].

The graphene/PANI nanofiber composite films prepared by the vacuum filtration method give better Cs of 210 F g^{-1}[47]. Hybrid films of SWNT and PANI also enhances the energy density value without deteriorating the power capabilities [48-50]. Carbon nanofiber (CNF)/PANI composite produces synergistic effect as both electric double layer and pseudocapacitance contributes to the charge storage mechanism and hence, an increased capacitance value (638 F g^{-1}) (Fig. 8) [51]. For a composite material of carbon (any form) and CPs, thickness of both kinds of material (base or core material and shell material) plays a vital role in defining the electrochemical properties. It is indeed observed that the electrochemical performance of the GNR/PANI composite material is better than that of the base material (GNRs) but if the thickness of the PANI exceeds a certain limit then the Cs start decreasing because more loading of PANI in the composite material leads to reduction in the conductivity. The optimized GNR/PANI composite exhibits high Cs, e.g., 264 Fg^{-1} [52].

It needs to be noted here that the 2D carbon materials such as graphite nanoflakes (GFs),

graphene oxide (GO), and reduced graphene oxide (rGO) also have high surface area and can act as good substrate for making composite material with CPs. GO has a good compatibility with the CPs due to the presence of oxygenated groups such as hydroxyl, carboxyl, and epoxide functional groups on its basal planes and edges [53]. The comparative morphological and electrochemical studies on 1D PANI, GO and PANI/Go nanocomposite reveal that the ratio of aniline to GO plays the main role in determining the morphology of the final composite material. In terms of electrochemical performance, the PANI/GO nanocomposite gives better results, e.g., (555 F g^{-1}) [54].

Further, the 3D carbon materials such as carbon cloth, carbon fibers, activated carbon, and carbon aerogels provide good distribution of macro, meso and micropore sizes. Such activated carbons (AC) also provide charge transport pathways. Thus, *in situ* polymerized PANI/AC composite exhibits Cs value (943 Fg^{-1}) (Fig. 9) higher than that (371 Fg^{-1}) of the pure PANI material at low scan rate [55].

Although loading of PANI on AC decreases the specific surface area but Cs value enhances because

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now capacitance is given by both processes, i.e., electric double layer formation due to AC and redox reactions due to the PANI. Cs decreases with increase in scan rate because high scan rate restricts low diffusion of electrolyte ions.

Similarly, the PEDOT (i.e., polyethylenedioxy thiophene)-coated carbon provides 181 Fg^{-1} of Cs for the solid-state device [56]. In a similar manner, the 3D porous polypyrole film synthesized by template-assisted method exhibits a high capacitance of 313 Fg^{-1} and 81.3% retention after 10,000 cycles by three electrode system. Here $CaCO_3$ is used as template as it creates more pores. That increases the surface area and hence, aids the diffusion-controlled process. In addition, it enhances the total amount of redox reactions [57].

It follows that this composite design philosophy works mainly on the concept of a perfect match of the pore size of the 3D carbon material with the electrolyte ion size. When that happens, it gives rise to charge accumulation by the electric double layer formation. That is why, the CP (i.e., CPs)-3D carbon composites provide improved electrochemical properties [58, 59]. Further, the RuO_2 shell-PANI nanofiber core composites are reported [60] to have the highest Cs of 710 Fg^{-1} at 5 mVs^{-1} along with 94% retention from 5 to 100 mVs^{-1} coupled with 88% cycling stability improvement (*ca.* 65% for PANI nanofiber), (Fig. 10).
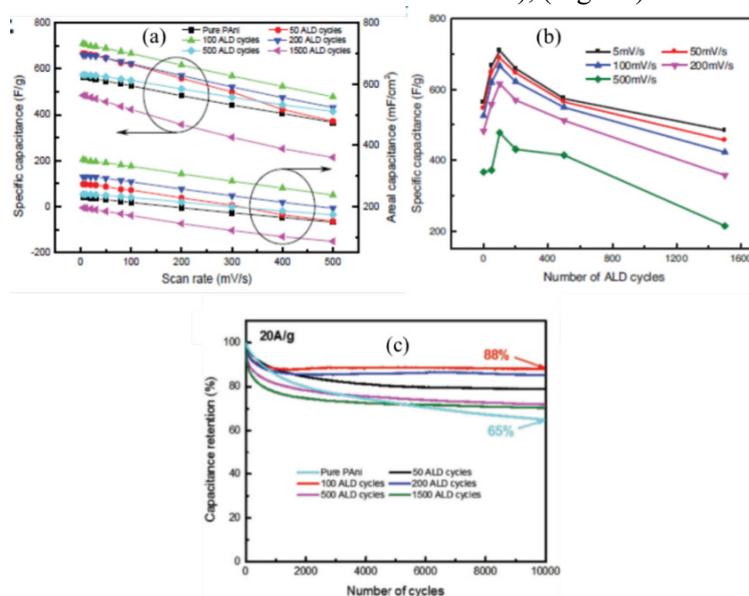

Fig. 9. Variation of Cs values of PANI and PANI/AC composite at varying (a) scan rates and (b) current density. (c) Energy density and power density of PANI and composite materials.
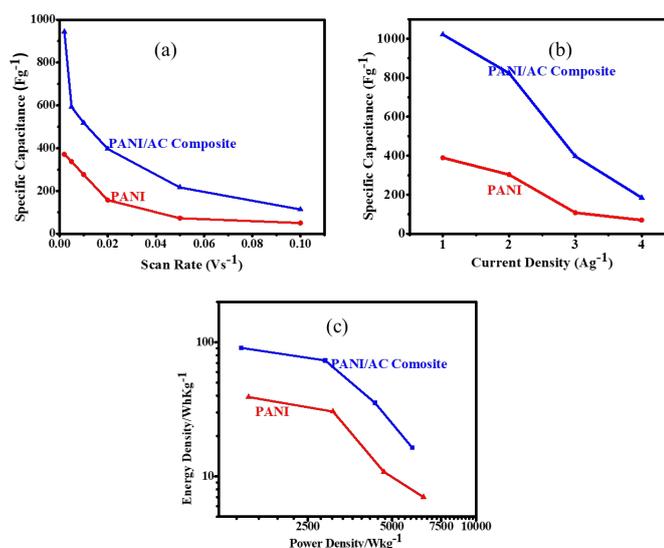

Fig. 10. Electrochemical performance of PANI/RuO_2 core shell (a) Variation of Cs and areal capacitance with scan rate, (b) variation of Cs with atomic layer deposition ALD: atomic layer deposition), (c) cyclic stability of pure PANI and core shell structure [60].

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Table 1. Cs, energy and power density, and cyclic performance of CPs and its composites.

Electrode Material	Electrolyte	Cs (F g^{-1})	Power density (kW kg^{-1})	Energy Density (Wh kg^{-1})	Cyclic Stability	Ref.
PANI-benzoquinone	H$_2$SO$_4$ (1M)	524	-	-	>5000	14
Poly(isothianaphthene)	Propylene carbonate+ 1 M Bu$_4$NBF$_4$	40				22
PPy	H$_2$SO$_4$ (0.5 M)	586	-	-	-	31
PANI/CNT	H$_2$SO$_4$-polyvinyl alcohol	350			1000	32
PPy /Polyethylene geotextile	LiCl$_4$ (1M)	545				38
PANI/MWNT	LiPF$_6$ (1M) + ethylene carbonate and dimethyl carbonate	238 (F/cm^3)	220	100 kW	-	43
SWNT/Polyaniline	H$_2$SO$_4$ (0.5 M)	706				44
PANI/Carbon cloth	H$_2$SO$_4$ (1M)	724			10,000	46
PPy/Carbon cloth	H$_2$SO$_4$ (1M)	99			10,000	46
Graphene/PANI nanofiber	-	210			800	47
SWNT/PANI	-	236	62.5	131		48
PANI/SWNT		541				50
PANI/CNF	H$_2$SO$_4$ (1M)	638			1000	51
PANI/GNRs	H$_2$SO$_4$ (1M)	340	3.2	7.56	4200	52
PANI/GO	H$_2$SO$_4$ (1M)	555			1000	54
PANI/AC	Na$_2$SO$_4$ (1M)	937	5.9	16.3	2000	55
PEDOT/CF	PVA-H$_2$SO$_4$	112	-	5.1	12000	56
PPy	-	313	-	-	10000	57
PANI/RuO$_2$		710	42.2	10	10000	60
PPy/CA	KOH (mol L^{-1})	433			500	61
PANI/Cdots	676					66
PPy/Cdots	529					66

Though pure PPy has low Cs in comparison to PANI but composites of PPy/carbon material gives enhanced performance. For instance, the PPy/carbon aerogel composites synthesized by the chemical oxidation polymerization method gives many times increment in the Cs value (433 Fg^{-1}) in comparison to that of the pure PPy. Doping PPy with organic molecules (such as *p*-toluenesulfinate) exhibits a 96% retention after 500 cycles [62]. In addition, the ccombination of CPs with inorganic material gives a synergistic effect to provide better plastic property and electrical conductivity [63-65]. The Cs values are reported to be 529 Fg^{-1} for PANI doped with carbon dots and 676F g^{-1} for PPy doped carbon dots [66]. This work uses the *in situ* chemical oxidative polymerization method. Polythiopene has low conductivity and usually shows lower Cs values in comparison to those of PANI and PPy but it can work for a wider potential window [67, 68]. Due to its high environmental stability [69, 70] the PEDOT CP is also gaining popularity as a supercapacitor electrode material. Table 1 shows the

electrochemical performance (Cs, energy and power density, and cyclic performance) of few CPs and their composites.

Future challenges

The future developmental challenges of pseudocapacitors are deeply linked with the development of CPs and CP-(1D/2D/3D) Carbon composites. The future of CPs lies in exploring new chemistry and new molecular design along with the exploration of both existing and new fields for commercialization. Despite great progress, the n-doped CPs are yet to be able to meet the ambient stability and conductivity level of p doped polymers. Another important factor that will govern this emerging field is the development of efficient synthesis methodologies for development of new CPs. Despite the immense progress in recent research, the relationship between chain structure morphology, and conductivity is yet to be comprehensively understood. However, the immense importance of this aspect stems very much from the fact that the properties of the CPs are hugely affected by the chain length distribution of the monomers and hence, even a small amount of bond connectivity defects and undesirable crosslinking may drastically change the charge transport properties. The most obvious need of the hour is that the cycling stability of the CP based pseudocapacitors must be significantly enhanced. The rate and cycling performance of CP based electrodes can be improved by making composites of CP with other materials (e.g., carbon-based materials, nanomaterials, hydroxides, sulfides or oxides).

The major challenge is to develop these new hybrid materials in a pre-designed fashion so that they can deliver the required output for future generation of supercapacitors. Both AI and ML can play a big role here in defining the design of such exotic materials.

Thus, there can't be any doubt that there is a plenty of room for these hybrid material in supercapacitors. PANI is the most explored CPs foe energy storage application [32, 43,4 6-55, 60]. Other CPs such as poly(isothianaphthene) [22], PPy [31, 38, 46, 57, 61, 66], PEDOT [56], and PIn also have the potential for energy-storage applications. The current topic of research for carbon materials is zero dimensional (nanosized) carbon materials. Although C-dots are less conductive in comparison to conductive polymers but the synergistic effect of electric double layer and redox oxidation phenomenon may lead to better electrochemical phenomenon of the hybrid materials synthesized form the C-dots and CPs [66]. For instance, as mentioned above; if a nanocomposite of CPs and carbon material is synthesized then both electric double layer formation and pseudocapacitance can enhance the performance of the energy storage device. As and when this dream is realized, the CPs composite electrodes may play a vital role in smart, economical, and flexible energy storage applications in the future generations of pseudocapacitors.

Summary and Conclusions

This review focuses on the current state of the knowledge on existing and new materials for development of better pseudocapacitors as efficient energy storage devices. It specifically describes the developments that has taken place to enhance the specific capacitance (Cs) of CPs and their composites with (e.g., 0D, 1D, 2D, and 3D carbon), C-dots, and suitable metal oxides, e.g. RuO_2, etc. Further, it identifies the future challenges that need to be addressed for further development of CPs (PANI, PPy, PEDOT, PIn, etc.) and their composites with (0D, 1D, 2D, 3D carbon), C-dots, and suitable metal oxides, e.g. RuO_2, etc. Finally, it also suggests the need for more efficient scalable synthesis technologies for large-scale production of pseudocapacitor materials, especially the CPs so that more efficient energy storage devices can be developed in days to come.

REFERENCES

1. B. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum Publishers, New York, 1999.
2. E. Frackowiak, *Phys. Chem. Chem. Phys.,* **9,** 1774 (2007).
3. F. Beguin, E. Frackowiak, M. Lu, Supercapacitors: Materials, Systems and Applications, Wiley-VCH, 2012.
4. R. Kotz, M. Carlen, *Electrochim. Acta,* **45**, 2483 (2000).
5. A. Burke, *J. Power Sources*, **91**, 37 (2000).
6. K. H. An, W. S. Kim, Y. S. Park, J.-M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee, Y. H. Lee, *Adv. Funct. Mat.*, **11**, 387 (2001).
7. S. Arepalli, H. R. Fireman, P. G. Moloney, C. B. Huffman, P. Nikolaev, L. Yowell, C. D. Higgins, S. P. Turano, K. Kim, P. A. Kohl, W. J. Ready, *JOM*, **57**, 26 (2005).
8. Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, *Int. J. Hydrogen Energy*, **34**, 4889 (2009).

9. H. Chen, T. N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, *Prog. Nat. Sci.*, **19**, 291 (2009).

10. J. Y. Lee, K. Liang, K. H. An, Y. H. Lee, *Synth. Met.*, **150**, 153 (2005).

11. S. Rawal, B. Joshi, Y. Kumar, *J. Energy Storage*, **20**, 418 (2018).

12. S. Balasubramaniam, A. Mohanty, S. K. Balasingam, S. J. Kim, A. Ramadoss, *Nano-Micro Lett.*, **12**, 1, (2020).

13. P. Simon, Y. Gogotsi, *Nat. Mater.*, **7**, 845 (2008),

14. D. Vonlanthen, P. Lazarev, K. A. See, F. Wudl, A. J. Heeger, *Adv. Mater.*, **26**, 5095 (2014).

15. A, M. Bryan, L. M. Santino, Y. Lu, S. Acharya, J. M. D'Arcy, *Chem. Mater.*, **28**, 5989 (2016).

16. L. L. Zhang, X. S. Zhao, *Chem. Soc. Rev.*, **38**, 2520 (2009).

17. I. Shown, A. Ganguly, L. C. Chen, K. H. Chen, *Eng. Sci. and Eng.*, **3**, 2 (2015).

18. G. Wang, L. Zhang, J. Zhang, *Chem. Soc. Rev.* **41**, 797 (2012).

19. Y. Kumar, S. Rawal, B. Joshi, S. A. Hashmi, *J. Solid State Electrochem.*, **23**, 1118 (2019).

20. V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* **7**, 1597 (2014).

21. G. A. Snook, P. Kao, A. S. Best, *J. Power Sources,* **196**, 1 (2011).

22. S. Sivakkumar, R. Saraswathi, *J. Power Sources,* **137**, 322 (2004).

23. C. S. Park, C. Lee, O. S. Kwon, *Polymers,* **8**, 249 (2016).

24. F. S. Omar, N. Duraisamy, K. Ramesh, S. Ramesh, *Biosens. Bioelectron.,* **79**, 763 (2016).

25. V. K. Thakur, G. Ding, J. Ma, P. S. Lee, X. Lu, *Adv. Mater.,* **24**, 4071 (2012).

26. R. Brooke, P. Cottis, P. Talem, M. Fabretto, P. Murphy, D. Ewans, **86**, *Front. Chem.,* 127 (2017).

27. C. S. Park, D. H. Kim, B. J. Shinm, D. Y. Kim, H. K. Lee, H. S. Tae, *Materials,* **9**, 812 (2016).

28. Q. Tang, J. Wu, X. Sun, Q. Li, J. Lin, *Langmuir,* **25**, 5253 (2009).

29. A. Deronzier, J. C. M., C.C. R. *Photo Chemical,* **147**, 339 (1996).

30. Y. Shi, L. Peng, Y. Ding, Y. Zhao, Y. Guihua, *Chem. Soc. Rev.,* **44**, 6684 (2015).

31. D. P. Dubal, S. H. Lee, J. G. Kim, W. B. Kim, C. D. Lokhande, *J. Mater. Chem.,* **22**, 3044 (2012).

32. C. Meng, C. H. Liu, L. Z. Chen, C. H. Hu, S. S. Fan, *Nano Lett.,* **10**, 4025 (2010).

33. T. Kombayashi, H. Honeyama, *J. Electroanal. Chem.* **177**, 281 (1984).

34. C. Choi, D.S. Ashby, D. M. Butts, R. H. DeBlock, Q. Wei, J. Lau, B. Dunn, *Nature Review Materials,* **5**, 5 (2019).

35. R. B. Choudhary, S. Ansari, B. Purty, *J. Energy Storage*, **29**, 101302 (2020).

36. Y. Huang, H. Li, Z. Wang, M. Zhu, Z. Pei, Q. Xue, Y. Huang, C. Zhi, *Nano Energy,* **22**, 422 (201),.

37. M. Gross, D. C. Muller, H. G. Nothofer, U. Scherf, D. Neher, C. Brauchle, K. Meerholtz, *Nature,* **405**, 661 (2000).

38. A. Yavuz, N. Ozdemir, H. Zengin, *Int. J. Hydrog. Energy*, **451**, 8876 (2020).

39. M. H. Naveen, N. G. Gurudatt, Y. B. Shim, *Appl. Mater. Today*, **9**, 419 (2017).

40. M. Gerard, A. Chaubey, B. D. Malhotra, *Biosensors, Bioelectron.* **17**, 345 2002).

41. S. K. Dhawan, N. Singh, D. Rodrigues, *Sci. Technol. Adv. Mater.* **4**, 105 (2003).

42. G. Yu, X. Xie, L. Pan, Z. Bao, Y. Cui, *Nano Energy,* **2**, 213 (2013)

43. M. N. Hyder, S. W. Lee, F. Ç. Cebeci, D. J. Schmidt, Y. Shao-Horn, P. T. Hammond, *ACS Nano,* **5**, 8552 (2011).

44. J. Liu, J. Sun, L. Gao, *J. Phys. Chem. C,* **114**, 19614 (2010).

45. J. Ge, G. Cheng, L. Chen, *Nanoscale,* **3**, 3084 (2011).

46. T. Y. Liu, L. Finn, M. H. Yu, H. Y. Wang, T. Zhai, X. H. Lu, Y. X. Tong, Y. Li, *Nano Lett.,* **14**, 2522 (2014).

47. Q. Wu, Y. X. Xu, Z. Y. Yao, A. R. Liu, G. Q. Shi, ACS *Nano,* **4**, 1963 (2010).

48. Z. Q. Niu, P. S. Luan, Q. Shao, H. B. Dong, J. Z. Li, J. Chen, D. Zhao, L. Cai, W. Y. Zhou, X. D. Chen, S. S. Xie, *Energy Environ. Sci.*, **5**, 8726 (2012).

49. K. L. Klein, A. V. Melechko, T. E. McKnight, S. T. Retterer, P. D. Rack, J. D. Fowlkes, D. C. Joy, M. L. Simpson, *J. Appl. Phys.*, **103**, 061301 (2008).

50. I. V. Panasenko, M. O. Bulavskiy, A. A. Iurchenkova, Y. Aguilar-Martinez, F. S. Fedorov, E. O. Fedorovskaya, B. Mikladal, T. Kallio, A. G. Nasibulin, *J. Power Sources,* **541**, 231691 (2022).

51. X. Yan, Z. Tai, J. Chen, Q. Xue, *Nanoscale,* **3**, 212 (2011).

52. L. Li, A. R. O. Raji, H. Fei, Y. Yang. E. L. Samuel, J. M. Tour, *ACS Appl. Mater. Interfaces,* **5**, 6622 (2013).

53. B. Genario, W. Lu, A.M. Dimiev, Y. Zhu, A. R. O. Raji, B. Novosel, L. B. Alemany, J. M. Tour, *ACS Nano,* **6**, 4231 (2012).

54. J. J. Xu, K. Wang, S. Z. Zu, B. H. Han, Z. X. Wei, *ACS Nano,* **4**, 5019 (2010).

55. S. Rawal, U.K. Mandal, A. Kumar, Y. Kumar, B. Joshi, *Nano Express,* **2**, 010013 (2012).

56. B. Anothumakkool, A. Torris, S. N. Bhange, M. V. Badier, S. Kurungot, *Nanoscale,* **6**, 5944 (2014).

57. T. Wang, Y. Wang Di, Zhang, X. Hu, L. Zhang, C. Zhao, Y. S. He, W. Zhang, N. Yang, Z. F. Ma, *ACS Appl. Mater. Interfaces*, **13**, 17726 (2021).

58. F. Fu, H. Wang, D. Yang, X. Qiu, Z. Li, Y. Qin, *J. Colloid Interface Sci.,* **617**, 694 (2022).

59. M. Seredych, D. Hulicova-Jurcakova, G. Q. Lu, T. J. Bandosz, *Carbon,* **46**, 1475 (2008).

60. C. Xia, W. Chen, X. Wang, M. N. Hedhili, N. Wei, H. N. Alshareef, *Adv. Energy. Mater.*, **5**, 1401805 (2015).

61. H. An, Y. Wang, X. Wang, L. Zheng, X. Wang, L. Yi, X. Zhang, *J. Power Sources,* **195**, 6964 (2010).

62. A. Kumar, R. K. Singh, H. K. Singh, P. Srivastava, R. Singh, *J. Power Sources,* **246**, 800 (2014).

63. L. Shao, J.-W. Jeon, J. L. Lutkenhaus, *Chem. Mater.*, **24**, 181 (2011).

64. G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang, W. Yang, *Adv. Mater.,* **23**, 4679 (2011).

65. Y. E. Miao, W. Fan, D. Chen, T. Liu, *ACS Appl. Mater. Interfaces*, **5**, 4423 (2013).

66. B. Devadas, T. Imae, *ACS Sustainable Chem. Eng.,* **6**, 127 (2018).

67. L. Yuan, B. Yao, B. Hu, K. Huo, W. Chen, J. Zhou, *Energy Environ. Sci.*, **6**, 470 (2013).

68. A. Laforgue, P. Simon, C. Sarrazin, J. F. Fauvarque, *J. Power Sources*, **80**, 142 (1999).

69. K. Lota, V. Khomenko, E. Frackowiak, *J. Phys. Chem. Solids*, **65**, 295 (2004).

70. Z. Su, C. Yang, C. Xu, H. Wu, Z. Zhang, T. Liu, C. Zheng, Q. Yang, B. Li, F. Kang, *J. Mater. Chem. A*, **1**, 12432 (2013).