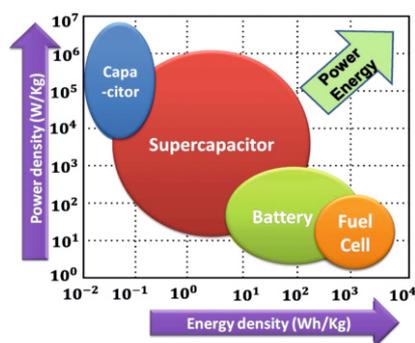


Super Capacitors

Review on Electrochemical Capacitor Technology: Role of Transition Metal-based Oxides

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Ragone Plot: Power vs Energy Density.

ABSTRACT

Electrochemical capacitors constitute an important class of energy storage devices that has been on the forefront of research in materials science in the last decade. The article presents the overview of recent progress in the field of supercapacitor materials with special emphasis on electrode materials. Even though the commercial supercapacitors presently available in market are based on carbon materials, there is a huge impetus on research on other materials including transition metal-based oxides, hydroxides and polymers to obtain better energy density. The charge storage mechanisms of different kind of electrodes along with their advantages and disadvantages and the strategies that are adopted to improve the capacitive performance have also been discussed. The article provides the synthesis challenges of the electrode materials with better electrochemical performance using environmental friendly, facile and low-cost methods for development of efficient and cost-effective electrochemical capacitors for energy storage applications.

KEYWORDS: Energy storage, Supercapacitor, Electrode, Carbon, Transition metal oxide, Layered double hydroxide

Introduction

The development of mankind is intrinsically related to energy supply and demand[1]. With continuous increase in technological growth, there has been unprecedented increase in energy demand as well. This calls for developing efficient, clean and sustainable sources of energy production, storage and conversion given the state of non-renewable fossil fuels which are still the primary energy providers worldwide. This has prompted the scientific and technical community to focus its research in the areas of solar, nuclear, hydrogen and other renewable and sustainable energy forms. However, for the intermittent nature of energy sources like solar energy there is a necessity for developing inexpensive and efficient energy storage and conversion devices. In fact, these devices shall become absolutely necessary as these renewable energy technologies become more widespread, and are integrated into the electrical grid. Among different energy storage technologies, the role of those based on electrochemical techniques such as batteries and electrochemical supercapacitors has been considered paramount in overcoming fossil fuel exhaustion[2]. Common features among these two are that the underlying chemical processes take place at the interface of electrode/electrolyte and the electron and ion transport occur through different routes. However, there are certain differences in the charge storage mechanisms of batteries and supercapacitors that bestows them with different features and makes them useful for different purposes. Batteries, like Li-ion batteries were introduced in 1990 by Sony, following pioneering work by Whittingham, Scrosati and Armand. They are excellent in terms of performance, with energy densities up to 180 watt hours/Kg but they suffer from slow power delivery or uptake (power

densities), and hence are not much helpful when faster and higher-power energy storage systems are needed. This is where the electrochemical capacitors fill in the bridge as they can be fully charged or discharged in seconds. As a result, their energy density (about 5 Wh kg⁻¹) is lower than batteries, but they deliver such higher power delivery or uptake (power density~10 kW kg⁻¹) and that can be achieved in very short durations (a few seconds). Hence, they could play an important role in complementing batteries in the energy storage applications, such as back-up power supplies to protect against power disruption and load-levelling. Due to features such as fast charging, long charge-discharge cycles, and broad operating temperature ranges, electrochemical supercapacitors find widespread applications in hybrid/electric vehicles, electronics, and smart grids. Fig.1 gives the plots of specific energy vs specific power for various electrical energy storage devices. The specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge.

Strictly speaking, depending on working mechanism, electrochemical capacitors may be classified as (1) Electrical Double layer Capacitor (EDLC or supercapacitor) and (2) Pseudocapacitors. While EDLCs depend on formation of an ionic double layer at the electrode-electrolyte interface for electrical energy storage, pseudocapacitors store energy due to reversible redox reactions based on Faradaic charge transfer, in which the concentration of redox sites on the surface of electrodes is a governing factor of the specific capacitance. Supercapacitors or EDLCs are cheap and widely available but suffer from low E density. On the other hand, pseudocapacitors are costly but provide better energy and power density. From the materials point of view, the materials used/researched for supercapacitor applications fall in three main categories: a) Carbon-based materials for electric double-

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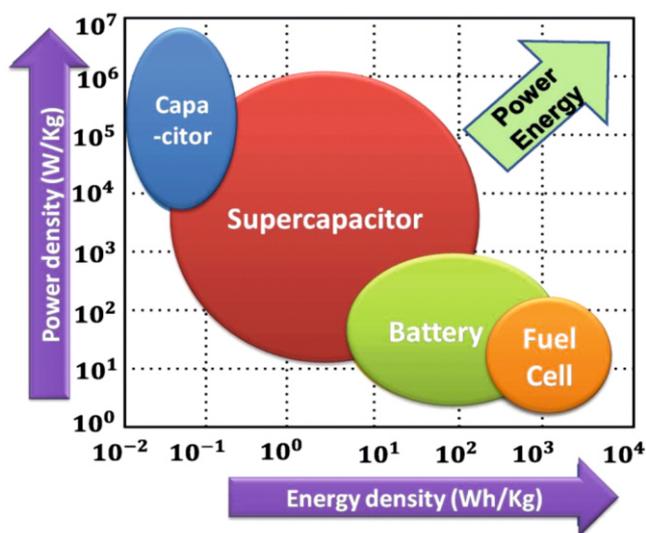


Fig.1: Ragone Plot: Power vs Energy Density of different electrochemical energy storage devices.

Carbon based Supercapacitors

Carbon-based materials are well documented as efficient electrode materials for supercapacitor applications and till now all the commercial supercapacitors available in market are based on carbon materials only. The major advantages of carbon based supercapacitors are possibility of larger surface area and higher conductivity of carbon based material apart from their low cost and easy processibility[4]. The major challenge of carbon based super capacitor research is to increase the energy density keeping the total cost comparable with the existing one. For that numerous strategies have been adopted, such as, increase in surface area, optimization of pore size of carbon electrode materials and increase of operating voltage by using different electrolyte materials[5]. It has been reported that the co-existence of micro and meso pores facilitate the mobility of ions within the electrode materials because of superior inter pores connectivity. In recent times, several carbon structures with interconnected hierarchical pores were synthesized, which show better electrochemical performances due to high surface area and optimized diffusion pathway for easy conduction or movement of ions[6].

layer capacitors (EDLCs): For this class of materials, the charge storage is due to the electrostatic separation between the ions of the electrolyte and the high-surface area electrodes; b) Electronically conducting polymers: These materials store energy through fast reversible doping/de-doping processes; c) pseudocapacitive transition-metal-based oxides/hydroxides: These materials store energy by virtue of fast reversible multi-electron surface redox Faradaic reactions. This is in addition to the double layer capacitance that is due to high surface area of the electrode material. This particular class include materials that mostly belong to oxides and hydroxides based on transition-metal, such as MnO_2 , NiO , CoO_x , $Co(OH)_2$, and $Ni(OH)_2$ [3]. They exhibit rich redox states, which can provide considerably improved specific capacitance than typical carbon-based EDLCs. Some of the materials that find application in electrochemical capacitors based on carbon, transition metal oxides and hydroxides are discussed in details in the following sections.

Doping of carbon materials with boron (B), nitrogen (N), oxygen (O), sulfur (S) and phosphorus (P) have tremendous effect on the supercapacitive properties by increasing the energy density of carbon based EDLCs[7]. Nitrogen is the most accepted doping element because of its greater electronegativity, similar size and easy synthesis methodology. Primarily, two different synthesis strategies have been adopted for nitrogen containing porous carbons, viz. (a) post-treatment of pre-synthesized carbons in nitrogen atmosphere, like ammonia or urea and (b) pyrolysis of nitrogen-containing precursors, namely polyaniline, polypyrrole, polyimide, melamine, polyvinyl pyridine etc for in-situ nitrogen doping[8]. We have synthesized nitrogen doped porous carbon with hierarchical interconnected pore structure by single step annealing of EDTA precursor, where the nitrogen doping and pore diameter were varied by changing the annealing temperature [Fig. 2]. The optimized sample can provide high energy density of 9.5 Whkg^{-1} at a power density of 64.5 Wkg^{-1}

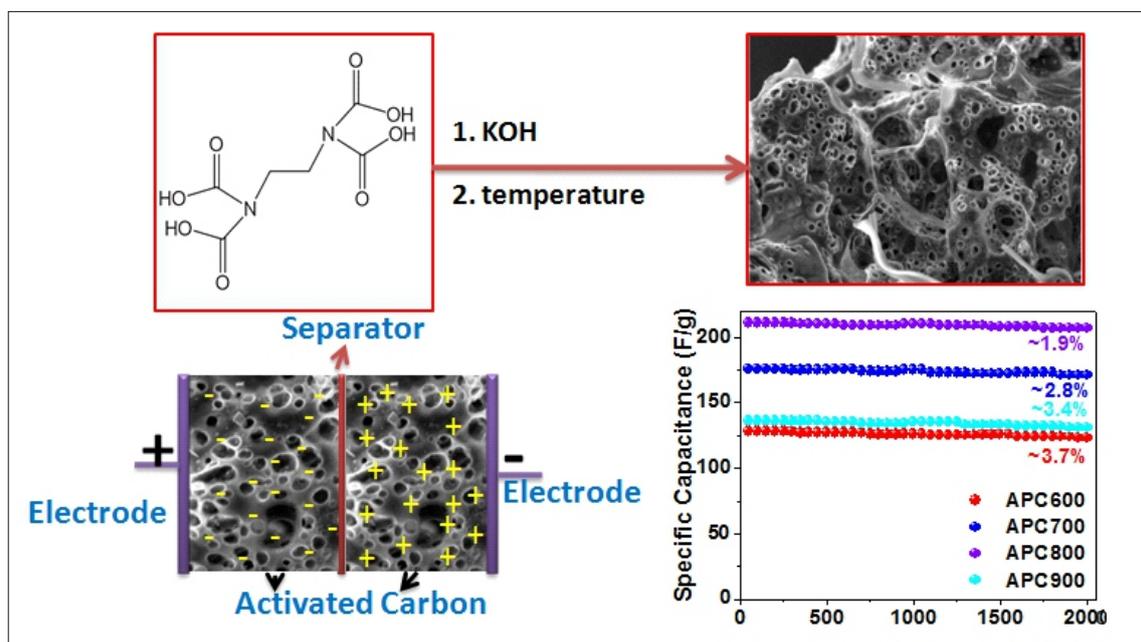


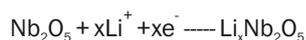
Fig.2: N-doped porous carbon prepared from the pyrolysis of EDTA.

within a voltage window of 1.0 V with very high capacity retention[9]. Similarly, Kang *et. al.* has synthesized hierarchical interconnected carbon which demonstrated high capacitance of 268.4 Fg^{-1} confirming the increased ions transport in presence of interconnected larger micropores and mesopores[10].

Transition Metal Oxides-based Supercapacitors

The significance of transition metal based supercapacitor rely on the fact that, due to the existence of variable oxidation states, they can store more amount of charge by reversible Faradic reaction near the surface of the active material, leading to more energy density compared to the traditional carbon based supercapacitor. The main difference from the battery material is that in pseudo capacitor, the change in the oxidation state does not led to the phase change of the material. The initial reports on the pseudocapacitor behaviour of transition metal based system are mostly on ruthenium oxide (RuO_2) which exhibits high theoretical specific capacitance value around $1300\text{-}2200 \text{ Fg}^{-1}$. Due to the high cost of RuO_2 afterwards different systems were studied and reported including other transition metal oxides, hydroxides, and doubled layer hydroxides. Apart from that, recently several derivatives were also studied such as sulfides, and selenides for their supercapacitive application[11]. The main research objective of transition metal based supercapacitor study is the optimisation of synthesis procedure to get better electrochemical performance by varying the composition, morphology and structural parameters by using different synthetic methodologies. The main advantage here is that the TM based supercapacitors can be combined with carbon based supercapacitor to make a hybrid capacitor, which ultimately leads to both higher specific and current density along with the long term cyclic stability.

The major charge storage mechanism of the pseudocapacitor can be divided in two major categories, the redox based pseudo capacitance and intercalation based pseudocapacitance[12]. In the redox based pseudocapacitor redox reactions typically take place at the surface and near surface region and the GCD (galvanostatic charge discharge) curve exhibit triangular shape similar to the EDLC. Typical electrodes, where these types of mechanisms are seen are RuO_2 and MnO_2 . Here during the charging process the electrolyte gets absorbed on the electrode and the metal ions get oxidised to their higher oxidation states. For example, in acidic medium the Ru(II) gets converted to Ru(IV), where as Mn(III) gets oxidised to Mn(IV). During the discharging the reverse process occurs. In the intercalation based pseudo capacitance the electrolyte goes into the voids and also in the interlayer spacing of the electrode materials and gets intercalated. A very well known example for that is hexagonal $\text{T-Nb}_2\text{O}_5$ oxide, which in virtue of its layer structure allow Li^+ ion to transport within it without any activation barrier [13]. The reaction occurs during the charging process is given by



The major benefits for these kinds of systems are very high specific capacitance and energy density due to the utilisation of the complete bulk material but the application is limited by poor cyclic stability. Another major drawback is the poor conductivity of the electrode material where improvement has been achieved by making composite with carbon. Jiawen *et al.* demonstrated that Nb_2O_5 @mesoporous carbon hollow core-shell nanostructures exhibits an initial reversible specific capacity of 410 Cg^{-1} at 1 Ag^{-1} with rate capability of 173 Cg^{-1} at 50 Ag^{-1} [14]. Apart from the cation intercalation (Li^+ , Na^+), perovskite oxide anionic intercalated supercapacitors are also

reported, where O^{2-} ions gets intercalated. It can be easily achieved in the aqueous medium and due to higher charge storage capacity of O^{2-} ions, these kinds of supercapacitors show higher charge density[15].

RuO_2 is considered as the ideal pseudocapacitor material due to its good electrical conductivity and high power and energy density. In spite of its excellent electrochemical properties the material has been rarely used due to its toxic nature, low abundance and high cost. Apart from that, there are issues regarding the agglomerations of RuO_2 nanoparticles which lead to the decrease in energy and power density of the system. This problem can be taken care by dispersing RuO_2 nanoparticles on carbon surface. Different carbon materials have been studied for this purpose and it has been found that the presence of carbon support does not only prevent the agglomeration of the nanoparticles, but also provides more active sites by increasing the surface area of the electrode material and reduces the overall cost. For example, RuO_2 and electrospun carbon composite, with very low RuO_2 loading concentration, shows excellent pseudo capacitance performances with high energy density of $22\text{-}15 \text{ W h kg}^{-1}$ in the power density range of $400\text{-}4000 \text{ W kg}^{-1}$ [16]. Han *et al.* also established that a solid-state supercapacitors with RuO_2 /Vertical Graphene hybrids and polymer gel electrolyte shows excellent capacitance retention with at least 10,000 cycles[17]. Flexible supercapacitor synthesized by homogeneously dispersing RuO_2 nanoparticles on carbon nano anion (CNO) support by sol gel route shows a high energy and charge density of 10.62 Whkg^{-1} and 4.456 kWkg^{-1} with excellent cyclic stability, where CNO acts both as the electrical conducting material as well as the support for the oxide nanoparticles[18].

Though there is commanding advancement on the supercapacitor work of RuO_2 , still the toxicity and cost of the material are found to be the limiting parameters. Development of cheaper and environmental friendly counter parts with comparable supercapacitive behaviour with RuO_2 is in progress and the most potential material till now is MnO_2 , due to its low cost, high theoretical capacitance. The major issue in the phase pure MnO_2 is its very poor thermal conductivity. Change in the morphology and structural parameters and making nanocomposite with other metal oxides and conducting carbons are some of the routes for the improvements of their supercapacitive performances. For example, to obtain nanosize and high surface area materials, Xiao *et al.* had implemented salt-templated approach for synthesis of 2D- MnO_2 sheets[19].

Mixed Transition Metal Oxide

Mixed transition metal oxides have obtained enormous significance for pseudocapacitor applications[20]. In the mixed transition metal oxide the synergistic effect by different metal ions play a vital role to increase the electron transportation, which finally leads to higher specific capacity and conductance.

One of the very interesting and widely explored mixed oxides of Ni and Co is NiCo_2O_4 , where contribution of redox properties of both Ni and Co ions, giving rise to excellent electrochemical behaviour. Different morphological structures have been synthesized for NiCo_2O_4 and depending on the morphology vast difference in the supercapacitive performance are reported. NiCo_2O_4 nanosheets and nanowires with oxygen vacancy on the surface promote specific capacitance by facilitation the absorption of OH^- ion and are reported to have high specific capacitance (1590 and 1280 Fg^{-1}) at current density of 1 Ag^{-1} [21]. It is important to note that

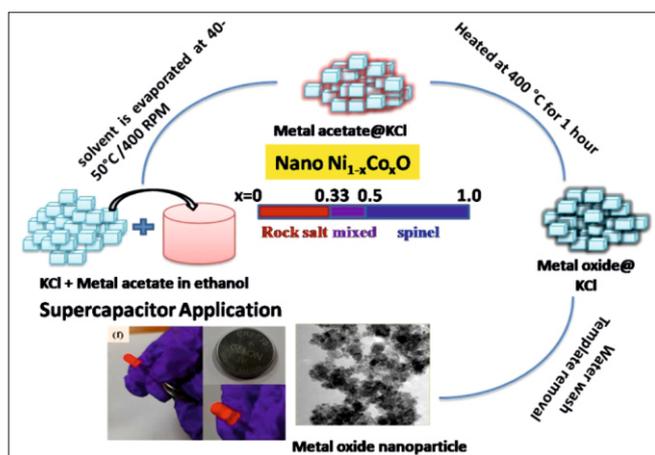


Fig.3: Synthesis and supercapacitor application of $Ni_{1-x}Co_xO$ ($0.0 \leq x \leq 1.0$) oxide.

NiO adopts rock salt structure whereas Co_3O_4 crystallizes in a spinel structure. The structure of the mixed oxide depends on their calcinations temperature as well as their preparation method. In general in very low Co content the mixed oxide stabilizes in the rock salt structure but with increase in the Co content it forms spinel or inverse spinel structure. In our recent study we have seen that $Ni_{1-x}Co_xO$ ($0.0 \leq x \leq 1.0$) system synthesized by salt templated route, formed a biphasic mixture of fcc and spinel-type phases upon 33 mol% of cobalt-substitution, but gets converted to single-phasic spinel-type phase field which continued up to 100 mol% Co_3O_4 [22]. [Fig.3] Among the range of composition it has been found that due to the combined effect of both Ni and Co ions, the $Ni_{0.5}Co_{0.5}O_x$ exhibits highest specific capacitance of 146 F g^{-1} at 1 A g^{-1} with 97% retention up to 1000 cycles[22].

Apart from the mixed Ni-Co oxides, zinc cobaltites and copper cobaltites[23] are two emerging electrode materials for supercapacitor application. The major advantage of zinc cobaltite ($ZnCo_2O_4$) is that it possesses good redox activity and conductivity along with high theoretical specific capacitance of 2650 F g^{-1} . Electrode made with urchin-like $ZnCo_2O_4$ microspheres prepared by Jadav *et al.* shows a high specific capacitance of 677 F g^{-1} at 1 A/g current density[24]. $ZnCo_2O_4$ nanorods deposited on Nickel-foam via co-precipitation method exhibits a specific capacitance value of 604.52 F/g [25]. Binder free $ZnCo_2O_4$ deposited on stainless steel prepared by the hydrothermal method was reported to exhibit a specific capacitance value of 593 F/g at 10 mV/s .

$CuCo_2O_4$ (CCO) also has emerged as one of the potential materials for supercapacitor application as it possesses inherently high specific capacity. But the semiconducting nature of the $CuCo_2O_4$ materials is the major hindrance to its electrochemical application. So for the practical application, composite with other conductive material or introduction of conductive skeleton in the structure is needed. Aliovalent metal ion doping has also been reported to increase the conductivity by introduction of oxygen vacancy in the structure. An electrode prepared by core shell nanocomposite of $CCO@CuO$ synthesized by hydrothermal method and deposited on flexible stainless steel mesh substrate exhibited a high specific capacitance of 713 F g^{-1} at a current density of 11 mA cm^{-2} , which was higher than that of the individual components[26].

Layered Double Hydroxides as Supercapacitors

Layered double hydroxides (LDHs) multi-metal clay materials that consist of layers of metal cations (mostly

transition metal ions) that octahedrally surrounded by hydroxyls forming $M(OH)_6$ ($M: M^{2+}/M^{3+}/M^{4+}$) octahedra[27]. The layers are positively charged and are held together by charge balancing negative ions and many a times neutral species like water molecules. A considerable amount of research is being dedicated towards LDH materials as pseudocapacitors because of the following factors:

- (1) High redox activities, green and environmentally-friendly nature and efficient utilization of transition metal atoms that are dispersed homogeneously in LDH structure.
- (2) Easy tunability of cations in the host layers of LDH and possibility of anion exchange without altering the crystal structure.
- (3) Easy and facile exfoliation of LDH structure into monolayer nanosheets and possibility of chemical modification.

Plenty of research studies have been carried out on the electrochemical behaviors of LDHs in recent years. Most of these studies focus on the effect composition, structure design and device assembly[14–19].

The general formula of LDH compounds is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]A_{x/n}^{n-} \cdot nH_2O$. There is wide variety of interlayer anions present in the LDH. The wide tunability option available for tuning M^{2+}/M^{3+} in addition to choosing the interlayer anion, yields a range of host-guest combinations and nano-architecture and this provides a huge data set for electrochemical properties. Thus, there is a lot of scope for varying the electrical behaviour of these materials by varying any of the above parameters and hence in the recent years a tremendous amount of research has been dedicated to this area. The open two-dimensional structure of transition metal based LDHs enables highly efficient Faradaic redox reactions at the near-surface transition metal sites with fast kinetics.

LDH based on Ni and Co ions have been widely explored due to their high theoretical specific capacitance of more than 2000 F g^{-1} [28]. Electrochemical behavior of Ni, Al and Co, Al-based LDH have also been widely explored. In case of Ni-Al-LDH, two redox peaks were observed in the cyclic voltammetry (CV) curves, as represented by the following reaction:



The charge transport inside the material is due to electron hopping along the layers and “proton transfer” from hydroxyl attached to Ni^{2+} ions from host layers to electrolyte solution when the anodic potential is applied. Co-Al-LDH however shows different behaviour[29]. In order to understand the effect of M^{2+}/M^{3+} ratio on structural and energy storage response, several studies have tried to adjust the amount of Al^{3+} in Co-Al-LDH. It has been observed that etching the Co-Al-LDH with KOH leads to loss of non-electroactive Al^{3+} and results in porous morphology that enhances the capacitive performance[30]. In fact, the synthesis routes are being modified and controlled to obtain monometallic LDH by making use of different oxidation states of Ni (Ni^{2+} - Ni^{3+} - LDH) and Cobalt (Co^{2+} - Co^{3+} - LDH)[31].

It is understandable that LDH containing different electroactive ions within a single double hydroxide structure shows better capacitive performance owing to wider inter layer space and reduced mechanical stress during the charge/discharge process. Many dually active metal-based LDHs (e.g. NiMn-LDHs, CoMn-LDHs and CoFe-LDHs)[32] have also been studied for electrode application of pseudo-supercapacitors owing to redox activity of both the ions within the same structure. In such cases, the capacitive performance

parameters such as specific capacitance, rate performance and cycling stability are affected by a variety of factors. The atomic ratio of the cations is one of the biggest influencing factors that controls not just the crystal phase but also the morphology, structure and capacitive behaviour. Several studies have shown the effect of Ni/Co ratio on the morphology of the Ni-Co LDH [33]. In addition, the content of Co makes the nanostructures thicker. The thickness has an adverse effect on capacitive behaviour as larger thickness would limit their surface area, make lesser surface sites accessible and affect surface-dependent redox reactions. The ratio of Ni and Co ions also affect the electrochemical behaviour as this determines the position of redox peaks. In addition, the presence of Co increases the electronic conductivity because of conversion of $\text{Co}(\text{OH})_2$ to CoOOH which is more conductive and hence aids the e^- transfer during electrochemical process[34]. However, higher Ni amounts leads to better specific capacitance. Thus, an optimal ratio of Ni and Co ions is required for designing efficient layered double hydroxide for this application. Similarly, a lot of studies have been reported on LDH containing other electrochemically active ions such as Fe and Mn[35]. Other than manipulating the cations and their ratio in LDH structures, tuning the anions present in the interlayer gallery of LDH is also a strategy employed for designing materials with enhanced electrochemical behaviour. The ionic movement of OH^- ions (from electrolyte) inside the layers of LDH is hindered that leads to increase in resistance. In order to circumvent this, many organic anions (sodium dodecyl sulfate) can be exchanged with inorganic anions such as CO_3^{2-} , NO_3^- etc. usually present in the interlayers of LDH leading to increase in the gallery height that promotes ionic diffusion and lesser ohmic resistance resulting in superior electrochemical behaviour such as better specific capacitance and rate capabilities[36]. Sometimes the neutral organic moieties such as ethylene glycol, glucose etc. are also used for this purpose that have yielded encouraging results[37]. LDHs belongs to one of the most technologically promising structural families for application as electrode materials for electrochemical capacitors owing to their low cost, facile synthesis and high theoretical specific capacitance. Due to their inherently layered structure, possibility of choosing a wide variety of host metal ions and the ease of exchange of interlayer anions, they have tremendous potential in energy storage applications.

Conclusion and Prospects

Transition metal-based oxides have been frontrunners for oxides for energy storage applications. The advantages are higher relative natural abundance, low production cost, higher specific capacitance as compared to other candidates such as carbon-based materials and conductive polymers. There has been a lot of research in tuning the composition and concomitant structure to optimise the electrochemical behaviour. This has direct bearing on redox behaviour exhibited by the material. In case of layered materials, the interlayer spacing of the material provides an additional parameter to control the electrochemistry. Control on nanoarchitecture aids in improving the capacitive performance as it enhances the utilization of active sites and promotes fast ion transport. The biggest roadblock in their large scale application is that they possess relatively low electrical conductivity which restricts the charge/ discharge kinetics. A multi-pronged approach is followed to overcome this problem, which includes synthesis of electrode materials with nanostructure possessing larger active surface area, combining with conductive materials (i.e., conducting polymers and carbon materials) as well as employing multiple metals composite with synergistic effect. Despite a lot of research being carried out in all the aspects of

developing viable electrochemical capacitors, their practical capacitance and energy densities leave scope for exploration. The synthesis of electrode materials with good electrochemical performance by an environmentally friendly, facile and low-cost method is need of the day for developing efficient and cost-effective electrochemical capacitors for energy storage applications.

References

- [1] F. Wang, X. Wu, X. Yuan, Z Liu, Y Zhang, L Fu, Y. Zhu, Q. Zhou, Y. Wu and W. Huang, *Chem. Soc. Rev.*, 2017, 46, 6816.
- [2] [(a) C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 2015, 44, 7484–7539; (b) W. Tang, Y. Zhu, Y. Hou, L. Liu, Y. Wu, K. P. Loh, H. Zhang and K. Zhu, *Energy Environ. Sci.*, 2013, 6, 2093–2104; (c) F. Wang, X. Wu, C. Li, Y. Zhu, L. Fu, Y. Wu and X. Liu, *Energy Environ. Sci.*, 2016, 9, 3570–3611; (d) R. Li, Z. Lin, X. Ba, Y. Li, R. Ding and J. Liu, *Nanoscale Horiz.*, 2016, 1, 150–155.
- [3] Y. Wang, J. Guo, T. Wang, J. Shao, D. Wang and Y.-W. Yang, *Nanomaterials*, 2015, 5, 1667-1689.
- [4] Ling Miao, Ziyang Song, Dazhang Zhu, Liangchun Li, Lihua Gan and Mingxian Liu, *Mater. Adv.*, 2020, 1, 945-966.
- [5] S. Kondrat, C. R. Pérez, V. Presser, Y. Gogotsi and A. A. Kornyshev, *Energy Environ. Sci.*, 2012, 5, 6474-6479.
- [6] Ruben Heimböckel, Frank Hoffmann and Michael Fröba, *Phys. Chem. Chem. Phys.*, 2019, 21, 3122-3133.
- [7] Lijing Xie, Fangyuan Su, Longfei Xie, Xiaoqian Guo, Zhenbing Wang, Qingqiang Kong, Guohua Sun, Aziz Ahmad, Xiaoming Li, Zonglin Yi and Chengmeng Chen, *Mater. Chem. Front.*, 2020, 4, 2610-2634.
- [8] Polyacrylonitrile/polyvinyl alcohol-based porous carbon nanofiber electrodes for supercapacitor applications, Yasin Altin, Ayse Celik Bedeloglu, *Int. J. of Energy Research*.
- [9] Das TK, Banerjee S, Sharma P, Sudarsan V, Sastry PU. *Int J Hydrogen Energy*, 2018, 43, 8385–94.
- [10] Min Seok Kang, Incheol Heo, Kyung Gook Cho, Hyuna Kyung, Hee Soo Kim, Keun Hyung Lee, Won Cheol Yoo, 2022, 45, 380-388.
- [11] Cong Wang Zehao Song Houzhao Wan, Xu Chena, Qiuyang Tan, Yi Gan, Pei Liang, Jun Zhang, Hanbin Wang, Yi Wang, Xiaoni Peng, Peter A. van, Akenb Hao Wang, *Chemical Engineering Journal*, 2022, 400, 125955.
- [12] (a) Yuqi Jiang, Jinping Liu, *Energy and environmental materials*, 2019; 2:30-37. (b) Y. Liu, S. P. Jiang, Z. Shao, *Materials Today Advances*, 2020, 7, 100072.
- [13] (a) J. W. Kim, V. Augustyn, B. Dunn *Adv. The effect of crystallinity on the rapid pseudocapacitive response of Nb2O5 Energy Mater.*, 2012, 2, 141; (b) V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, B. Dunn, *Nat. Mater.*, 2013, 12, 518.
- [14] Songmin Zhang, Jiawen Wu, Jitong Wang, Wenming Qiao, Donghui Long, Licheng Ling, *Journal of Power Sources*, 2018, 396, 88-94.
- [15] L. Zhu, Y. Liu, C. Su, W. Zhou, M. Liu, Z. Shao, *Angew. Chem.*, 2016, 128, 9728-9731.
- [16] Sohyun Jeon, Ji Hwan Jeong, Hyomin Yoo, Hak Ki Yu, Bo-Hye Kim*, and Myung Hwa Kim, *ACS Appl. Nano Mater.*, 2020, 3, 3847–3858.
- [17] Zhao Jun Han, Shafique Pineda, Adrian T. Murdock, Dong Han Seo, Kostya (Ken) Ostrikov, Avi Bendavid, *J. Mater. Chem. A*, 2017, 5, 17293-17301.
- [18] VEDIKUYIL AZHAGAN MUNIRAJ, CHAITANYA KRISHNA KAMAJA, and MANJUSHA V. SHELKE, *ACS Sustainable Chem. Eng.* 2016, 4,

- 2528–2534.
- [19] X. Xiao, H Song, S. Lin, *et al.* Nature Communications, 2016, 7, 11296.
- [20] (a) T.-Y. Wei, C.-H. Chen, H.-C. Chien, S.-Y. Lu, C.-C. Hu, *Adv. Mater.*, 2010, 22, 347–351; (b) P.F. Teh, Y. Sharma, S.S. Pramana, M. Srinivasan, *J. Mater. Chem.*, 2011, 21, 14999–15008.
- [21] D. Yan, W. Wang, X. Luo, C. Chen, Y. Zeng, Z. Zhu, *Chem. Eng. J.*, 2018, 334, 864–872.
- [22] S. Banerjee, A. Chowdhury, A. Chandra, V. Grover, *Mat. Chemi. and Physics*, 2022, 286, 126202.
- [23] S. Vijayakumar, S.-H. Lee, K.-S. Ryu, *Electrochim. Acta*, 2015, 182, 979–986.
- [24] H. Chen, J. Wang, X. Han, F. Liao, Y. Zhang, X. Han, C. Xu, *Ceram. Int.*, 2019, 45, 4059–4066.
- [25] T. Huang, C. Zhao, R. Zheng, Y. Zhang, Z. Hu, *Ionics (Kiel)*, 2015, 21, 3109–3115.
- [26] Gokul P. Kamble, Akash S. Rasal, Samadhan B. Gaikwad, Vivek S. Gurav, Jia-Yaw Chang, Sanjay S. Kolekar, Yong-Chien Ling, and Anil V. Ghule, *ACS Appl. Nano Mater.* 2021; 4: 12702–12711.
- [27] J. Zhao, J. Chen, S. Xu, M. Shao, D. Yan, M. Wei, D. G. Evans and X. Duan, *J. Mater. Chem. A*, 2013, 1, 8836.
- [28] (a) Z. Lu, Z. Chang, W. Zhu and X. Sun, *Chem. Comm.*, 2011, 47, 9651–9653; (b) H. Chen, J. Jiang, Y. Zhao, L. Zhang, D. Guo and D. Xia, *J. Mater. Chem. A*, 2015, 3, 428–437.
- [29] X. Li, D. Du, Y. Zhang, W. Xing, Q. Xue and Z. Yan *J. Mater. Chem. A*, 2017, 5, 15460.
- [30] (a) Z. Lu, W. Zhu, X. Lei, G. R. Williams, D. O'Hare, Z. Chang, X. Sun and X. Duan, *Nanoscale*, 2012, 4, 3640–3643; (b) Y. Wang, W. Yang, C. Chen and D. G. Evans, *J. Power Sources*, 2008, 184, 682–690; (c) N. Abushrenta, X. Wu, J. Wang, J. Liu and X. Sun, *Sci. Rep.*, 2015, 5, 13082.
- [31] (a) F. Gu, X. Cheng, S. Wang, X. Wang and P. S. Lee, *Small*, 2015, 11, 2044–2050; (b) P. Vialat, C. Mousty, C. Taviot-Gueho, G. Renaudin, H. Martinez, J. C. Dupin, E. Elkaim, F. Leroux, *Adv. Funct. Mater.*, 2014, 24, 4831–4842.
- [32] (a) H. Chen, F. Cai, Y. Kang, S. Zeng, M. Chen and Q. Li, *ACS Appl. Mater. Interfaces*, 2014, 6, 19630–19637; (b) J. Zhao, J. Chen, S. Xu, M. Shao, Q. Zhang, F. Wei, J. Ma, M. Wei, D. G. Evans and X. Duan, *Adv. Funct. Mater.*, 2014, 24, 2938–2946.
- [33] (a) J. Yang, C. Yu, X. Fan and J. Qiu, *Adv. Energy Mater.*, 2014, 4, 1400761; (b) X. Sun, G. Wang, H. Sun, F. Lu, M. Yu and J. Lian, *J. Power Sources*, 2013, 238, 150–156.
- [34] (a) X. Zheng, Z. Gu, Q. Hu, B. Geng and X. Zhang, *RSC Adv.*, 2015, 5, 17007–17013; (b) Y. Cheng, H. Zhang, C. V. Varanasi and J. Liu, *Energy Environ. Sci.*, 2013, 6, 3314–3321.
- [35] (a) K. Y. Ma, J. P. Cheng, J. Zhang, M. Li, F. Liu and X. B. Zhang, *Electrochim. Acta*, 2016, 198, 231–240; (b) A. D. Jagadale, G. Q. Guan, X. M. Li, X. Du, X. L. Ma, X. G. Hao and A. Abudula, *J. Power Sources*, 2016, 306, 526–534.
- [36] X. Wu, L. Jiang, C. Long, T. Wei and Z. Fan, *Adv. Funct. Mater.*, 2015, 25, 1648–1655.
- [37] (a) C. Wang, X. Zhang, Z. Xu, X. Sun and Y. Ma, *ACS Appl. Mater. Interfaces*, 2015, 7: 19601–19610; (b) L. Lv, K. Xu, C. D. Wang, H. Z. Wan, Y. J. Ruan, J. Liu, R. J. Zou, L. Miao, K. Ostrikov, Y. C. Lan and J. J. Jiang, *Electrochim. Acta*, 2016, 216, 35–43.