A Review on Transition-metal Oxalate Based Electrode for Supercapacitors

Abhijeet Kumar Singh1, Piyush Jaiswal1 and Preetam Singh2

1Nanotechnology Program, Centre for Advanced Studies, Abdul Kalam Technical University, Lucknow, 226031, Uttar Pradesh, INDIA
E-mail: ak110singh@rediffmail.com (Abhijeet Kumar Singh)
E-mail: piyushj@cas.res.in (Piyush Jaiswal)

2Department of Ceramic Engineering, IITBHU, Banaras Hindu University, Varanasi, 221005, Uttar Pradesh, INDIA
E-mail: preetamsingh.cer@itbhu.ac.in (Preetam Singh)

Abstract. Transition-metal oxalates have been significantly showing the potential for charge storage in supercapacitor as an energy material. Transition-metal oxalate materials with framework structures, morphology and electrochemical properties offer an opportunity for sustainable energy storage material. Recently, transition metal oxalates, witnessed pseudocapacitive or battery type behaviour when it has been used as electrode for supercapacitor applications. In this review, we mainly address the recent study of transition metal oxalates as potential energy storage materials such as Co, Ni, Mn and Fe based oxalates and composites in the context of supercapacitors with electrochemical performances. Although, electrochemical performances of TMOx electrode can be enhanced through various methodology such as by preparing mixed TMOx structures or preparing nanocomposite with highly conductive secondary materials such as graphene and CNT. The generated idea after reading this paper will help the researchers to explore further usage of transition metal oxalates in the field of electrochemical energy storage devices.

Keywords: Transition Metal Oxalates, Open structure, Electrode, Pseudocapacitor

1. Introduction

Burning of fossil fuel leads to the emission of CO2 which is one of the greenhouse gases that causes global warming. It has been observed that there is decrement in fossil fuel while an accompanying huge demand of energy increased in the society [1–3]. These issues can be minimized as the required society will utilize the sustainable and renewable resources. Electrochemical energy storage devices (EESD) as an alternative source which is more energy efficient and environmentally friendly [2, 4]. These EESD work on the principal of conversion of electrical energy into chemical energy and vice versa. Rechargeable batteries and supercapacitor are one of the peculiar EESD are currently being developed to resolve the issue of global demand of energy [5, 6].

Supercapacitors are EESD devices which has lower energy density as compare to batteries but it can deliver higher power [2, 3, 6]. Supercapacitor can also overcome the limitation of
batteries such as rate capability at higher current as well as cyclic stability [7, 8]. Supercapacitors, categories in double layer capacitors (EDLCs) and pseudocapacitors. EDLC performs by storing the ions on the surface of electrodes by electrostatic storage of charges. Mainly the carbon based electrode such as, porous carbon, activated carbon, graphene, Carbon Nanotube (CNT) has been used as an electrode for EDLC [3] [9]. Pseudocapacitor exhibits faradic redox reactions occurring at or near the surface of an appropriate electrode material lead to EDLC-like electrochemical features but the redox processes lead to much greater charge storage [10, 11]. Transition-metal-oxides, conducting polymer, and nanocomposite materials have been also extensively used as an electrode for pseudocapacitor application [3, 12–15].

RuO$_2$ has been extensively studied as pseudocapacitive material for energy storage [12, 16]. Although RuO$_2$ exhibits having specific capacitance 600F/g with operating potential 1.2V in acidic medium [16]. Ruthenium is a costly element, therefore utilizing ruthenium in commercial supercapacitor is not feasible economically. Similarly, MnO$_2$ display in both amorphous and crystalline phase have been investigated for high-rate energy storage in aqueous electrolytes [12, 14]. MnO$_2$ have poor electrical conductivity which one of the reason having low specific capacitance [17]. In addition to that transition metal oxides suffer from irreversibility during charging and discharging due to the phase change [12, 18]. Layered material such as Ni(OH)$_2$ shows higher specific capacitance as compare to other oxides such as RuO$_2$ and MnO$_2$ but it has smaller potential window [19]. A part from that layered materials also have lower cyclic stability due to continuous phase change [20]. Transition Metal Dichalcogenide (TMDS) are usually two dimensional layered material which will offer both EDL as well as intercalation/deintercalation of ions for faradic reaction [21]. Moreover, due to poor electronic conductivity, TMDs electrochemical performance decreases as electrolyte couldn’t access more number of active sites which results poor capacitance. TMDs also suffer from rate capability and cyclic stability during charging/dis-charging cycle [22]. Conducting polymer exhibit large pseudocapcitance in the range of ~ 300F/g which is more than few carbon material and metal oxide. Due to their high resistance by ion diffusion within the electrode slows down. As a result of that swelling and shrinking of polymers occurred during cyclic process [3, 13, 23].

![Figure 1. Bar chart for transition metal oxalates and their derivatives for LIBs and Supercapacitor.](image)

Figure 1. Bar chart for transition metal oxalates and their derivatives for LIBs and Supercapacitor.
In the recent years, the number of research has been conducted on transition metal oxalate (TMOx) materials and their electrochemical characteristics which defines the feasibility of TMOx as an energy storage material. Fig 1 clearly shows the recent work related to synthesis of nanostructured oxalate and oxalate-derived materials and their application in Lithium ion batteries (LIBs) and supercapacitors is a main focus [24]. Tarascon et al. has mentioned the reversible Li$^{+}$ insertion capability in Fe(III) Oxalate tetrahydrate as an anode for Lithium ion batteries (LIBs) [25]. Reddy et al. reviewed that of oxalates and oxyanions based anodes for LIBs [26]. The electrochemical performance of TMOx has displayed equivalently capable, and offers higher specific capacities as compared to the identical oxide [27]. TMOx showed a great potential in the field of electrochemistry, mainly batteries and supercapacitors to acquire high energy and power density. Moreover, transition metal oxalates as an energy material offers an opportunity to explore electrodes that can possibly exhibits good capacity for charge storage. In account of that TMOx require more emphasised and in-depth study in the field of EESD more specifically supercapacitors. Thereby, we believe that presenting a concentrated review to summarize the significance of TMOx-based energy storage materials the further developments for pseudocapacitor applications. This review, consists comprehensively addressed the usage of oxalates and nanocomposites based on oxalate as an electrode for supercapacitors. In addition to that we have describe the type of electrode materials and structure of TMOx for charge storage mechanism.

2. A short briefing regarding the type of electrode materials

Electrochemical signatures including Cyclic voltammograms (CV) accompanied by galvanostatic charge/discharge (GCD) curves, the electrode materials can be categorised as EDLC, pseudocapacitive and battery-like as shown in fig2 which has been used for the fabrication of supercapacitors [28]. EDLC mainly show rectangular CV with scan rate response as well as linear charge discharge profile with respect to time. Pseudocapacitance electrode materials, such as MnO$_2$ and RuO$_2$ exhibits surface redox which produces approximately rectangular CV in aqueous media with almost-linear GCD with some inflation [12]. Mostly Co/Ni based oxide, double layer hydroxide, and sulphide shows intercalation type also termed as battery-type electrode materials, with reversible redox peaks in their CV. In addition to battery type material show plateau in GCD curve.

3. Transition Metal Oxalates

Transition-metal oxalates compounds inculcates transition metal sites are coordinated with oxygen atoms of oxalate group (C$_2$O$_4$)$^{2-}$. Transition metal site exhibits redox coupling while oxalate group creates a framework structure that promote the diffusion of ions inside the structure during charge/discharge process. Moreover, different morphology of 2D TMOx nanomaterials also exhibits large number of redox active sites due to larger surface area. Hence, high surface area, framework structure, low price oxalates and their composites bring TMOx as sustainable candidate for electrode materials.

3.1. Cobalt based Oxalate

2D porous CoC$_2$O$_4$ thin sheet has been synthesised by Chen et al. by using simple hydrothermal method at 220°C with different reaction time as shown in fig 3(a) which exhibits schematic diagram of synthesis of CoC$_2$O$_4$ thin sheet [29]. Sample S1, S2 and S3 of CoC$_2$O$_4$ 2D thin sheet were prepared with reaction time of 5h, 10h and 20h respectively. Fig 3(b) display the FESEM image of S1(left), S2(right) and S3(bottom) of CoC$_2$O$_4$ which has a sheet like morphology. Electrochemical performance of CoC$_2$O$_4$ 2D thin sheet has been measured using Ni foam as current collector in 6M KOH. From the fig 3(c) it has been S3 has higher discharge time as compare to S1 and S2 Fig 3(d) and (e) shows the CV and GCD of S3-CoC$_2$O$_4$ 2D porous thin
Figure 2. CV and GCD of EDLC, pseudocapacitive and battery type materials. Reproduced (adapted) with permission [28]. Copyright 2018, Royal Society of Chemistry

sheet determines specific capacitance 1.631 F/cm² at the current 1.2 mA/cm² with excellent rate capability. Moreover, 2D porous thin sheet of S3-CoC₂O₄ was assembled with activated carbon to prepare complete cell as shown in fig 3(f) which exhibits maximum energy density and power density of 17.6 Wh/Kg and 9000 W/kg respectively. Cheng et al synthesised CoC₂O₄ by facile anodization strategy directly growing CoC₂O₄ on the cobalt foil [30]. From GCD fig 3(g) calculated specific capacitance for CoC₂O₄ was 1269 F/g at 6 A/g of current density in 2M KOH. In addition, to that electrode displays good rate capability and cyclic stability i.e. 8.1% of decay after 100000 cycle as shown in fig 3(h).

3.2. Nickel based Oxalates
Nanostructure nickel oxalate can be prepared by dissolving Nickel foil in oxalic acid with various organic solvent and water [31]. Fig. 4 (a)-(e) exhibits change in the morphology of nanostructures nickel oxalate that are prepared in various solvents containing 1M oxalic acid.

The electrochemical test of nickel oxalate nanostructures conducted in 2M KOH medium for the pseudocapacitance application as shown in fig 4(f). Subsequently, nickel oxalate annealed at higher temperature and converted into NiO which shows less intense peak as compare to nickel oxalate. Jung et al also investigated that the specific capacitance of the nickel oxalate structures is higher than that of the nickel oxide [31]. Zhao et al introduced 2D porous nickel oxalate (Ni–OA) thin sheets synthesized by a simple hydrothermal method [32]. NiC₂O₄ thin sheet were synthesised by hydrothermal method at constant temperature of 200 °C for 6, 12 and 24 h corresponding to sample was marked as S1, S2 and S3, respectively. Electrochemical test including CV and GCD were conducted in 6M KOH for S1, S2 and S3 at different scan rates and current densities respectively as shown in fig 4(g) and (h). Fig 4(i) CV curves reveals that as scan rates increases, peak current also increases for S1 Ni-OA. As a result of that it has been inferred that the 2D porous nickel oxalate based electrode exhibits the battery-type behavior. Further, fig 4(j) displays S1 Ni-OA electrode exhibits specific capacitance of 2835 F/g for 1 A/g of current density, and excellent cyclic stability which remains 92.5% at 10 A/g after 5000 charge–discharge cycles for supercapacitor as shown in fig 4(k).
**Figure 3.** (a) Schematic diagram of the preparation of 2D porous CoC$_2$O$_4$ thin sheets. (b) FESEM image of S1, S2, and S3 of CoC$_2$O$_4$ thin sheets. (c) GCD of S1, S2, and S3. (d) CV of S3 CoC$_2$O$_4$ thin sheets at different scan rates. (e) GCD of S3 CoC$_2$O$_4$ thin sheet at different areal current. Reproduced a, b, c, d, e, and f with permission [29]. Copyright 2018, The Royal Society of Chemistry. (g) Galvanostatic charge/discharge curve at various current densities. (f) Nanostructured cobalt oxalate electrode after CV treatment of 100,000 cycles along with SEM image showing the changed morphologies after number of cycle. Reprinted g and h with permission [30]. Copyright 2016, Elsevier.
Figure 4. FE-SEM images of nickel oxalate nanostructures with different morphology prepared in 1M oxalic acid dissolved in different solvents: (a) deionized water, (b) methanol, (c) ethanol, (d) n-propanol, (e) n-butanol. (f) CV of Nickel oxalate in 1M KOH. Reproduced a, b, c, d, e and f with permission [31]. Copyright 2010, The Royal Society of Chemistry. (g) CV of S1, S2 and S3 sample of Nickel Oxalate thin sheet. (h) GCD curves of S1, S2 and S3 at 1.0 A/g, respectively. (i) CV curves of S1 at different scan rate (j) GCD curves of S1 at different current densities. (k) Cyclic performance of S1 at a current density of 10 A·g⁻¹. Reproduced g, h, i, j and k with permission [32]. Copyright 2020, The Royal Society of Chemistry.
3.3. Other Oxalates

Recently Liu and co-workers [33] reported of MnC$_2$O$_4$/GO materials as an electrodes in supercapacitor application. Hydrothermal decomposition of KMnO$_4$ with ascorbic acid leads to the uniform distribution of the olive-like MnC$_2$O$_4$ particles on the surface of the GO sheets. The composite electrodes indicated a capacity of 122 F/g at 0.5 A/g of current density. Although from the CV as shown in Fig 5 (a) there was humps due to the presence of MnC$_2$O$_4$ which conclude the pseudocapacitance behaviour of MnC$_2$O$_4$/GO. Mixed oxalate the Co$_{0.5}$Mn$_{0.4}$Ni$_{0.1}$C$_2$O$_4$*$n$H$_2$O micro polyhedrons prepared by single step co-precipitation method [34]. The specific capacitances attain by microployhedrons 990F/g at 0.6 A/g, in 3.0 M KOH solution. Subsequently Co$_{0.5}$Mn$_{0.4}$Ni$_{0.1}$C$_2$O$_4$*$n$H$_2$O micro polyhedrons based electrode exhibited stable cycling performance maintaining specific capacitance of 968 F/g even after 6000 cycles.

Liu et al reported FeC$_2$O$_4$/rGO hydrogel composite as a negative electrode for supercapacitors[35]. The electrochemical performance of FeC$_2$O$_4$/rGO was conducted in aqueous Na$_2$SO$_4$ solution (1mol/L) using three electrode steup. The CV curves of rGO hydrogels were rectangular as rGO shows EDLC behaviour while redox peaks evidently appear for the FeC$_2$O$_4$/rGO hydrogel as shown in fig 5(b) indicating the pseudocapacitive of iron oxalate. The specific capacitance in Na$_2$SO$_4$ solution were 591F/g at 2A/g of current density with good rate capability.

![Figure 5](image)

**Figure 5.** 5 (a) CV of MnC$_2$O$_4$/GO electrode in 6M KOH at different scanrate, (b) CV of FeC$_2$O$_4$/rGO in 1mol/L of Na$_2$SO$_4$solution at different scan rate. Reproduced (a) with permission [33]. Copyright 2013, Springer-Verlag Berlin Heidelberg; (b) Reproduced with permission [35]. Copyright 2018, Chinese Physical Society

Transition metal based oxalate has great potential of pseudo-capacitance applications as it showed the higher specific capacitance. Various type of electrode based on TMOx has been compared in Table 1.

4. Conclusion

In summary, the prime objective of this paper emphasised on the usage of TMOx based electrode for supercapacitors. In addition, TMOx synthesis process, morphology of nanostructures, as well as electrochemical performances has been conferred. Transition-metal oxalates emerges as a relevant energy material in the field of supercapacitor due to their cost effectiveness, environmental begin and open structure for ion transportation. Although, TMOx also have some...
Table 1. Transition-metal oxalates based electrodes for Supercapacitor

| Material | Morphology         | Specific capacitance (F/g) | Electrolyte  | Operating Potential(V) | Ref.  |
|----------|--------------------|-----------------------------|--------------|------------------------|-------|
| CoC₂O₄   | Thin sheet         | 1269                        | 6M KOH       | 0 to 0.5               | [30]  |
| NiC₂O₄   | 2D thin sheet      | 2835                        | 6M KOH       | 0 to 0.4               | [32]  |
| MnC₂O₄/GO| Olive-like         | 122                         | 6M KOH       | -0.1 to 0.55           | [33]  |
| Co₀.₅Mn₀.₄Ni₀.₁C₂O₄·nH₂O| Micro polyhedrons | 990                         | 3M KOH       | 0 to 0.4               | [34]  |
| FeC₂O₄/rGO| Porous rod        | 591                         | 1M Na₂SO₄    | -1.3 to 0              | [35]  |

shortcoming such as less conductive and accumulation of particles degrades the electrochemical performance. In account of that, electrochemical performances of TMOₓ electrode can be enhanced through various methodology such as by preparing mixed TMOₓ structures or preparing nanocomposite with highly conductive secondary materials such as graphene and CNT. Hence, it is valuable to investigate more stable structures and highly electrochemically active oxalates for energy storage applications.

Acknowledgements

This work is supported by Nanotechnology program at Centre for Advanced Studies, AKTU and Department of Ceramic Engineering, IIT (BHU).

References

[1] Goodenough J B 2018 Nat. Electron 1 204–204
[2] Winter M and Brodd R J 2004 Chemical Reviews 104 4245–4270 URL 10.1021/cr020730k
[3] Simon P and Gogotsi Y 2010 Mater. Sustain. Energy A Collect. Peer-Reviewed Res. Rev. Artic. from Nat. Publ. Gr 138–147
[4] Li H B, Yu M H, Wang F X, Liu P, Liang Y, Xiao J, Wang C X, Tong Y X and Yang G W 2013 Nature Communications 4 1–7 URL 10.1038/ncomms2932
[5] Cao X 2019
[6] Service R F 2006 Science 313 902–902 URL 10.1126/science.313.5789.902
[7] Lee T H, Pham D T, Sahoo R, Seok J, Luu T H T and Lee Y H 2018 Energy Storage Materials 12 223–231 URL https://doi.org/10.1016/j.ensm.2017.12.009
[8] Liu X, Shi C, Zhai C, Cheng M, Liu Q and Wang G 2016
[9] Liu X, Shi C, Zhai C, Cheng M, Liu Q and Wang G 2016 URL 10.1021/acsami.5b10781
[10] Chmiola J, Largeot C, Taberna P L, Simon P and Gogotsi Y 2008 Angewandte Chemie International Edition 47 3392–3395 URL 10.1002/anie.200704894;https://dx.doi.org/10.1002/anie.200704894
[11] Costentin C, Porter T R and Savéant J M 2017 ACS Applied Materials & Interfaces 9 8649–8658 URL 10.1021/acsami.6b14100;https://dx.doi.org/10.1021/acsami.6b14100
[12] Augustyn V, Simon P and Dunn B 2014 Energy & Environmental Science 7 1597–1597 URL 10.1039/c3ee44164d;https://dx.doi.org/10.1039/c3ee44164d
[13] González A, Goikolea E, Andoni J and Mysyk R 2016 *RSC Adv* **3** 13059–13084

[14] Wang F, Xiao S, Hou Y, Hu C, Liu L and Wu Y 2013 *Prog. Nat. Sci. Mater. Int* **23** 245–255

[15] Zheng J P, Cygan P J and Jow T R 1995 *ACS Applied Materials & Interfaces* **8** 33732–33740 URL 10.1021/acsami.6b12518

[16] Jabeen N, Xia Q, Savilov S V, Aldoshin S M, Yu Y and Xia H 2016 *J. Power Sources* **312** 184–149 URL 10.1016/j.jpowsour.2015.12.249

[17] Salavati-Niasari M, Mir N and Davar F 2009 *Polyhedron* **28** 1111–1114 URL 10.1016/j.poly.2009.01.026

[18] Du H, Pan Y, Zhang X, Cao F, Wan T, Du H, Joshi R and Chu D 2019 *Nanoscale Advances* **1** 140–146 URL 10.1039/c8na00110c

[19] Tyagi A, Joshi M C, Shah A, Thakur V K and Gupta R K 2019 *ACS Omega* **4** 3257–3267 URL 10.1021/acsomega.8b03618

[20] Liu W, Song Y, Wang H, Wang H and Yan L F 2018 *Chinese J. Chem. Phys* **31** 707–716 URL 10.1039/d0cj00268b