

Electrode materials for supercapacitors synthesized by sol–gel process

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This review article on synthesis of various carbonaceous and transition metal oxide based supercapacitor electrode materials and their electrochemical performance shows that though a potential method, the sol–gel process needs to be extensively explored and practiced on a large extent. The carbonaceous materials possess high electrochemical stabilities but they demonstrate lower capacitance compared to the ruthenium-based materials. Overall excellence in electrochemical behaviour was exhibited by a binary metal oxide NiCoO₄ in thin film form with a value of 2157 F/g.

Keywords: Specific capacitance, sol–gel process, supercapacitor materials.

ONE of the next generation energy storage devices, supercapacitors, has a great demand in the market and extensive research is being pursued on in the field of electrode materials for supercapacitors and device fabrication. Instead of using a conventional dielectric as in capacitors to store electrical energy, supercapacitors use either mechanism, viz. double layer capacitance or pseudocapacitance. Double layer capacitance has electrostatic form and pseudocapacitance is electrochemical in nature. Supercapacitors can be considered as a blend of the regular capacitor and the working principle of an ordinary battery. Supercapacitors, popularly known as ultracapacitors can be typified by electrode materials with high accessible surface area and storage of large amounts of electrical charge operating at considerably low voltage. The large surface area of the electrode is a key factor for the large capacitance value of a supercapacitor. Larger surface area guarantees better access for the electrolyte that enhances the capacitance value. The electrode materials utilized for supercapacitor are metal oxides and carbon in various forms which possess greater extent of surface action. Today, the challenge is to produce economical but efficient electrodes for supercapacitors which should exhibit chemical and electrical compatibility with electrolytes.

With rapidly progressing nanoscience and nanotechnology, a range of materials are available for the fabrication makeover of a supercapacitor and its performance.

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Advancement in nanotechnology makes it possible to synthesize nanostructured materials, such as nanotubes, nanorods, nanoflakes, nanoparticles, etc. These nanoforms demonstrate considerable improvement in electrochemical performance by virtue of large accessible surface area. They facilitate shorter transport–diffusion paths for charge carriers making the kinetics quicker. Also, it offers efficient interaction among electrode surface and electrolyte ions, and large number of electroactive sites for faradaic energy storage¹.

Today several methods and techniques such as sol–gel method, hydrothermal method, electrodeposition, chemical bath deposition, successive ionic layer adsorption and reaction (SILAR) method, and spray coating, ink jet printing are followed to synthesize the materials to their most efficient form, suitable for the desired application. Sol–gel process is regarded as a versatile method of material synthesis as it can best be applied to produce materials in a variety of forms such as coatings, films, glasses, fibres, powders, monoliths, etc. with a high active surface area.

Considering the market demands, novel and efficient but economic supercapacitor materials need to be explored. Since the sol–gel method is an advantageous chemical method, this review focuses on compilation of results on specific capacitance (SC) of a wide variety of materials in bulk form as well as in thin film form synthesized by sol–gel process from selective citations.

Sol–gel process: advantages in synthesis of supercapacitor electrode material

Sol–gel science, a new term coined in the 1950s, points to an approach of material synthesis which involves preparation of a sol followed by its gelation and removal of the solvent. The term sol–gel applies to a process in which sols are gelled and also to the process in which it is not certain whether discrete colloidal particles exist at a point of time during reaction. When such is the case, the term sol–gel can be understood as an acronym of solution–gelation²!

Turner³ points to a number of advantages of the sol–gel process over conventional processes. (i) better chemical homogeneity in multicomponent systems; (ii) relatively low sintering temperatures due to high surface area of the

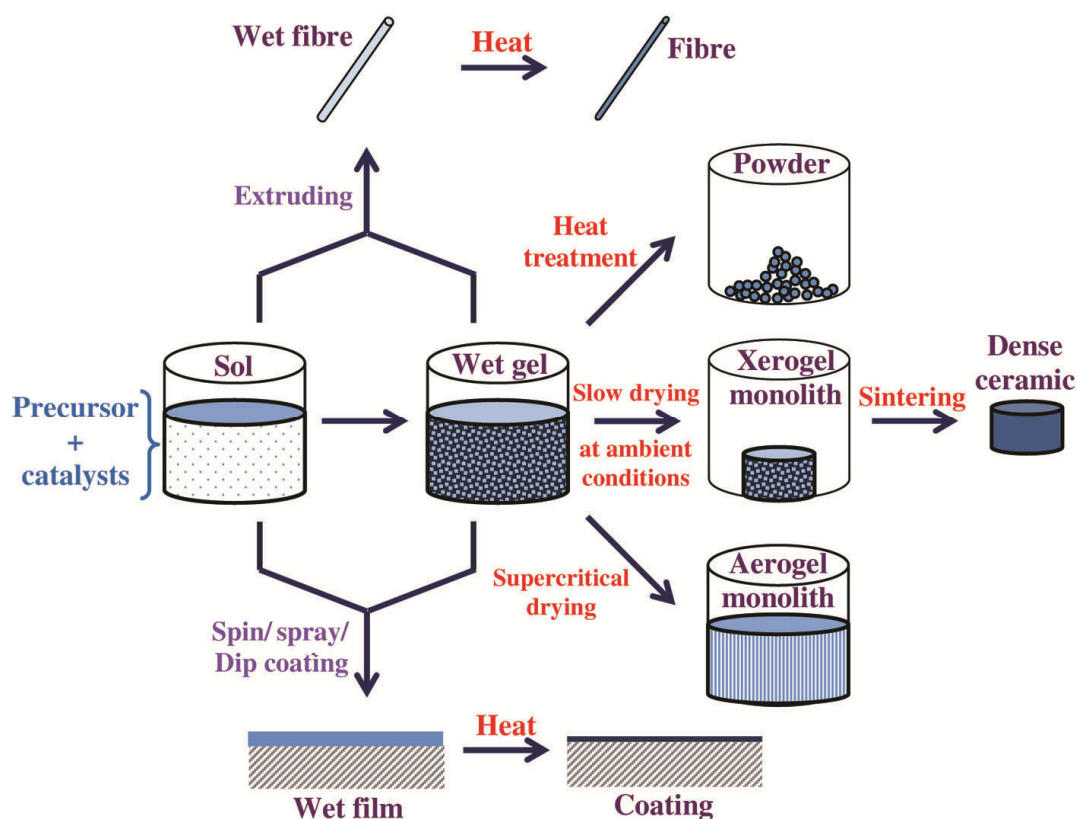


Figure 1. Synthesis of various forms of materials by versatile sol-gel process.

product; (iii) ability to maintain relatively high chemical purity as the processes of grinding, pressing etc. are not involved; and (iv) versatility to produce a variety of products in the form of monoliths, fibres, particles, coatings, following a simple solution method as shown schematically in Figure 1.

Large specific surface area and high degree of purity of materials are requirements of electrode materials for supercapacitor applications. Taking the aforementioned advantages of the sol-gel process into account, it can be regarded as the most suited method for synthesizing these materials. Generally, transition metal-oxide based electrodes follow pseudocapacitance (redox) mechanism while carbon-based electrodes store the charge via electric double layer capacitance (EDLC). The materials to incorporate both types of charge storage mechanism can be produced by the versatile sol-gel process which is a soft chemical method. This has been practised for production of highly porous oxides at moderate temperatures⁴. The properties of supercapacitors rely on electrochemical properties such as stability, conductivity and structural properties such as porosity and surface area of the electrode materials. Sol-gel synthesized materials have been greatly explored over the couple of preceding decades.

High specific capacitance (F/g) at low resistance enables construction of high energy and high power density supercapacitors from transition metal oxides (TMOs)

making them promising electrode materials. Electrochemical behaviour of oxides such as RuO_2 , MnO_2 , etc. is pseudocapacitive due to either reversible surface chemical reactions or fast and reversible lattice intercalation⁵. Excellent structural stability and the high SC value of TMOs and the ability to adopt varied oxidation states make them competent materials for supercapacitor electrodes. These metal oxides having various nanostructures have been synthesized by sol-gel method to enhance the performance of supercapacitors. TMOs in bulk as well as in thin film form synthesized by sol-gel process were investigated for application as supercapacitor electrodes and include oxides of ruthenium, nickel, cobalt, manganese, tin, iron, vanadium, etc. which exhibit considerable specific capacitance values⁶⁻⁸. Ceramic oxides have been used as supercapacitor materials owing to their stability in different electrochemical systems, ability to attain high capacitance and importantly their low production cost.

‘Carbon aerogels and xerogels are a kind of carbon in nano-form’ with a substantial mesoporous networked structure extended in 3-dimensions. ‘Both of them can be regarded as competent electrode materials for supercapacitors due to their large specific surface area, low/moderate-low density and electrical conductivity’⁹. An added advantage of carbon-based electrode material is that they may not require any extra binding material. Carbon aerogels are binderless electrodes which show

lower equivalent series resistance (ESR) than activated carbons.

Carbon

The fundamental requirements of materials which follow EDLC mechanism to attain the best performance are^{10–12}: (i) high ionic electrolyte conductance; (ii) high ionic separator conductance; (iii) high electronic separator resistance; (iv) high electronic conductance; (v) large electrode surface area; (vi) low separator and electrode thickness.

Porous carbonaceous materials owing to their high specific surface area and good electrical conductivity are being used to fabricate electrodes for supercapacitors^{5,13,14}. Studies find carbon xerogels and aerogels of interest as they are potential candidates for supercapacitor electrode materials by virtue of their conductive network of carbon nanoparticles and porosity. Due to the continuous network and ability of carbon to bond chemically, there is no need for adding any binding agent which may alter the electrochemical properties. Apart from carbon xerogel and aerogel, graphene, carbon nanotubes have also been found to enhance the enactment of supercapacitors by improving electron transport and modifying the charge transfer process. The carbon electrodes for EDLC should possess high specific areas, appropriate intra- and inter-particle conductivity in porous matrix and ease of access for the electrolyte to the area available in the pores^{15,16}. As it is popularly known, the sol–gel process can tailor materials with high porosity and it is a convenient way of producing porous carbons for supercapacitor applications. It is usually noticed that EDLCs exhibit better stability and power densities than pseudocapacitors¹⁷.

One of the high specific surface areas that carbonaceous electrode materials are synthesized via sol–gel process is carbon xerogel/aerogel^{18,19}. Higher the percentage of pores, the more facile the ion transport through pores. This makes carbon xerogels/aerogels suitable for high-power supercapacitor applications.

The steps involved in carbon xerogel/aerogel synthesis are transformation of sol to gel, exchange of solvent, ambient drying or supercritical drying of wet gel and heat treatment. Carbon xerogels are produced by following conventional drying method and not using supercritical drying in CO₂. Xerogel is formed by drying wet gel without hindrance in shrinkage of the three-dimensional cross-linked gel networks. Though the network shrinks under ambient conditions, considerably high porosity and large surface area is retained because of availability of nano/micro-pores in the network. On the other hand, when the solvent is removed under supercritical conditions, there is little network shrinkage. This drying process produces highly porous and low density material,

categorized as aerogel. The synthesis parameters to be monitored in sol–gel route such as pH, pyrolysis temperature, time, etc. affect the textural properties of carbon xerogels/aerogels^{20–24} and thus the performance. Generally, the measured capacitances of carbon materials in existing supercapacitors fall short compared to the values reported in the literature²⁵. SC values roughly measure over 20 to 300 F/g for aqueous and organic electrolytes. The storage of energy in supercapacitors is due to ionic charge build-up across the double-layer occurring at the interface of electrode and electrolyte. There is quick attainment of double-layer in carbon material electrodes due to high porosity and large accessible surface area. In general, carbon materials with more specific surface areas and porosity possess greater ability for accumulation of charges at the electrode/electrolyte interface²⁶. As not all pores in the electrode material are necessarily accessible to electrolyte ions, specific capacitance may not be in direct proportion with the specific surface area^{27–29}.

Job *et al.*³⁰ report synthesis of porous carbon material produced by pyrolysis of resorcinol formaldehyde (RF) aquagels and evaporative drying. Texture of the material can be effectively controlled by adjusting pH of the precursor. It is also reported that Na₂CO₃ functions as a polymerization catalyst (C). But Job *et al.*³⁰ state that Na₂CO₃ involves pH regulation. Thus, instead of using commonly used Na₂CO₃, NaOH was used as pH regulator³⁰.

The specific surface areas (SBET) of RF gels after drying and after pyrolysis at 800°C under N₂ flow are presented in Table 1. After pyrolysis of dried gels, SBET increase considerably for the sample with pH = 5.80 to a value of 635 m²/g. Specific surface area, being a key aspect in deciding the probable application of material such as fuel cell electrode, supercapacitor, etc., carbon xerogel can stand as a potential candidate for supercapacitor applications.

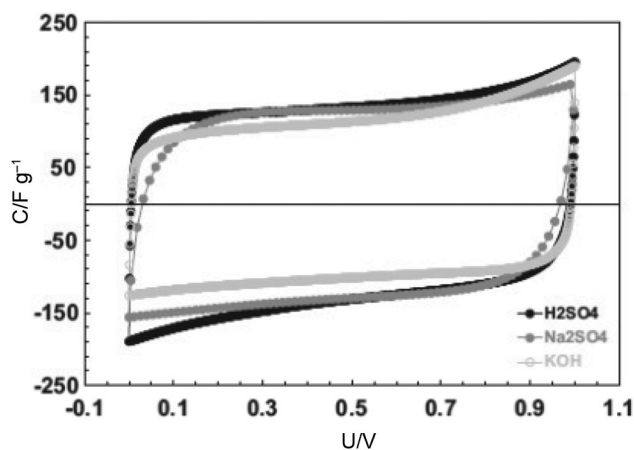
Calvo *et al.*³¹ also report synthesis of RF-based carbon xerogel via the microwave assisted sol–gel process. Subjecting the sol to microwaves induces and accelerates polymerization reactions between monomers.

The electrodes were prepared using activated carbon xerogels and the electrochemical properties in various aqueous media, viz. H₂SO₄ (acidic), Na₂SO₄ (neutral) and KOH (basic) were studied. Figure 2 demonstrates typical rectangular voltammograms as expected of ideal supercapacitors with a slight distortion appearing probably due to contact resistance. The maximum value of SC, 196 F/g, was reached with acidic electrolyte, H₂SO₄.

Mezzavilla *et al.*³² report electrodes based on RF polymerized heat-treated carbon xerogels with resorcinol to catalyst (R/C) ratio as high as 1000, that corresponds to a single-electrode SC of 100 F/g in 6 M KOH and energy density 3.1 Wh/kg. Jun Li *et al.*²¹ produced carbon aerogel from RF gel by following similar sol–gel route as mentioned by Mezzavilla *et al.*³², but the drying process

Table 1. pH dependence of specific surface area³⁰

pH ± 0.05 S _{BET} (m ² /g) ± 5	After drying						After pyrolysis					
	5.45	5.8	6	6.25	6.5	7.35	5.45	5.8	6	6.25	6.5	7.35
	330	435	475	505	510	470	625	635	610	565	<40	<40

**Figure 2.** Voltammograms of R-F based carbon xerogel electrode in aqueous electrolytes of different pH³¹.

was altered to get carbon aerogel. Attempts were needed in reducing the contraction of RF gels while carrying out ambient drying. Acetone is a drying solvent with low surface tension and further to decrease drying stress, drying was done using a stream of pure Ar gas. SEM revealed porous morphology of the carbon aerogel and hence improved specific surface area. The maximum SC of ~110 F/g in 6 M KOH was reported. Though the specific surface area of xerogels in the report of Mezzavilla *et al.*³² is comparatively lower, SC does not differ (100 F/g) considerably from that of aerogel (110 F/g) as reported by Jun Li²¹.

Zanto *et al.*³³ analysed the effect of synthesis parameters on the surface area, pore volume, EDLC for 16 samples of carbon aerogels and xerogels from RF gel. The study included the effect of pH (5.5 and 7.0), temperature at which pyrolysis was done (800 and 1050°C), etc. They concluded that carbon aerogels, on average, exhibit higher values of surface area, pore volume, electrochemical capacitance than carbon xerogels (Table 2).

Figure 3 shows a schematic of the synthesis of RF gel and subsequent drying and pyrolysis to obtain well developed carbon aerogel (C-aerogel) without any activation³⁴.

Though the carbon aerogel electrode exhibited modest SC of 21.8 F/g along with superior power density (2.4 kW/kg) and specific energy (22.1 Wh/kg), the electrochemical stability is considerably high, that the specific capacitance was retained to 87% at the end of 10,000 cycles. This superior electrochemical performance was

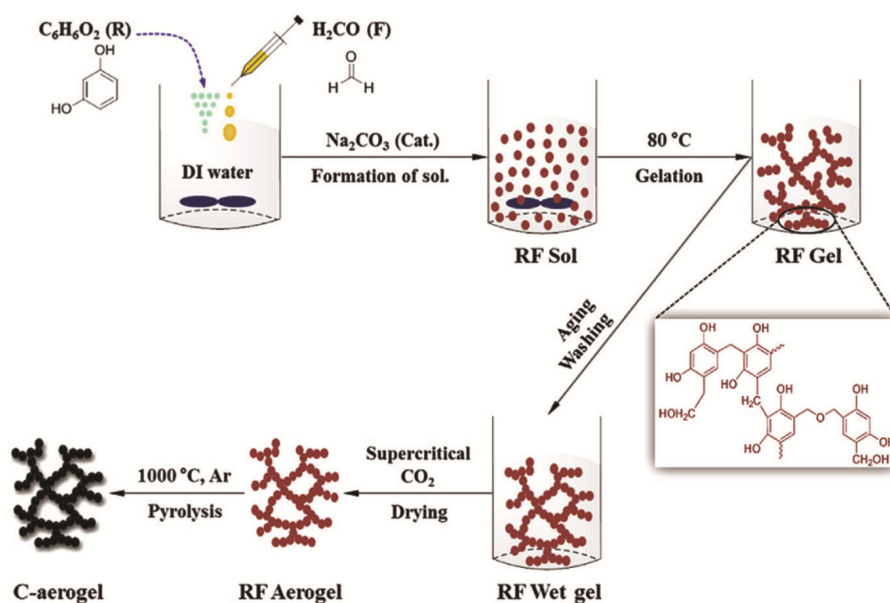
credited to the dual three-dimensional mesoporous network which provides more active sites. Efficient transfer of charges through such a network is a reason for steady electrochemical performance.

The specific surface area of carbonaceous electrodes is considered as a key aspect for development of electrical double layer. There are activation methods such as physical activation (e.g. use of CO₂) to achieve higher value of specific surface area in porous carbon^{22,35,36}. Even if the specific surface area is a deciding factor for supercapacitor performance, the pore size distribution, textural properties are also crucial in inducing better electrical conductivity in carbon electrode material and thus the electrochemical performance³⁷. Chuan Lin *et al.*²⁴ reported an attention-grabbing systematic study regarding pore size distribution of RF-based carbon xerogel with carbonization time and temperature. With increase in carbonization temperature, a reduction in quantity of micropores of the order of 6 Å was noticed. This reduction was accompanied with no effect on the size distribution of mesopores and thus no change in cumulative surface of mesopores. An increase in the number of micro- and mesopores was noted with increase in activation time with carbon dioxide (CO₂). The pores in the range of width of 6 Å over the time broaden to that of ~12 Å. They concluded that pores less than about 8 Å in width did not contribute to DLC¹⁹.

Various electrochemical, chemical and physical ways of modifying carbon electrode surface involve oxidation, reduction and pre-adsorption of various functional groups. Micropores in bulk and defects in surface can be included for increasing the specific surface area. Also, the electrochemical capacitance exhibited by carbonaceous materials improves on grafting of functional groups and/or doping with heteroatoms. Supercapacitor electrode materials based on carbon activated with hetero-atoms of elements such as N³⁸, P³⁹ into the networked carbons show improved electrochemical properties. Particularly, doping nitrogen in porous carbon materials improved the functional properties of supercapacitor material³⁸. The carbon-based electrode materials, as stated earlier, follow EDLC charge storage mechanism and the grafted functional groups/heteroatoms contribute to pseudocapacitance. Carbonaceous electrodes exhibit modest specific capacitance, while they possess enormous electrochemical stability. Thus, incorporation of heteroatoms possessing high specific capacitance efficiently improves the electrochemical properties of the electrode material as a whole.

Table 2. Comparison of carbon xerogel and aerogel properties with respect to synthesis parameters³³

Initial solution pH	Solid content (wt%)	Pyrolysis temperature (°C)	Surface area (m ² /g)		Pore volume (cm ³ /g)		Electrochemical capacitance (F/g)	
			Aerogel	Xerogel	Aerogel	Xerogel	Aerogel	Xerogel
5.5	5	800	561	569	0.32	0.36	128	161
5.5	5	1050	508	521	0.30	0.28	68	105
5.5	20	800	517	493	0.24	0.26	86	63
5.5	20	1050	474	460	0.23	0.25	59	74
7.0	5	800	900	591	0.92	0.20	179	113
7.0	5	1050	753	540	1.32	0.40	142	106
7.0	20	800	929	586	1.31	0.44	146	124
7.0	20	1050	804	515	1.42	0.44	144	104
Average			680.8	534.4	0.758	0.329	119.0	106.3
Standard deviation			186.6	46.1	0.539	0.093	42.9	29.9

**Figure 3.** Schematic of synthesis of RF gel and subsequent development of carbon aerogel³⁴.

Fang *et al.*⁴⁰ report synthesis of carbon aerogel (CA) by following a similar route mentioned earlier in the late nineties⁴¹. To obtain activated carbon aerogels (ACA), carbonization of CA with KOH was done by keeping the mass ratio of KOH : CA at 3 : 1. Apart from only activating CA, the samples were subjected to a process of surface modification using vinyltrimethoxysilane (VTMOS). For VTMOS-modified carbons high SC (~140 F/g) was noticed. This may be caused by more rapid ion transport. Also, energy density of 37 Wh/kg was measured at 2.5 mA/cm². Surface modification with VTMOS of the activated carbon aerogel enables more accessible surface area to the ions of the electrolyte because of improved wettability towards propylene carbonate-based electrolyte and thus quicker charge propagation.

Liu *et al.*³⁷ report the designing of nitrogen-doped carbonaceous porous materials with hierarchical micro-

structures. The co-polycondensation of RF with melamine for nitrogen doping to obtain three-dimensional porous structures via sol-gel process was done and the PEO76–PPO29–PEO76 micelles were used in optimizing the formation of micron-channels of porous structure. Breakdown of PEO76–PPO29–PEO76 micelles during carbonization created microchannels which facilitate traversing of the ions of the electrolyte. Further, CO₂-assisted activation (at 950°C for 8 h) produced hierarchical porosity. The presence of well-connected abundant meso/micropores with micro-channels (Figure 4) (specific surface area = 4279 m²/g) and the effective nitrogen doping resulted in high electrochemical performance with SC value of 271 F/g (ref. 37).

Pyrolysis of poly(acrylic acid)/methylated melamine-formaldehyde resin aqueous solution by sol-gel process was done to produce rich nitrogen-doped nanoporous

carbon, possessing large specific surface area using activation by KOH. The specific surface area of the material with a nitrogen content of 8.8 wt% was reported up to 2674 m²/g. Because of both, EDLC and pseudocapacitance, the material presented fascinating electrochemical performance in 1 M H₂SO₄ with SC of 280 F/g and excellent stability over 9000 cycles as seen in Figure 5 (ref. 42).

A report gives details of ruthenium composited carbon xerogels having high surface area obtained by sol-gel process. Specific capacitance of 256 F/g (corresponding power density = 1000 W/kg and energy density = 30 Wh/kg) was reported for a carbon xerogel holding Ru to 14 wt% and stability over 2000 charge/discharge cycles²⁴. It is estimated that about 40% of the capacitance was contributed by double layer generated within pores in the carbon xerogel matrix during charge/discharge, and about 60% of the capacitance was attributed to RuO₂ dispersed in the matrix undergoing reversible redox reactions.

A novel composite electrode material, composed of sol-gel synthesized three-dimensional graphene (3DG),

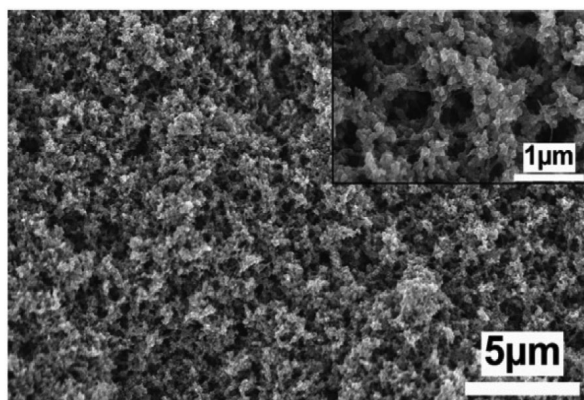


Figure 4. Scanning electron microscopy picture showing activated nitrogen doped carbon xerogel³⁷.

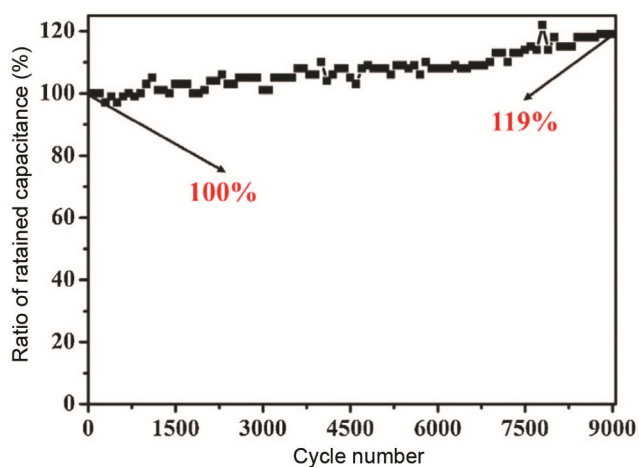


Figure 5. Cycling stability of N-doped porous carbon activated with KOH at 700°C (ref. 42).

carbon black (CB) as conductive particles, and MnO₂ nanoparticles on 3DG surface, is produced by a hydrothermal method. In the electrode material (3DG/CB/MnO₂), the synergistic reaction between 3DG and MnO₂ occurs to the optimum which favourably increased the supercapacitor performance of the combination. The composite showed superior electrochemical properties over only MnO₂ due to the existence of enhanced effective surface area carbons with pseudocapacitive MnO₂. The SC of the 3DG/CB/MnO₂ composite recorded for 0.3, 1 and 3 A/g current densities are 590, 433 and 247 F/g respectively⁴³.

Sun *et al.*⁴⁴ synthesized carbon aerogels with pore structure which can be tuned, and possess high specific surface area by substitute route via polycondensation of RF on Fe-containing ionic liquid, hexadecyl-2,3-dimethylimidazolium tetrafluoroborate ([C₁₆Im]BF₄). Spherical micelles produced in water by the ionic liquid serve as a sol-gel polymerization template. The SC of 188 F/g was reported for mesoporous carbon aerogel formed by this method. The corresponding energy and power density values are 9.08 Wh/kg and 6250 W/kg respectively⁴⁴.

Apart from the advantages of sol-gel route of material synthesis, Laheäär *et al.*⁴⁵ compared two porous carbon materials. Of the two, one is obtained from organic aerogel prepared by sol-gel process followed by its pyrolysis and another is synthesized using molybdenum carbide by the method of chlorination at high temperature. The obtained materials were tested as a supercapacitor electrode in tetraalkylammonium which is a salt-based electrolyte (nonaqueous). The report mentions that the gravimetric capacitance value for carbon-based electrode derived from carbide (C(Mo₂C)) was ~125 F/g which is almost double that of carbon aerogel-based electrode (~55 F/g). Similar trend of energy density was also observed with values 32 Wh/kg for carbon aerogel-based electrode and 63 Wh/kg for C(Mo₂C)-based electrode⁴⁵.

The sol-gel process is an efficient way to synthesize transition metal oxides. In the beginning, it used metal alkoxides as the precursor and organic media as homogenizing means. Various forms of desired metal oxides such as monoliths, thin films, powders, etc. were produced. In general, the organometallic precursors of metals are expensive. Even then, the sol-gel-derivative methods use these precursors often because of their purity and good results. Use of inorganic or organo-inorganic precursors in organic or aqueous media is a general practice.

Ruthenium

Alternatively, oxides of transition metals such as Ru⁴⁶, Ni^{47,48}, Co^{49,50}, Mn^{51,52} have already been reported to exhibit good electrochemical properties. Also, they possess high theoretical specific capacitance values and fast rate of reversible metal-ion redox transitions over wide potential range. Among the various TMOs, RuO₂ is the most

studied pseudocapacitive material and reported to exhibit very high capacitance values. Owing to high specific capacitance, it challenges the carbon-based electrode material for supercapacitors.

Zheng *et al.*⁵³ give details of amorphous RuO₂ (RuO₂·1/2H₂O) produced by sol–gel process for which notably high SC of 720 F/g was reported. The corresponding surface area was 68.6 m²/g (energy density 26.7 Wh/kg)⁵³. This better performance was observed due to hydrous surface layers, which enable mixed protonic–electronic conductivity. However, it was also reported that the charge storage ability of amorphous RuO₂ drops when the scan rate is increased. This can be because of proton depletion during charge–discharge cycles⁵⁴.

A comparative study on RuO₂·xH₂O synthesized via modified sol–gel process was carried out. The annealing of the product was done with air and water at different temperatures. The corresponding variation in textural and electrochemical properties was compared by Chang *et al.*⁴⁶. Distinctive textural properties of RuO₂·xH₂O were observed for annealing at 225°C for 24 h with 16 wt% water (termed as hydrothermal annealing). The high pressure, water-enriched surrounding that controls the agglomeration of RuO₂·xH₂O nanocrystallites produced distinctive textural properties. An average particle size of about 7 nm and specific capacitance of 390 F/g was reported for RuO₂·xH₂O.

A study discusses preparation of sol–gel derived hydrous RuO₂ impregnated with carbon black of low and high surface areas to produce nanocomposites of different particle size. The capacitive properties showed that there exists a relationship between the specific capacitance and the surface area of carbons used in the composite and the particle size of RuO₂. There is a decrease in capacitance of composites containing high surface area carbon and also due to aging of oxide sol. This happens due to the growth of oxide particles over time. On the other hand, capacitance of low surface area carbon composites enhances as the sol ages. This is due to the small efficiency of impregnation of oxide particulates. Increase in proportion of the oxide phase leads to the increase in capacitance of the composites⁵⁵.

Chen *et al.*⁵⁶ report sol–gel synthesized RuO₂ nanoparticles (30–60 nm), which are amassed petite RuO_x clusters of dimensions less than 10 nm. Composite of 10 wt% RuO_x nanoparticles and 90 wt% of activated carbon showed the SC of 111.7 F/g. Enhanced performance of activated carbon (AC) was attributed to the mixing of two process, viz. the adsorption of RuO_x clusters and the ultrasonic wetting in NaOH⁵⁶.

An attempt was made reported to synthesize ruthenium oxide-graphene (RuO₂–G) nanocomposite by the sol–gel technique. The RuO₂–G with a 10 : 1 ratio had better specific capacitance due to larger surface area of graphene and RuO₂ available to interact with the ions of the electrolyte. The SC of bare RuO₂ was reported to be

7.3 mF/cm² while the nanocomposite of RuO₂–G 10 : 1 showed considerable improvement in SC to 187.5 mF/cm² (ref. 57).

Another study on RuO₂–graphene composite mentions hydrous ruthenium oxide/graphene sheet composite (ROGSCs) with variation in the mass of Ru. The method followed for the preparation was a combination of sol–gel process and low temperature annealing. Due to the existence of RuO₂ particles, the graphene sheets were maintained at 5–20 nm from each other. Also, RuO₂ nanoparticles were clinched at the oxygen-rich functional groups on chemically activated graphene sheets. The collective effect of both materials, viz. graphene and RuO₂ was observed to improve SC up to 570 F/g for 38 wt.% of RuO₂. There was 98% retention in capacitance value after 1000 cycles while the energy density was reported to be 20.1 Wh/kg. An interesting mention in the report is that the specific capacitance of ROGSCs is superior to the SC values of separate components GSs and RuO₂ (ref. 58).

The composite of sol–gel processed RuO_x with exfoliated graphite (EG) was prepared for application as a binderless electrode for the supercapacitor. The SC value measured was 176 F/g for 16.5 wt.% Ru loading⁵⁹. Also, a specific mention that the capacitance values were normalized with respect to the mass of the composite used and not to the mass of RuO_x.

The sol–gel method was followed to deposit RuO₂ onto well-aligned CNTs grown by CVD using ethylenediamine on stainless steel. To make the substrate noble, a thin coat of gold was deposited, followed by deposition of cobalt as catalyst for CVD of ethylenediamine. Electrochemical properties of RuO₂ thus produced were studied⁶⁰.

The pseudocapacitive response of (Ru–Ti)O_x aerogels, RuO₂, and hydrous RuO₂ in acidic electrolyte was examined⁶¹. The (Ru–Ti)O_x aerogel exhibits higher surface area compared to RuO₂ and hydrous RuO₂, but controversially presents small value of specific capacitance. This lowering was associated with the formation of RuO₂ nanocrystallites in rutile form produced during heat treatment of the Ru/Ti gel. An important conclusion from the study is that when high specific capacitances are desired for RuO_x-based aerogels, formation of crystalline RuO₂ should be avoided.

High cost and toxicity limits the exploration of ruthenium as a commercial material for supercapacitor electrodes⁶². Cost concerns and toxicity of ruthenium led researchers to investigate the properties of TMOs such as Co₃O₄, NiO, and MnO₂ which possess theoretically high SC values. Thus, owing to high SCs, these TMOs are worth considering as electrode material for supercapacitor.

Cobalt

Wei *et al.*⁶³ were the first to report the epoxide addition procedure via sol–gel route for synthesis of cobalt oxide

(Co₃O₄) aerogels. They tested two precursors of cobalt, viz. CoCl₂·6H₂O and Co(NO₃)₂·6H₂O with different polar protic solvents, viz. water, methanol, ethanol, isopropyl alcohol and acetone. An important observation made in this study is that CoCl₂ could not undergo gelation which was attributed to the fast increase in solution pH due to consumption of protonated epoxide and promotion of the proton scavenging of epoxide from hydrated metal ions that led to precipitation instead of gelation. The aerogels heat-treated at 200°C have specific surface 235 m²/g and exhibited SC of 623 F/g.

Wang *et al.*⁶⁴ reported on the synthesis of nanoscale Co₃O₄ cryogel posing macroporous network along with hierarchical mesoporosity for energy storage devices. A triblock polymer/ice crystal double templated sol–gel method was used for the first time in this synthesis. The freeze-drying process was shown to be superior compared to conventional sol–gel process. It involves optimum maximum use of material, production of ultrafine Co₃O₄ nanocrystals and hierarchical structures. The Co₃O₄ cryogel showed considerable SC of 742.3 F/g and excellent energy density (25.8 Wh/kg) and power density (125.12 W/kg) values⁶⁴.

Nickel

Ni(OH)₂ gels were produced by the sol–gel process using nickel sulphide and subsequent drying at ambient pressure at 80°C followed by heating under air, that produced NiO_x xerogels possessing mesoporous structure leading to high surface area. The effect of heating on specific capacitance was studied and was reported to increase with increase in temperature from 110°C to 250°C (696 F/g at 250°C) and then again decrease at elevated temperatures⁶⁵.

High porosity possessing NiO was synthesized by sol–gel process followed by supercritical drying of Ni(OH)₂. The product was subjected to heat treatment at different temperatures in air to obtain oxides. The aerogel-like NiO possesses maximum surface area of 325.6 m²/g and SC of 125 F/g. The enhanced capacitive behaviour of the material was due to ordered mesopores which favour diffusion of electrolyte into electrode material ensuring maximum extent of redox reactions⁶⁶.

Morphology-dependent electrochemical properties of sol–gel synthesized NiO nanostructures with distinct morphologies, viz. flower, slice and particle have been reported⁶⁷. The morphologies were tailored by the preparation conditions as shown in Figure 6. Among various nanostructures, at current density 0.5 A/g highest SC of 480 F/g was recorded for the NiO nanoflower.

Padmanathan *et al.*⁶² report thermostable nanostructured CeO₂ with the combination of NiO synthesized by sol–gel process. Equimolar solutions of nitrates of Ni and Ce in deionized water were used as precursors. The subsequent additions of other reagents lead to the formation

of a gel which was then slowly decomposed to ash, which was then subjected to high temperature to eliminate the unreacted citric acid used for polymerization. Pristine NiO and CeO₂ synthesized by following the same procedure were compared and NiO–CeO₂ nanoparticles were compared to confirm the enhanced electrochemical performance (305 F/g) of the combination over the pristine oxide components. The supercapacitor behaviour was ascribed to the Ce⁴⁺/Ce³⁺ and Ni³⁺/Ni²⁺ redox switching of the separate oxide phases⁶².

There is an excellent report on the fabrication of a complete assembly of asymmetric supercapacitor based on sol–gel synthesized ‘cerium (Ce) doped NiO (1% Ce:NiO) as positive electrode and reduced graphene oxide (rGO) as negative electrode’ and its electrochemical testing in aqueous KOH. The device displayed SC of 110 F/g and highest energy density of 26.27 Wh/kg with 91.6% electrochemical stability over 1000 cycles⁶⁸.

Ternary-mixed oxides

It is now well accepted that to improve electrochemical activity, blending of pristine electrode materials and other electroactive moieties such as polymers, TMOs has to be attempted. As TMOs show multiple oxidation states, elevated energy density and specific capacitance values, mixed oxide systems are potential candidates in supercapacitors.

There is a first ever attempt reported on synthesis of spinel MnCo₂O₄ via economic sol–gel method. Supercapacitive performance of this spinel was studied in alkaline electrolyte⁶⁹. Also, electrochemical properties of single components, viz. MnO₂ and Co₃O₄ and MnCo₂O₄ were compared, and as anticipated, better properties such as high SC (405 F/g) and excellent cycle stability (95.1% retention after 1000 cycles) were displayed by the spinel MnCo₂O₄.

Ni–Co oxides comprising different ratios were effectively prepared via sol–gel process⁷⁰. Strong influence of Ni and Co concentrations on the nano and microstructure and thus on the supercapacitive performance was also reported. Raising the amount of Co alters the sample from NiO dominant to Co₃O₄ dominant structure, but with a reduced surface area. A maximum SC of 1539 F/g at a current density of 1 A/g was reported for Ni–Co oxide in the ratio 1 : 2.

Spinel nickel cobaltite (NiCo₂O₄) is an inexpensive and environment friendly mixed transition metal oxide which can be synthesized by simple, low-cost sol–gel process resulting in homogeneous materials. Wei *et al.*⁷¹ established ‘a novel epoxide-driven sol–gel process to prepare mixed valence oxide nickel cobaltite aerogel’, NiCo₂O₄, that displays high SC of 719 F/g for the sample calcined at 200°C. Interestingly, at a cycle number of 500, SC of the material attained a maximum of 1400 F/g

which indicates that for full activation of the sample, 500 cycles are required. There is insignificant (9%) decay in SC after 2000 cycles which demonstrates outstanding reversibility and constancy of the aerogels produced.

Systematic sol-gel synthesis of different nanofoms of NiCo_2O_4 , viz. 'coral-like porous crystals, nanoparticles and submicron-sized particles' was reported wherein 'citric acid was used as chelating ligand and H_2O -DMF served as solvent'. The results showed that submicron-sized NiCo_2O_4 particles (170 nm) exhibit SC value of 217 F/g at a high mass loading (5.6 mg/cm^2) and 96.3% of which is retained after 600 charge-discharge⁷².

Spinel NiCo_2O_4 nanoparticles were synthesized by a chelating agent 'citric acid, oxalic acid, ethylenediamine tetraacetic acid' by assisted sol-gel method. The particle and pore size is scalable by varying the chelating agent involved in the sol-gel synthesis which thereby alters the electrochemical performance. The characterizations revealed that the spinel nickel cobalt oxide produced using oxalic acid demonstrates the highest SC of 1254 F/g, while that prepared using EDTA showed the best cycling stability⁷³.

A composite, $\text{NiO/NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$, demonstrating fairly high SC of 1717 F/g and excellent electrochemical constancy with 94.9% retention after 1000 cycles was fabricated by a sol-gel process⁷⁴.

As already stated, the sol-gel process is one of the effective methods for thin film deposition. Nanoporous NiCo_2O_4 thin films on ITO were synthesized using plain sol-gel method for probable application as pseudocapacitor electrode. More specific surface area was available for effective reversible redox reactions because of hierarchical nanoporous structure that enhances the capacitive character. The nanoporous NiCo_2O_4 thin film electrode exhibited extremely appreciable ultrahigh value of SC of 2157 F/g and 96.5% retention after 10,000 cycles⁷⁵.

Manganese

Nanostructured $\gamma\text{-MnO}_2$ was prepared using sol-gel route with manganese acetate ($\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$) as a precursor. Pseudocapacitive behaviour with SC of 317 F/g in 1 M LiOH electrolyte measured at current density 100 mA/g was mentioned⁷⁶. Sol-gel template synthesis method was used by Wang *et al.*⁷⁷ to obtain highly ordered MnO_2 nanowire arrays in thin film form. The anodic aluminum oxide (AAO) was used as template which has periodically arranged pores of uniform diameter. The length of the nanowires thus produced was 500–700 nm while the diameter was approximately 70 nm. The specific capacity of the electrode in $(\text{NH}_4)_2\text{SO}_4$ electrolyte was 165 F/g (ref. 77).

MnO_2 thin films synthesized via sol-gel method on graphite substrates by dip coating technique which showed SC of 230.5 F/g after heat treating at 300°C were reported. Interesting changes in surface profile of the

MnO_2 coatings subjected to heat, before and after cyclic voltammetry test, are shown in Figure 7 (ref. 78). MnO_2 thin films on nickel foils were obtained by two ways, one is sol-gel method (dip and drop-coating) followed by subsequent gelation and calcination and the other is electrodeposition⁷⁹. The CV diagrams of nanoparticulate thin films obtained using dip-coating technique derived from sol-gel-process demonstrated superior performance. Also, the specific capacitance was noted to be as high as 698 F/g. These values when judged against values for electrodeposited films were noted to be around half. The comparison of specific capacitances of sol-gel and electrodeposited thin films is given in Table 3.

Pang *et al.*⁷⁹ compares the textural and electrochemical properties of sol-gel-derived and electrodeposited MnO_2 thin films. Porosity of sol-gel-derived nanoparticulate thin films was as high as 80%, while electrodeposited films showed random irregular macropores with porosity 67%. Not only the SC (698 F/g), but also the cycling stability and reversibility of sol-gel-derived MnO_2 films was reported to be superior compared to electrodeposited MnO_2 films⁷⁹.

Reddy *et al.*⁸⁰ synthesized xerogel and ambigel of MnO_2 , following simple sol-gel method. The MnO_2 ambigel showed high capacitance (130 F/g) compared to that of the xerogel (73 F/g). Also, the effect of electrolyte concentration, NaCl and MnO_2 exhibited electrochemical stability up to 800 cycles⁸⁰.

The spinel MnCo_2O_4 possessing porous structure was synthesized by simple sol-gel route and its capacitive behaviour in aqueous electrolyte KOH with specific capacitance of 405 F/g was reported. The cycling stability was observed to be 95.1% over 1000 cycles⁸¹.

Hybrid films were synthesized by mixing a range of concentrations of 'meso-carbon microbeads' (MCMB) in sol-gel processed MnO_2 . 'The 300°C heat-treated hybrid Mn-oxide coating with a Mn/MCMB ratio of 10/1 exhibited specific capacitance of 350 F/g', while the unadded counterpart of the films showed specific capacitance of 209 F/g. This increase was attributed to the excess active surface area offered by mesocarbon microbeads⁸².

Tin

SnO_2 is also one of the actively studied materials owing to its economy and ecologically genial nature. Research articles on sol-gel prepared SnO_2 for supercapacitors can be found in refs 83–85.

SnO_2 -based supercapacitors in two sets were synthesized⁸³. The first set involves doping of Sb into nanocrystalline SnO_2 produced by a sol-gel process which typically exhibits double-layer (DL) capacitance. Surface-grafting technique was followed to prolong grain coarsening which resulted in a maximum of 16 F/g in 1M aqueous KOH. For another set, composite electrodes

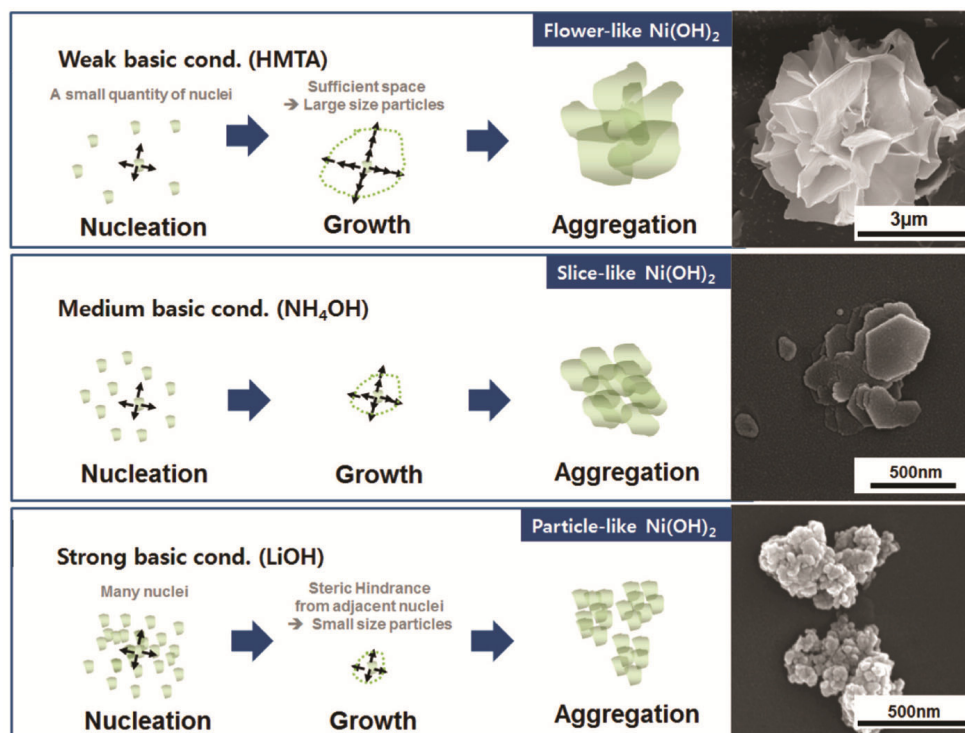


Figure 6. Synthesis of $\text{Ni}(\text{OH})_2$ tailored under different preparative conditions and corresponding SEM⁶⁷.

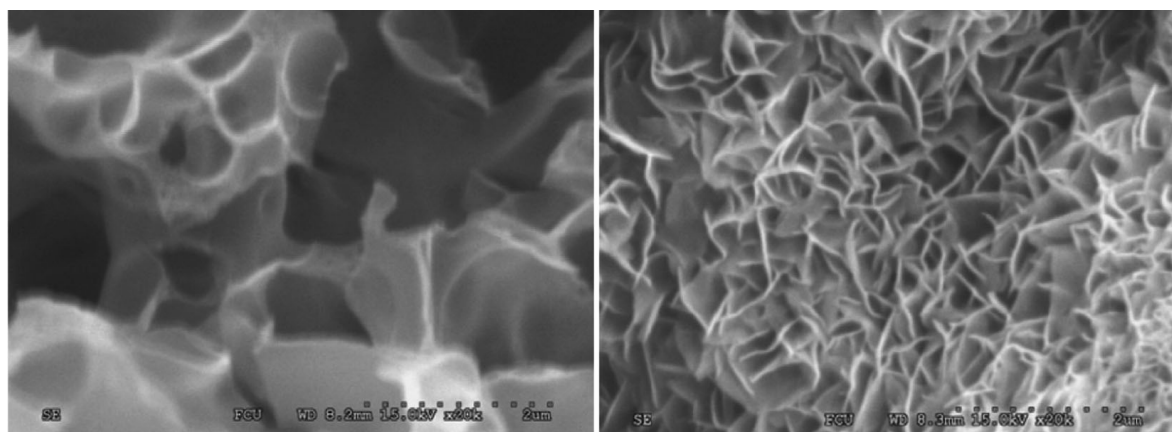


Figure 7. Change in surface morphology before and after subjecting MnO_2 thin film to CV measurement⁷⁸.

comprising the nanocrystalline SnO_2 and RuO_2 or Fe_3O_4 were studied which follow pseudocapacitive mechanism of charge storage. Electrochemical performance of $\text{Fe}_3\text{O}_4\text{-SnO}_2$ composite electrodes was reported to be 33 F/g in 1 M sodium sulphide solution. Refer to Table 4 wherein, ' SnO_2 U xerogel= Sb doped SnO_2 xerogel powder untreated with HMDS prior to calcination, SnO_2 H xerogel= Sb doped SnO_2 xerogel powder treated with HMDS prior to calcination'⁸³.

Tin spheres with binary oxidation states cling on carbon surface of organic RF gels were synthesized via sol-gel method. Cyclic voltammogram revealed that $\text{Sn}/\text{SnO}_2@\text{C}-(1.0, 800)$ composite reached the highest

specific capacitance of 906.8 F/g in 6M KOH over 2000 cycles. The reasons for high capacitance value could be: (i) binary oxidation states of metal composite; (ii) stratified micro-meso porous structure and (iii) unique structure of $\text{Sn}/\text{SnO}_2@\text{C}$ (ref. 86).

Others

Iron oxide ($\alpha\text{-Fe}_3\text{O}_4$) nanoparticles were synthesized using simple sol-gel-hydrothermal route. Ferratrane precursor was subjected to oxide one-pot synthesis (OOPS) and then to heat treatment. The material could

Table 3. Comparison of average specific capacitance of electrodeposited (ED) and sol-gel synthesized (SG) MnO₂ thin films⁷⁹

Sample ^a	Active electrode mass (μg/cm ²)	Average specific capacitance (F/g)	
		CV ^b	CCD ^c
SG300 (300 C)	1.05	678	698
SG200 (200 C)	1.08	607	566
ED300 (25 C)	8.83	350	418
ED300 (300 C)	8.83 ^d	389	–
ED600 (25 C)	13.37	311	438
ED600 (300 C)	13.37 ^d	359	–

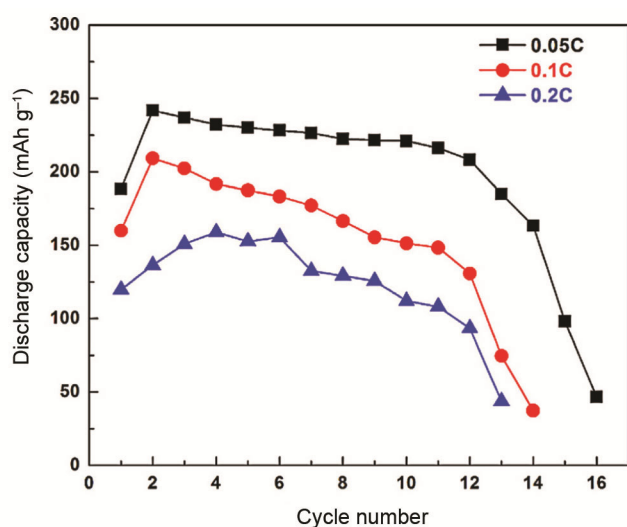
^aValues in parentheses indicate the post-deposition calcination temperatures. Numbers after SG and ED designate calcination temperature and deposition time respectively. ^bCyclic voltammetry. ^cConstant current discharge. ^dAssuming no active mass loss after calcination.

Table 4. Comparison of specific capacitance of Sb-doped SnO₂ composites with Fe₃O₄ and RuO₂ (ref. 83)

	4 mV/s		100 mV/s	
	Specific capacitance (F/g)	Capacitance density ^a (F/cm ³)	Specific capacitance (F/g)	Capacitance density (F/cm ³)
SnO ₂ U-Xerogel	5.0	20	3.2	13
SnO ₂ H-Xerogel	10–16	40–64	9–14	36–56
SnO ₂ –RuO ₂	15	60	9.6	38
SnO ₂ –Fe ₃ O ₄	–	–	33 (50 mV/s)	130 (50 mV/s)
Carbon	20–200	10–100	10–100 ^b	5–50 ^b

^aCalculated based on the geometric densities of 4.0 and 0.5 g/cm³ for the oxide xerogel and carbon electrodes respectively.

^bThe data are calculated based on a reduction of 50% in capacitance as the voltage sweeping rate was increased from 4 to 100 mV/s.


Figure 8. Cycle life of carbon-coated nanostructured Li₂MnSiO₄ (ref. 91).

achieve a maximum specific capacitance of 532.80 F/g, energy density of 74 Wh/kg along with power density of 0.5 W/kg (ref. 87).

Nanocrystalline ceria oxide (CeO₂) nanoarchitectures in the form of aerogels and ambigels possessing high porosity and thus large active surface area were prepared⁸⁸ for probable electrochemical applications. It is advised that the

mode of traversing of charges in these nanoarchitectures is through ‘the connected networks of void volume’.

A hierarchical porous vanadium pentoxide (V₂O₅)/graphene hybrid aerogel was synthesized by the *in situ* development of V₂O₅ nanofibres on graphene laminas. The supercapacitors based on these hybrids exhibit significant electrochemical properties with specific capacitance 486 F/g and energy density 68 Wh/kg (ref. 89).

Sol-gel synthesis of SnVO₄ for supercapacitor applications using acetone/water solution, VO(OC₂H₅)₃ and stoichiometric amount of SnCl₄ has been reported. Electrochemical performance in 2M KCl solution displayed specific capacitance of 150 F/g with good cycle stability⁹⁰.

Devaraj *et al.*⁹¹ reported on obtaining ‘carbon-coated Li₂MnSiO₄ (LMS/C)’ possessing morphological nanostructures by sol-gel method in presence of a chelating carbonizing source, ‘glucono-1,5-lactone (GAL)’. From the electrochemical performance profile of LMS/C it is seen that there exists a flat charge/discharge plateau for the storage processes at room temperature at different C-rates up to 10 cycles (Figure 8).

The constancy of cycle-life and the enhanced electrochemical performance was due to the ‘phase retention’ in LMS/C nanocomposite⁹¹.

The networking and grafting of Li₄Ti₅O₁₂ nanocrystals on carbon nano-fibres (nc-Li₄Ti₅O₁₂/CNF) was studied using mechano-chemical sol-gel reaction. The reaction

was carried out under centrifugal force field (65,000 N) and the product was then subjected directly to instant heat-treatment (900°C for 3 min) in vacuum. Compared to bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the prepared nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF stands superior in view of intrinsic material properties such as Li^+ diffusivity and electron conductivity. Supercapacitors comprising electrodes nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF and activated carbon reached an energy density as high as 40 WhL^{-1} and power density of 7.5 kWL^{-1} (ref. 92).

Summarizing remarks

The technological advancements and needs of modern society strongly demand the development of improved methods for storing energy whenever it is available and retrieving it when needed. The electrochemical energy storage systems can be the best option for effective storage of energy⁹³. Supercapacitors are potential and proven energy storage systems at present because of high energy density and specific power ($>10 \text{ kW kg}^{-1}$), fast charge-discharge processes (fraction of a second) and extended cycle life ($>10^5$) (ref. 94). The superior electrode materials with high electrochemically active area for SCs are the thrust area of research now-a-days as the performance of SCs is principally determined by the properties of electrode materials. Sol-gel synthesized materials based on carbon and several transition metal oxides have been broadly studied as electrode materials for SCs with notable development in the recent years^{8,95,96}. Obtaining mesoporous structures with vast surface area, chemical modification and their association with conductive nanostructures are the key factors in the development of latest, high-performance supercapacitor electrodes.

Considering the values of capacitance mentioned in this article, in general, though carbonaceous materials possess high electrochemical stabilities, they demonstrate lower capacitance compared to the ruthenium-based materials. Overall excellence in electrochemical behaviour was exhibited by a binary metal oxide NiCoO_4 in thin film form with a value of 2157 F/g. This review on important attributes from reports in the last two decades on synthesis of various carbonaceous and transition metal oxide-based supercapacitor electrode materials and their electrochemical performance, puts into place the fact that, though being a potential method, sol-gel process needs to be extensively explored and practised to a large extent. Considering the features of sol-gel derived materials and the reported encouraging specific capacitance values, emphasis may be given on research in the field of material synthesis for highly efficient and cost-effective supercapacitor electrodes via the versatile sol-gel process.

1. Wang, G., Zhang, L. and Zhang, J., A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.*, 2012, **41**, 797–828.

2. Johnson, D. W., Sol-gel processing of ceramics and glass. *Ceramic Bull.*, 1985, **64**(2), 1597–1602.
3. Turner, C. W., Sol-gel process—principles and applications. *Ceramic Bull.*, 1991, **70**, 1487–1490.
4. Hamdani, M., Singh, R. N. and Chartier, P., Co_3O_4 and co-based spinel oxides bifunctional oxygen electrodes. *Int. J. Electrochem. Sci.*, 2010, **5**, 556–577.
5. Jagadale, A. D., Kumbhar, V. S. and Lokhande, C. D., Supercapacitive activities of potentiodynamically deposited nanoflakes of cobalt oxide (Co_3O_4) thin film electrode. *J. Colloid Interf. Sci.*, 2013.
6. Balakrishnan, A. and Subramaniam, K. R. V. (eds), *Nanostructured Ceramic Oxides for Supercapacitor Applications*, CRC Press, Taylor & Francis Group, ISBN 13: 978-1-4665-7691-9, 2014, pp. 119–145.
7. Wang, F., Xiao, S., Hou, Y., Hu, C., Liu, L. and Wu, Y., Electrode materials for aqueous asymmetric supercapacitors. *RSC Adv.*, 2013, **3**, 13059–13084.
8. Lokhande, C. D., Dubal, D. P. and Joo, Oh-Shim, Metal oxide thin film based supercapacitors. *Curr. Appl. Phys.*, 2011, **11**, 255–270.
9. Kiamahalleh, M. V., Zein, S. H. S., Najafpour, G., Sata, S. A. and Buniran, S., Multiwalled carbon nanotubes based nanocomposites for supercapacitors: A review of electrode materials. *Nano: Brief Rep. Rev.*, 2012, **7**, 1230002–27.
10. Schnewly, A. and Gallay, R., Properties and applications of supercapacitors from the state-of-the-art to future trends. Proceedings of the Forty-Second International PCIM 2000 Power Electronics Conference, Adams/Intertec International, 2000, ISBN: 978-0931033780, p. 445.
11. Mittal, A. K. and Kumar, M. J., Electrochemical double layer capacitors featuring carbon nanotubes. In *Encyclopedia of Nanoscience and Nanotechnology* (ed. Nalwa, H. S.), 2011, vol. 13, pp. 263–271.
12. Jayalekshmi, S. and Anand Puthirath, *Supercapacitors: Fundamental Aspects, Nanostructured Ceramic Oxides for Supercapacitor Applications*, 2014; doi:10.1016/j.jpowsour.2010.06.036.
13. Inagaki, M., Konno, H. and Tanaie, O., Carbon materials for electrochemical capacitors. *J. Power Sources*, 2010, **195**, 7880–7903.
14. Zhang, L. L. and Zhao, X., Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.*, 2009, **38**, 2520–2531.
15. Conway, B. E., *Electrochemical Supercapacitors*, Springer US, softcover 1999, ISBN 978-1-4757-3060-9.
16. Frackowiak, E., Lota, G., Machnikowski, J., Vix-Guterl, C. and Béguin, F., Optimisation of supercapacitors using carbons with controlled nanotexture and nitrogen content. *Electrochim. Acta*, 2006, **51**, 2209–2214.
17. Chuang, C. M., Huang, C. W., Teng, H. and Ting, J. M., Effects of carbon nanotube grafting on the performance of electric double layer capacitors. *Energy Fuels*, 2010, **24**, 6476–6482.
18. Chang, Y. M., Wu, C. Y. and Wu, P. W., Synthesis of large surface area carbon xerogels for electrochemical double layer capacitors. *J. Power Sources*, 2013, **223**, 147–154.
19. Chuan, L., Ritter, J. A. and Popov, B. N., Correlation of double-layer capacitance with the pore structure of sol-gel derived carbon xerogels. *J. Electrochem. Soc.*, 1999, **146**, 3639–3643.
20. Fang, B. and Binder, L., A modified activated carbon aerogel for high-energy storage in electric double layer capacitors. *J. Power Sources*, 2006, **163**, 616–622.
21. Li, J., Wang, X., Huang, Q., Gamboa, S. and Sebastian, P. J., Studies on preparation and performances of carbon aerogel electrodes for the application of supercapacitor. *J. Power Sources*, 2006, **158**, 784–788.
22. Liu, N., Shen, J. and Liu, D., Activated high specific surface area carbon aerogels for EDLCs. *Microporous Mesoporous Mater.*, 2013, **167**, 176–181.
23. Liu, D., Shen, J., Liu, N., Yang, H. and Du, A., Preparation of activated carbon aerogels with hierarchically porous structures for

- electrical double layer capacitors, *Electrochim. Acta*, 2013, **89**, 571–576.
24. Chuan, L., Ritter, J. A. and Popov, B. N., Development of carbon-metal oxide supercapacitors from sol-gel derived carbon-ruthenium xerogels. *J. Electrochem Soc.*, 1999, **146**, 3155–3160.
25. Burke, A., Ultracapacitors: why, how, and where is the technology. *J. Power Sources*, 2000, **91**, 37–50.
26. Frackowiak, E., Carbon materials for supercapacitor application. *Phys. Chem. Chem. Phys.*, 2007, **9**, 1774–1785.
27. Li, W. C., Lu, A. H. and Guo, S. C., Characterization of the microstructures of organic and carbon aerogels based upon mixed cresol-formaldehyde. *Carbon*, 2001, **39**, 1989–1994.
28. Kim, S. J., Hwang, S. W. and Hyun, S. H., Preparation of carbon aerogel electrodes for supercapacitor and their electrochemical characteristics. *J. Mater. Sci.*, 2005, **40**, 725–731.
29. Schmitt, C., Probstle, H. and Fricke, J., Carbon cloth-reinforced and activated aerogel films for supercapacitors. *J. Non-Cryst. Solids*, 2001, **285**, 277–282.
30. Job, N., Pirard, R., Marie, J. and Pirard, J.-P., Porous carbon xerogels with texture tailored by pH control during sol-gel process. *Carbon*, 2004, **42**, 619–628.
31. Calvo, E. G., Lufano, F., Staiti, P., Brigandi, A., Arenillas, A. and Menéndez, J. A., Optimizing the electrochemical performance of aqueous symmetric supercapacitors based on an activated carbon xerogel. *J. Power Sources*, 2013, **241**, 776–782.
32. Mezzavilla, S., Zanell, C., Aravind, P. R., Volpe, C. D. and Soraru, G. D., Carbon xerogels as electrodes for supercapacitors. The influence of the catalyst concentration on the microstructure and on the electrochemical properties. *J. Mater. Sci.*, 2012, **47**, 7175–7180.
33. Zanto, E. J., Al-Muhtaseb, S. A. and Ritter, J. A., Sol-gel-derived carbon aerogels and xerogels: design of experiments approach to materials synthesis. *Ind. Eng. Chem. Res.*, 2002, **41**(13), 3151–3162.
34. Park, D.-W., Canas, N. A., Schwan, M., Milow, B., Ratke, L. and Friedrich, K. A., A dual mesopore C-aerogel electrode for a high energy density supercapacitor. *Curr. Appl. Phys.*, 2016, **16**, 658–664.
35. Chang, Y.-M., Wu, C.-Y. and Wu, P.-W., Synthesis of large surface area carbon xerogels for electrochemical double layer capacitors. *J. Power Sources*, 2013, **223**, 147–154.
36. Baumann, T. F., Worsley, M. A., Han, T. Y.-J. and Satcher, J. H., High surface area carbon aerogel monoliths with hierarchical porosity. *J. Non Cryst. Solids*, 2008, **354**, 3513–3515.
37. Liu, X. *et al.*, Porous structure design of carbon xerogels for advanced supercapacitor. *Appl. Energy*, 2015, **153**, 32–40.
38. Su, F. *et al.*, Nitrogen-containing microporous carbon nanospheres with improved capacitive properties. *Energy Environ. Sci.*, 2011, **4**, 717–724.
39. Wang, C., Zhou, Y., Sun, L., Wan, P., Zhang, X. and Qiu, J., Sustainable synthesis of phosphorus- and nitrogen-co-doped porous carbons with tunable surface properties for supercapacitors. *J. Power Sources*, 2013, **239**, 81–88.
40. Fang, B. and Binder, L., A modified activated carbon aerogel for high-energy storage in electric double layer capacitors. *J. Power Sources*, 2006, **163**, 616–622.
41. Pekala, R. W., Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J. Mater. Sci.*, 1989, **24**, 3221–3227.
42. Jiang, J., Bao, L., Qiang, Y., Xiong, Y., Chen, J., Guan, S. and Chen, J., Sol-gel process-derived rich nitrogen-doped porous carbon through KOH activation for supercapacitors. *Electrochim. Acta*, 2015, **158**, 229–236.
43. Cui, Y., Xu, S., An, J. and Yan, S., Application of 3DG/CB/MnO₂ electrode material in supercapacitors. *Int. J. Electrochem. Sci.*, 2016, **11**, 6297–6305.
44. Sun, G., Su, F., Xie, L., Guo, X. Q. and Chen, C., Synthesis of mesoporous carbon aerogels based on metal-containing ionic liquid and its application for electrochemical capacitors. *J. Solid State Electrochem.*, doi:10.1007/s10008-016-3170-2.
45. Laheäär, A., Peikola, A.-L., Koel, M., Jänes, A. and Lust, E., Comparison of carbon aerogel and carbide-derived carbon as electrode materials for non-aqueous supercapacitors with high performance. *J. Solid State Electrochem.*, 2012, **16**, 2717–2722.
46. Chang, K.-H., Hua, C.-C. and Chou, C.-Y., Textural and pseudocapacitive characteristics of sol-gel derived RuO₂·xH₂O: hydrothermal annealing versus annealing in air. *Electrochim. Acta*, 2009, **54**, 978–983.
47. Sathishkumar, K., Shanmugam, N., Kannadasan, N., Cholan, S. and Viruthagiri, G., Synthesis and characterization of Cu²⁺-doped NiO electrode for supercapacitor application. *J. Sol-Gel Sci. Technol.*, 2015, **74**, 621–630.
48. Meher, S. K., Justin, P. and Rao, G. R., Microwave-mediated synthesis for improved morphology and pseudocapacitance performance of nickel oxide. *ACS Appl. Mater. Interf.*, 2011, **3**, 2063–2073.
49. Meher, S. K. and Rao, G. R., Ultralayered Co₃O₄ for high-performance supercapacitor applications. *J. Phys. Chem. C*, 2011, **115**, 15646–15654.
50. Wang, X., Sumboja, A., Khoo, E., Yan, C. and Lee, P.-S., Cryogel synthesis of hierarchical interconnected macro-/mesoporous Co₃O₄ with superb electrochemical energy storage. *J. Phys. Chem. C*, 2012, **116**, 4930–4935.
51. Ghodbane, O., Pascal, J.-L. and Favier, F., Microstructural effects on charge-storage properties in MnO₂-based electrochemical supercapacitors. *Am. Chem. Soc. Appl. Mater. Interf.*, 2009, **1**, 1130–1139.
52. Beaudrouet, E., Le Gal La Salle, A. and Guyomard, D., Nanostructured manganese dioxides: synthesis and properties as supercapacitor electrode materials. *Electrochim. Acta*, 2009, **54**, 1240–1248.
53. Zheng, J. P., Cygan, P. J. and Jow, T. R., Hydrous ruthenium oxide as an electrode material for electrochemical capacitors. *J. Electrochem. Soc.*, 1995, **142**, 2699–2703.
54. McKeown, D. A., Hagans, P. L. and Carette, L. P. L., Structure of hydrous ruthenium oxides: implications for charge storage. *J. Phys. Chem. B*, 1999, **103**, 4825–4832.
55. Panic, V. V., Dekanski, A. B. and Stevanovic, R. M., Sol-gel processed thin-layer ruthenium oxide/carbon black supercapacitors: a revelation of the energy storage issues. *J. Power Sour.*, 2010, **195**, 3969–3976.
56. Chen, W.-C., Hu, C.-C., Wang, C.-C. and Min, C.-K., Electrochemical characterization of activated carbon-ruthenium oxide nanoparticles composites for supercapacitors. *J. Power Sources*, 2004, **125**, 292–298.
57. Hawaja, M. K., Sharma, S., Ram, M. K., Goswami, D. Y. and Stefanakos, E., Sol-gel synthesis of ruthenium oxide-graphene nanocomposites as electrode material for supercapacitor applications. *Graphene*, 2014, **2**(2), 117–122.
58. Wu, Z. S., Wang, D.-W., Ren, W., Zhao, J., Zhou, G., Li, F. and Cheng, H.-M., Anchoring hydrous RuO₂ on graphene sheets for high performance electrochemical capacitors. *Adv. Funct. Mater.*, 2010, **10**, 3595–3602.
59. Mitra, S., Lokesh, K. S. and Sampath, S., Exfoliated graphite-ruthenium oxide composite electrodes for electrochemical supercapacitors. *J. Power Sources*, 2008, **185**, 1544–1549.
60. Kahram, M., Asnavandi, M. and Dolati, A., Synthesis and electrochemical characterization of sol-gel-derived RuO₂/carbon nanotube composites. *J. Solid State Electrochem.*, 2014, **18**, 993–1003.
61. Long, J. W., Swider, K. E., Merzbacher, C. I. and Rolison, D. R., Voltammetric characterization of ruthenium oxide-based aerogels and other RuO₂ solids: the nature of capacitance in nanostructured materials. *Langmuir*, 1999, **15**, 780–785.
62. Padmanathan, N. and Selladurai, S., Electrochemical capacitance of porous NiO-CeO₂ binary oxide synthesized via sol-gel technique for supercapacitor. *Ionics*, 2014, **20**, 409–420.

63. Wei, T.-Y., Chen, C.-H., Chang, K.-H., Lu, S.-Y. and Hu, C.-C., Cobalt oxide aerogels of ideal supercapacitive properties prepared with an epoxide synthetic route. *Chem. Mater.*, 2009, **21**(14), 3228–3233.
64. Wang, X., Sumboja, A., Khoo, E., Yan, C. and Lee, P. S., Cryogel synthesis of hierarchical interconnected macro-/mesoporous Co_3O_4 with superb electrochemical energy storage. *J. Phys. Chem. C*, 2012, **116**, 4930–4935.
65. Cheng, J., Cao, G.-P. and Yang, Y.-S., Characterization of sol-gel-derived NiO_x aerogels as supercapacitors. *J. Power Sources*, 2006, **159**, 734–741.
66. Wu, M., Gao, J., Zhang, S. and Chen, A., Synthesis and characterization of aerogel-like mesoporous nickel oxide for electrochemical supercapacitors. *J. Porous Mater.*, 2006, **13**, 407–412.
67. Kim, S.-I., Lee, J.-S., Ahn, H.-J., Song, H.-K. and Jang, J.-H., Facile route to an efficient NiO supercapacitor with a three-dimensional nanonetwork morphology. *Am. Chem. Soc. Appl. Mater. Interf.*, 2013, **5**, 1596–1603.
68. Gawali, S. R. *et al.*, Asymmetric supercapacitor-based on nanostructured Ce-doped NiO (Ce:NiO) as positive and reduced graphene oxide (rGO) as negative electrode. *Chem. Select*, 2016, **1**, 3471–3478.
69. Kong, L.-B., Lu, C., Liu, M.-C., Luo, Y.-C., Kang, L., Li, X. and Walsh, F. C., The specific capacitance of sol-gel synthesized spinel MnCo_2O_4 in an alkaline electrolyte. *Electrochim. Acta*, 2014, **115**, 22–27.
70. Hu, G., Tang, C., Li, C., Li, H., Wang, Y. and Gong, H., The sol-gel-derived nickel-cobalt oxides with high supercapacitor performances. *J. Electrochem. Soc.*, 2011, **158**(6), A695–A699.
71. Wei, T. Y., Chen, C. H., Chien, H. C., Lu, S. Y. and Hu, C. C., Cost-effective supercapacitor material of ultrahigh specific capacitances: spinel nickel cobaltite aerogels from an epoxide-driven sol-gel process. *Adv. Mater.*, 2010, **22**, 347–351.
72. Wu, Y. Q., Chen, X. Y., Ji, P. T. and Zhou, Q. Q., Sol-gel approach for controllable synthesis and electrochemical properties of NiCo_2O_4 crystals as electrode materials for application in supercapacitors. *Electrochim. Acta*, 2011, **56**, 7517–7522.
73. Zhu, Y. *et al.*, Spinel NiCo_2O_4 for use as a high-performance supercapacitor electrode material: understanding of its electrochemical properties. *J. Power Sources*, 2014, **267**, 888–900.
74. Liu, M.-C., Kong, L.-B., Lu, C., Li, X.-M., Luo, Y.-C. and Kang, L., A sol-gel process for fabrication of $\text{NiO/NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$ composite with improved electrochemical behavior for electrochemical capacitors. *ACS Appl. Mater. Interf.*, 2012, **4**, 4631–4636.
75. Liu, Y., Wang, N., Yang, C. and Hu, W., Sol-gel synthesis of nanoporous NiCo_2O_4 thin films on ITO glass as high-performance supercapacitor electrodes. *Ceram Int.*, 2016, **42**, 11411–11416.
76. Wang, X., Yuan, A. and Wang, Y., Supercapacitive behaviors and their temperature dependence of sol-gel synthesized nanostructured manganese dioxide in lithium hydroxide electrolyte. *J. Power Sources*, 2007, **172**, 1007–1011.
77. Wang, X., Wang, X., Huang, W., Sebastian, P. J. and Gamboa, S., Sol-gel template synthesis of highly ordered MnO_2 nanowire arrays. *J. Power Sources*, 2005, **40**, 211–215.
78. Lin, C.-K., Chuang, K.-H., Lin, C.-Y., Tsay, C.-Y. and Chen, C.-Y., Manganese oxide films prepared by sol-gel process for supercapacitor application. *Surf. Coat Technol.*, 2007, **202**, 1272–1276.
79. Pang, S.-C., Anderson, M. A. and Chapman, T. W., Novel electrode materials for thin-film ultracapacitors: comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide. *J. Electrochem. Soc.*, 2000, **147**(2), 444–450; Pang, S.-C. and Anderson, M. A., Novel electrode materials for electrochemical capacitors: part II: material characterization of sol-gel-derived and electrodeposited manganese dioxide thin films. *J. Mater. Res.*, 2000, **15**(10), 2096–2116.
80. Reddy, R. N. and Reddy, R. G., Sol-gel MnO_2 as an electrode material for electrochemical capacitors. *J. Power Sources*, 2003, **124**, 330–337.
81. Kong, L. B., Lu, C., Liu, M. C., Luo, Y. C., Kang, L., Li, X. H. and Walsh, F. C., The specific capacitance of sol-gel synthesized spinel MnCo_2O_4 in an alkaline electrolyte. *Electrochim. Acta*, 2014, **115**, 22–27.
82. Chen, C.-Y., Wang, S.-C., Tien, Y.-H., Tsai, W.-T. and Lin, C.-K., Hybrid manganese oxide films for supercapacitor application prepared by sol-gel technique. *Thin Solid Films*, 2009, **518**, 1557–1560.
83. Wu, N. L., Nanocrystalline oxide supercapacitors. *Mater. Chem. Phys.*, 2002, **75**, 6–11.
84. Hu, C.-C., Wang, C.-C. and Chang, K.-H., A comparison study of the capacitive behavior for sol-gel-derived and co-annealed ruthenium-tin oxide composites. *Electrochim. Acta*, 2007, **52**(7), 2691–2700.
85. Wu, M., Zhang, L., Wang, D., Xiao, C. and Zhang, X., Cathodic deposition and characterization of tin oxide on graphite for electrochemical supercapacitors. *J. Power Sources*, 2008, **175**, 669–674.
86. Yang, Y. *et al.*, Sn@SnO_2 attached on carbon spheres as additive-free electrode for high-performance pseudocapacitor. *Electrochim. Acta*, 2016, **209**, 350–359.
87. Lorkit, P., Panapoy, M. and Ksapabutr, B., Iron oxide-based supercapacitor from ferratrate precursor via sol-gel-hydrothermal process. *Energy Proc.*, 2014, **56**, 466–473.
88. Laberty-Robert, C., Long, J. W., Lucas, E. M., Pettigrew, K. A., Stroud, R. M., Doescher, M. S. and Rolison, D. R., Sol-gel-derived ceria nanoarchitectures: synthesis, characterization and electrical properties. *Chem. Mater.*, 2006, **18**(1), 50–58.
89. Wu, Y., Gao, G. and Wu, G., Self-assembled three-dimensional hierarchical porous V_2O_5 /graphene hybrid aerogels for supercapacitors with high energy density and long cycle life. *J. Mater. Chem. A*, 2015, **3**, 1828–1832.
90. Gurunathan, K. and Manthiram, A., Sol-gel synthesis of SnVO_4 for supercapacitor. *International Materials Research Congress*, Cancun, Mexico, 2002.
91. Devaraj, S., Kuezman, M., Ng, C. T. and Balaya, P., Sol-gel derived nanostructured $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode with high storage capacity. *Electrochim. Acta*, 2013, **102**, 290–298.
92. Naoi, K., Ishimoto, S., Isobe, Y. and Aoyagi, S., High-rate nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ attached on carbon nano-fibers for hybrid supercapacitors. *J. Power Sources*, 2010, **195**, 6250–6254.
93. Yang, Z., Zhang, J., Kintner-Meyer, M. C. W., Lu, X., Choi, D., Lemmon, J. P. and Liu, J., Electrochemical energy storage for green grid. *Chem. Rev.*, 2011, **111**, 3577–3613.
94. Ghosh, A. and Lee, Y. H., Carbon-based electrochemical capacitors. *Chem. Sus. Chem.*, 2012, **5**, 480–499.
95. Basnayaka, P. A., Ram, M. K., Stefanakos, L. and Kumar, A., Graphene/polypyrrole nanocomposite as electrochemical supercapacitor electrode: electrochemical impedance studies, *Graphene*, 2013, **2**, 81–87.
96. Ketkar, S., Ram, M., Kumar, A., Weller, T. and Hoff, A., Stabilization of graphene-polyaniline based nanocomposite electrodes using barium strontium titanate for supercapacitor application. *AIP Conference Proceedings*, 2012.

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