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Review article

Vanadium based materials as electrode materials for high performance supercapacitors

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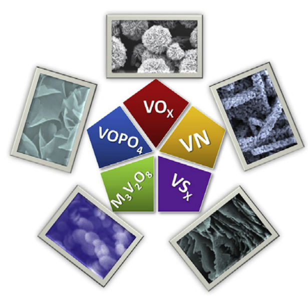
HIGHLIGHTS

- Vanadium based materials for high performance supercapacitor were reviewed.
- The advantages and disadvantages were discussed in details.
- Perspectives as to the future directions of vanadium based materials were provided.

GRAPHICAL ABSTRACT



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ABSTRACT

As a kind of supercapacitors, pseudocapacitors have attracted wide attention in recent years. The capacitance of the electrochemical capacitors based on pseudocapacitance arises mainly from redox reactions between electrolytes and active materials. These materials usually have several oxidation states for oxidation and reduction. Many research teams have focused on the development of an alternative material for electrochemical capacitors. Many transition metal oxides have been shown to be suitable as electrode materials of electrochemical capacitors. Among them, vanadium based materials are being developed for this purpose. Vanadium based materials are known as one of the best active materials for high power/energy density electrochemical capacitors due to its outstanding specific capacitance and long cycle life, high conductivity and good electrochemical reversibility. There are different kinds of synthetic methods such as sol-gel hydrothermal/solvothermal method, template method, electrospinning method, atomic layer deposition, and electrodeposition method that have been successfully applied to prepare vanadium based electrode materials. In our review, we give an overall summary and evaluation of the recent progress in the research of vanadium based materials for electrochemical capacitors that include synthesis methods, the electrochemical performances of the electrode materials and the devices.

1. Introduction

According to the energy crisis and greenhouse effect in the past few decades, many countries have not only been developing the strategies and rules but also have been developing a lot of high technologies to deal with the global warming effect [1–3]. Many

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energy storage devices, such as the solar energy, wind power, fuel cell, and biofuel have been taking an important role in the high tech industries recently. The most important goal for the energy storage device is to make them thin, small, and easy to carry for everyday use. The supercapacitors (SCs), also called ultracapacitors and electrochemical capacitors (ECs), compared with other storage devices, such as dielectric capacitor, secondary cell, fuel cells, lithium-ion batteries, have higher power density and broader range of working temperature [4,5]. Supercapacitors have not only a large power density of thousands of watts per kilogram, a long cycle life but also an enhanced efficiency of energy utilization.

If a supercapacitor integrates with secondary batteries in electronic devices, it will extend the lease and reduce the volume of devices. Take the mobile device for example, the mobile devices will be served by secondary batteries for common use [6,7]. However, when the devices need high-transient power which is the special characteristic of supercapacitors they will be provided by supercapacitors. Thus, if the supercapacitor links up with the secondary batteries in the mobile devices, the devices will not only lessen the volume of device but also prolong the batteries' life, especially in stabilizing the batteries' voltage [8,9].

Supercapacitors can store more energy, because the mechanism of double-layer gets larger interfacial area and the reaction between two electrodes involves the ions' transfer in the atomic range [10,11]. Dielectric capacitors get high power density but low energy density. However, supercapacitor can store higher energy density than traditional capacitor. The fuel cells have high energy density but low power density. The supercapacitor is in the middle of dielectric capacitor and fuel cell. Because of the ostensible characteristics of materials, the energy density is higher than the ceramic capacitors and electrolytic capacitors thousands to tens of thousands of times. The advantages of supercapacitors include [12–17], (1) The long life cycle (more than 50000 times of charge and discharge); (2) The wide application of temperature range (−40 °C–60 °C); (3) The wide range of voltage: The terminal voltage is 2.5 V for the only one supercapacitor; (4) Possessed of coulombic efficiency: the lost charges in charging and discharging process are close to zero in the supercapacitor; (5) The equivalent series resistance (ESR) is very tiny in the supercapacitor. Since the input and output current is very high, the supercapacitor can be charged and discharged very fast.

Selection of electrode materials plays a crucial role in determining the electrical properties of a supercapacitor. Most of the metal compound electrodes are transition metals, because they have changeable valence, which can provide ideal pseudocapacitance. The metal compounds must get three characteristics for applying on supercapacitor [18–20]. First, it is large conductivity. Second, there are more than two valences and the crystalline phase won't be changed with valence change. Third, the proton can intercalate into the lattice of metal compounds, especially for transition metal compounds [21,22].

The cyclic voltammogram of noble metal oxides (MOs) such as RuO_2 and IrO_2 electrodes have an almost rectangular shape and exhibit excellent capacitor behavior [23,24]. A very high specific capacitance of up to 750 F g^{-1} was reported for RuO_2 prepared at relatively low temperatures. Conducting metal oxides like RuO_2 or IrO_2 were ideal electrode materials in early ECs used for space or military applications [25]. The high specific capacitance in combination with low resistance resulted in very high specific powers. These capacitors, however, turned out to be too expensive. A rough calculation of the capacitor cost showed that 90% of the cost resides in the electrode material. In addition, these capacitor materials are only suitable for aqueous electrolytes, thus limiting the nominal cell voltage to 1 V. Several attempts were undertaken to keep the advantage of the material properties of such metal oxides at reduced cost. The dilution of the costly noble metal by forming perovskites was investigated by Lou et al. [26]. Other forms of metal oxides such as nickel oxides, cobalt oxides, manganese oxides, vanadium oxides and iron oxides are actively studied.16.

In the periodic table of the elements, vanadium (V) is element twenty-third, and is located in the position of VB, which belongs to 3d Sub family of transition metal elements, the structure of the valence electron layer is 3d34s2, the outermost layer has five valence electrons, and The five valence electrons can participate in bonding, therefore, valence of vanadium rich, is a multivalent metal element, such as +5, +4, +3, +2, which can provide excellent pseudocapacitance. Among the many compounds formed by vanadium, the valence of +5 is the most stable. The stability of +4 and + 2 are the worst, so the mostly studied vanadium compounds are VO_x, VN and vanadium bronze [27–29]. With flexible doping modification methods, the materials type and preparation methods are diverse. The material structure, conductivity, electrolyte, and material loading mass on the electrode have a crucial influence on the pseudocapacitance of vanadium-based materials. We could control the materials construction, form composites, and even develop new vanadium based materials to improve the supercapacitance performance. So as to promote future breakthroughs in this field, our review is dedicated to this important material group, providing a timely effort to comprehensively and critically evaluate the development.

2. Vanadium pentoxide

Vanadium oxide as a transition metal oxide (+2 to +5), has been widely applied to the electrode material of lithium batteries and sodium ion batteries [30–36]. It can not only produce the oxidation reduction reaction on the surface, but also can occur in the interior. However, because of the poor electrical conductivity and cyclic stability of vanadium oxide, the electrode material of electrochemical capacitor is limited. It is a main way to improve the electrical conductivity and cyclic stability of the electrode materials for electrochemical capacitors. At present, there are more studies on the vanadium oxide with V_2O_5, V_2O_3, VO_2 and so on [37].

2.1. Vanadium pentoxide

As one of the most representative vanadium oxide, vanadium pentoxide (V_2O_5) plays an important role in the field of electrochemical energy storage. David Lou's group have carried out extensive and in-depth research of V_2O_5, owing to their unique structure-determined physical and chemical properties, which can provide for facile Li ions insertion and good cycling stability for lithium-ion batteries and supercapacitors [38–42].

Lee et al. firstly used vanadium pentoxide as an electrode material that can be applied for the supercapacitors. They used melt-quenching method to prepare amorphous-$V_2O_5 \cdot nH_2O$ that can be an excellent electrode for a faradaic electrochemical capacitor [43]. Cyclic voltammograms versus SCE gave ideal capacitor behavior between 0.0 and 10.8 V at pH 6.67 and between 20.2 and 10.8 V at pH 2.32 with, respectively, a constant specific capacitance over 100 cycles of ca. 350 and 290 F g^{-1}, respectively. On short-circuit, α-$V_2O_5 \cdot nH_2O$ in 2 M KCl aqueous solution at pH 2.32 gave an initial current density of 0.28 A cm^{-2} and a total released charge of 4.5 C $cm^{-2,}$ which was to be compared with 0.32 A cm^{-2} and 11.1 C cm^{-2} for $RuOOH \cdot nH_2O$ in 5.3 M H_2SO_4. Moreover, half the stored charge was released 1.6 times faster from the α-$V_2O_5 \cdot nH_2O$ electrode.

Chemically pure vanadium pentoxide (V_2O_5) powders can be a good electrode material for supercapacitors [44]. Lao et al. found that the materials which was prepared by co-precipitation and