

CARBON - SUPPORTED RUTHENIUM OXIDE FOR ELECTROCHEMICAL DOUBLE LAYER CAPACITOR ELECTRODES

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Introduction

Electrochemical double layer capacitors (EDLCs) having electrodes made from activated carbon can theoretically deliver a large charge (100-200 F/g for a two electrode capacitor) due to amplification of the double layer capacitance ($\sim 20\mu\text{F}/\text{cm}^2$) by the large surface area of the carbon (1000-2000 m^2/g). Highly conductive electrolytes and high ionic concentrations (aqueous solution) are necessary to allow the movement of ions into the small pores of the carbon. The specific capacitance for a pseudocapacitor using ruthenium oxide can reach a value $330\mu\text{F}/\text{cm}^2$ or more [1]. Due to the high price of ruthenium, extensive work is being done to find less expensive pseudocapacitance materials [2]. Another approach is to combine the properties of activated carbon and ruthenium oxide to enhance the performance of EDLCs in which these carbons are used as electrode materials.

An investigation of the technique for the deposition of ruthenium oxide on high surface area carbons was initiated. The main focus of the work was the establishment of a reproducible technique for the introduction of ruthenium oxide into the porous carbon network. Standard methods for the production of catalysts by the deposition of metals and oxides on supports often involve heating to temperatures in excess of 300°C . When carbon is the material on which deposition is to take place, the temperature cannot be allowed to reach this value in order to prevent loss of carbon by oxidation. It is therefore necessary to develop a technique involving the introduction of a soluble ruthenium compound which can be decomposed at a temperature preferably as low as 200°C .

The main objective of the study was to determine whether the electrical energy storage capacity of EDLCs with porous carbon electrodes could be enhanced by the incorporation of substances such as ruthenium oxide which can undergo a surface redox reaction.

Experimental

Two commercial carbons (Calgon Corp. BPL, and Cabot Corp. Black Pearls 2000) have been used as the main

component of electrodes produced by compressing carbon particles with a Teflon binder. In order to study the characteristics of cells having ruthenium oxide impregnated carbon electrodes, the cell has recently been redesigned [3] with titanium disks replacing the nickel current collectors so as to allow sulphuric acid to be used as the electrolyte in place of aqueous potassium hydroxide solution.

Ruthenium (III) 2,4-pentadionate decomposes in air above 160°C to yield ruthenium oxide, RuO_2 . However the decomposition reaction is highly exothermic, resulting in a sudden increase in temperature that causes a significant amount of the starting material to sublime rather than decompose to give the desired product. Thermal gravimetric analysis (TGA) was used to determine the conditions under which the decomposition can be achieved in the presence of activated carbon with minimal loss of ruthenium. Ruthenium (III) 2,4-pentadionate was introduced into the carbon by mixing a dilute solution of the complex in acetone with the carbon. The resulting slurry is dried carefully at temperatures up to 110°C to remove the solvent. Small amounts of the dried product (approx. 10mg) are then decomposed, in a stream of air, in a thermogravimetric analyzer (TA Instruments) at temperatures up to 190°C . Larger amounts for use in electrodes have been heated in a temperature-controlled furnace under similar conditions.

To characterise the carbons, relevant properties such as surface area, pore size distribution, and ash content have been determined by the usual techniques. Also measured is the active area of the dispersed RuO_2 by chemisorption of H_2 .

Capacitance measurements have also been performed on electrodes produced from the impregnated carbons.

Results

When attempting to deposit metals and oxides within the pores of materials such as activated carbons, pore blocking is always a concern, particularly when much of the pore volume is in the micropore range ($> 2\text{ nm}$ in width). In order to ascertain the extent of pore blocking, nitrogen adsorption isotherms at 77 K were used to determine BET surface area and micropore volumes of impregnated BPL

and Black Pearls carbons, the two carbons on which most of the preliminary capacitance measurements had been made. In all cases Teflon binder was also used, since it is necessary to add this component to give sufficient mechanical stability to handle the EDLC electrode. The results summarise in Table I show that for BPL carbon there is considerable loss of surface area and pore volume following impregnation, but for Black Pearls the reduction in both of these parameters is not nearly as pronounced. Following this discovery, impregnation work has proceeded on Black Pearls alone.

Table I: Characteristics of BPL and Black Pearls carbons before and after RuO₂ deposition.

Carbon	Teflon %	BET Area m ² .g ⁻¹	Dubinín μpore volume mL.g ⁻¹
BPL		1118	0.45
BPL	6.8	469	0.18
BPL+RuO ₂	6.1	113	0.04
BP		1630	0.72
BP	5.6	1570	0.63
BP+RuO ₂		1470	0.66
BP+RuO ₂	5.2	1400	0.62

According to the TGA measurements, when the temperature is raised very slowly (0.1°C/min) the decomposition of ruthenium (III) 2,4-pentadionate in air starts at around 150°C and is completed at 180°C.

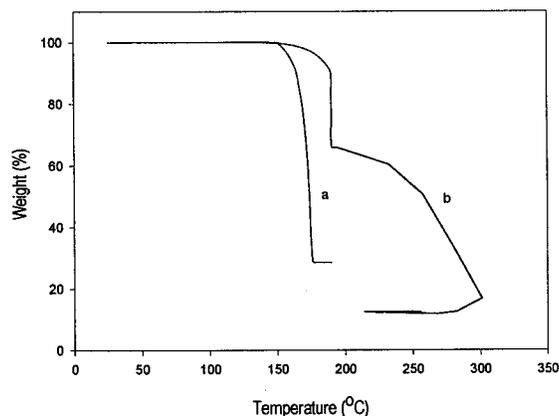


Figure 1: TGA of the decomposition of ruthenium (III) 2,4-pentadionate in air at two different heating rates: a - 0.1°C/min, b - 1°C/min.

However, if the heating rate is 1°C/min, the reaction rate becomes such that the temperature of the material increases dramatically, leading to considerable loss of the desired product. Sublimation of the complex is the likely explanation. Figure 1 shows TGA results at these two heating rates. The theoretical yield of RuO₂ is 34% of the starting mass.

It is important to control the decomposition conditions very carefully when processing larger amounts of material. The fact that the complex is “diluted” when distributed throughout a porous carbon structure may help to reduce this problem.

In order to establish that the impregnation technique has resulted in the deposition of ruthenium oxide, x-ray diffraction (XRD) measurements have been conducted on both the decomposition products of the pure ruthenium complex, and on the impregnated carbons.

To establish the amount of active ruthenium oxide surface area, chemisorption measurements were performed on ruthenium oxide deposited on Black Pearls.

Capacitance measurements performed on Black Pearls carbon with deposited ruthenium oxide, the presence of which was established by X-ray diffraction and chemisorption measurements, have not shown significant improvements in capacitance values. Further effort will be devoted to achieving greater dispersion of the RuO₂ on carbons with higher micropore and mesopore volumes.

Conclusion

Although a technique has been developed by means of which ruthenium oxide can be deposited on a high surface area carbon, either the method will have to be modified, or the type of carbon changed to allow greater dispersion of the oxide on the carbon surface. At present the ruthenium oxide does not significantly increase the capacity of the carbon electrode when used in a test cell containing sulphuric acid as electrolyte.

References

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