Performance investigations of $Pb_2Ru_2O_{6.5}$ oxide based pseudocapacitors

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Abstract

Lead Pb/Ru pyrochlore ($Pb_2Ru_2O_{6.5}$) was synthesized as a new electrode material for aqueous-electrolyte capacitors. This material was characterized using X-ray diffraction, BET area anhgalysis and cyclic voltammetry. Small laboratory-scale prototype capacitors were fabricated with $Pb_2Ru_2O_{6.5}$ oxide electrodes and tested for their electrochemical performance in terms of capacitance, rate-capabilities, and energy–power performance. These laboratory cells exhibited excellent performance under constant power discharge delivering >5 W h/kg specific energy at 750 W/kg power level based on electrode and electrolyte masses only. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to satisfy the high power requirement of an electric vehicle, it is logical to use an additional power system such as an electrochemical capacitor in conjunction with the electric vehicle battery. A hybrid system combination of a rechargeable battery and an electrochemical capacitor can provide the overall power and energy without sacrificing the energy density and cycle life of the battery. Thus, a high power density electrochemical capacitor with high energy density must be developed that possesses the ability to rapidly store and release large quantities of energy over several thousands of cycles. In the past several years, considerable interest [1–9] has been placed on developing high energy and power density electrochemical capacitors for pulse power and hybrid vehicle applications. To create a viable energy storage device for a hybrid vehicle, it is important to increase the energy storage capacity of existing double layer capacitors. This may be achieved by a concept called pseudocapacitance [1,2,8,9] that not only develops the typical double layer capacitance, but also exhibits pseudocapacitance due to surface redox couples providing net charge transfer. Owing to this redox reaction, the capacitance of these capacitors is significantly higher than a double layer capacitor. A key to increasing the energy density of an electrochemical capacitor is to develop materials containing metal centers capable of providing multiple redox reactions. Ruthenium is a remarkable element in that, it displays nine oxidation states ranging from 0 to VIII. One of the most promising ruthenium compounds, Pb/Ru pyrochlore oxide, is capable of providing several redox reactions [10,11] involving the oxidation states Ru(II), Ru(III), Ru(IV), Ru(V), and even Ru(VI). The work described in this paper is related to the electrochemical performance of the small laboratory-scale capacitors fabricated with Pb/Ru pyrochlore ($Pb_2Ru_2O_{6.5}$) electrodes.

2. Experimental

The Pb/Ru pyrochlore $Pb_2Ru_2O_{6.5}$ was synthesized and purified according to the method reported by Horowitz et al. [12]. This method involves an alkaline aqueous solution both as a means of reacting the appropriate metal cations by precipitation, and as a medium for the crystallization of the precipitate in the presence of oxygen. The KOH solutions were prepared from low-carbonate KOH pellets (Fluka). The salts Ru $(NO)(NO_3)_3$, 1.5% (w/v) (Aldrich) and $Pb(CH_3COO)_2·3H_2O$ (Aldrich) were mixed in the appropriate amounts to achieve the desired stoichiometries. The reaction was carried out for 24–72 h, until the supernatant solution was free of detectable amounts of the reactant metal

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ions. The suspension was filtered and washed with triply distilled water and glacial acetic acid in order to leach out any lead oxide formed during the reaction.

X-ray diffraction was done on a Philips Diffractometer. X-ray photoelectron spectroscopy was carried out using a Varian IEEE-15 instrument. The surface areas of the Pb/Ru pyrochlores were determined by the BET N_2 gas adsorption method, using a Quantasorb instrument (Quantachrome).

Cyclic voltammetry was carried out in a glass cell, which had separate compartments for the working electrode, counter electrode and reference electrode plus a Luggin capillary in order to minimize IR drop. A Pt screen was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The electrolyte was 0.5 M H_2SO_4. The working electrode $Pb_2Ru_2O_{6.5}$ was made on an ordinary pyrolytic graphite (OPG) disk electrode. The OPG disk was modified so that it was recessed slightly below the outer plane of the Teflon mounting to create a very small cavity. PTFE suspension (Teflon T30B, Dupont) was diluted with water and ultrasonically agitated with the Pb/Ru pyrochlore and filtered with a 1 μm pore size polycarbonate filter membrane. This semi-moist paste was kneaded with a spatula and then applied to the disk and spread evenly.

Electrochemical performance of the $Pb_2Ru_2O_{6.5}$ electrode was evaluated in terms of its capacitance, energy and power characteristics in laboratory-scale 2016 type (2 cm diameter and 1.6 mm height) coin cells. To fabricate the electrodes, a Teflon T30B suspension diluted approximately to about 2 mg/cm^3 in water, was slowly added to an aqueous suspension of active materials. The electrodes investigated in this study were 100% XC-72 carbon, 100% $Pb_2Ru_2O_{6.5}$ oxide, and 50 wt.% XC-72 carbon+50 wt.% $Pb_2Ru_2O_{6.5}$ oxide. The suspension was filtered using a 1 μm filter membrane. The resulting paste was kneaded with a spatula, until slightly rubbery, and applied to a tantalum substrate in the form of a thin layer. This was then pressed between two flat plates at about 300 kg/cm^2 and heat treated in an inert atmosphere. Symmetric 2016 type coin cells were fabricated by using two identical electrodes separated by a porous Celgard membrane. The electrodes were then impregnated with 0.5 M H_2SO_4 and sealed. These cells were tested with computer-controlled Arbin Cyclers. The electrochemical performance of these capacitors was investigated by constant current charge–discharge and constant power discharge.

3. Results and discussions

The X-ray diffraction pattern of the Pb/Ru pyrochlore ($Pb_2Ru_2O_{6.5}$) heat-treated at 100°C for 8 h is shown in Fig. 1. This X-ray diffraction pattern, when compared with literature data [12] confirmed the purity and the existence of the pyrochlore structure in $Pb_2Ru_2O_{6.5}$. The broadness of the diffraction peaks also indicates small particle size for
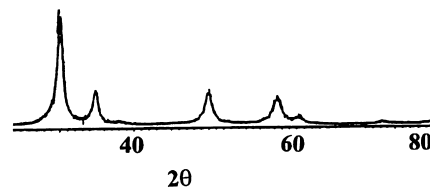

Fig. 1. X-ray diffraction pattern of $Pb_2Ru_2O_{6.5}$ pyrochlore oxide.

the oxide synthesized at lower temperatures. BET area measurement carried out on these powder shows a surface area of 35 m^2/g.

Cyclic voltammetry curve of $Pb_2Ru_2O_{6.5}$ oxide is shown in Fig. 2. The charge under the voltammetric curve in Fig. 2 is due to the double layer capacitance and a series of redox processes involving multiple electron transfers to ruthenium and lead cations. These redox processes, however, are not visible in Fig. 2. This is because the redox peaks in the cyclic voltammogram (Fig. 2) are buried under very large double-layer currents of the Pb/Ru pyrochlore electrode. However, for materials heat-treated at higher temperatures, the voltammetric peaks representing the redox reactions of Ru and Pb surface atoms are clearly observed [13] indicating better-defined Faradaic processes. This is because the double-layer capacitance is significantly decreased as a result of reduced surface area for the materials heat-treated at higher temperatures. The nature and extent of these surface redox reactions are highly dependent on the composition and synthesis conditions of the oxide. One of the advantages of the electrode materials heated at low temperature, however, is that the multiple surface redox processes merge smoothly, resulting in a relatively flat current voltage curve in the potential window. The capacitance is calculated to be about 400 μF/cm^2 for the Pb/Ru pyrochlore normalized to the surface area of the electrode materials, while the capacitance is usually in the range of 10–30 μF/cm^2 for a conventional electrochemical double layer capacitance.
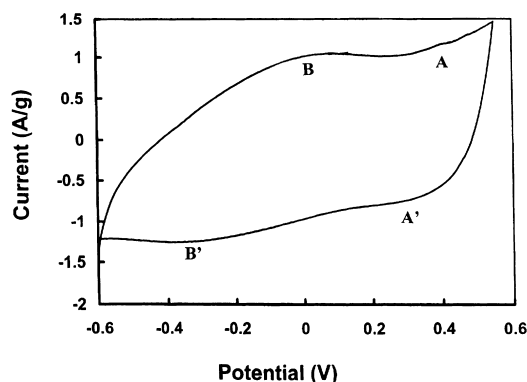

Fig. 2. Cyclic voltammogram of the $Pb_2Ru_2O_{6.5}$ electrode in N_2 saturated 0.5 M H_2SO_4 at room temperature, a Pt screen was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode, loading: 4 mg/cm^2 (5 wt.% Teflon), sweep rate: 20 mV/s, electrode area: 0.196 cm^2.
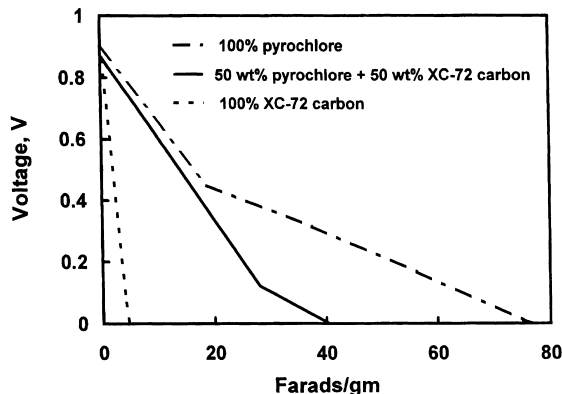
Fig. 3. Electrochemical performance of the symmetrical cell fabricated with electrodes containing 100% carbon, 100 wt.% Pb/Ru pyrochlore, and (50 wt.% $Pb_2Ru_2O_{6.5}$+50 wt.% XC-72 carbon) electrodes at a discharge current density of 400 mA/cm^2.
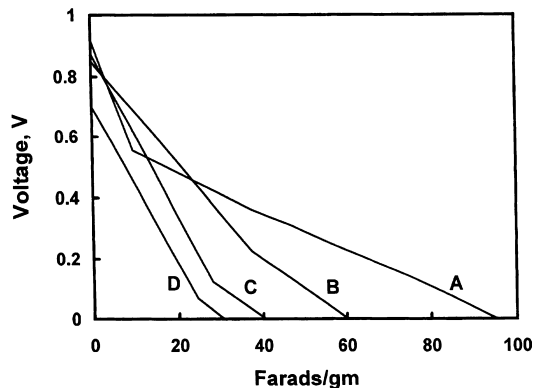

Fig. 4. Electrochemical performance of the symmetrical cell fabricated with electrodes containing 50 wt.% Pb/Ru pyrochlore and 50 wt.% XC-72 carbon at various current densities, the material loading is about 25 mg/cm^2, (A) 50 mA/cm^2; (B) 200 mA/cm^2; (C) 400 mA/cm^2; (D) 500 mA/cm^2.

The contribution of the redox processes to capacitance of the Pb/Ru pyrochlore materials is quite significant.

Fig. 3 shows a comparison of the performance of capacitors fabricated with 100% XC-72 carbon, 100% $Pb_2Ru_2O_{6.5}$ oxide, and a mixture of 50 wt.% XC-72 carbon+50 wt.% $Pb_2Ru_2O_{6.5}$ oxide at a 400 mA/cm^2 discharge current density. It is evident from this figure that the capacitance of XC-72 carbon electrode is only 6% of the capacitance observed for a 100% $Pb_2Ru_2O_{6.5}$ oxide electrode. The reason for the low capacitance of 100% carbon electrode is that carbon exhibits only the double layer capacitance, while the $Pb_2Ru_2O_{6.5}$ oxide exhibits both double layer and pseudocapacitance. The capacitance of the Pb/Ru pyrochlore oxide electrode in the capacitor fabricated with a mixture of 50 wt.% $Pb_2Ru_2O_{6.5}$+50 wt.% carbon is about the same to that of 100% $Pb_2Ru_2O_{6.5}$ oxide when normalized to the active material weight of $Pb_2Ru_2O_{6.5}$ oxide only. Due to ease of fabrication, the electrochemical performance of the $Pb_2Ru_2O_{6.5}$ electrode was investigated in the capacitors fabricated with 50 wt.% XC-72 carbon and 50 wt.% $Pb_2Ru_2O_{6.5}$ oxide. Fig. 4 shows the performance of such a capacitor made at various discharge current levels. The capacitance numbers in Fig. 4 are for one electrode and are normalized to the weight of the electrode including Pb/Ru pyrochlore, carbon, and binder. A close inspection of Figs. 3 and 4 show that the discharge curves show a change of slope. The discharge curves in Figs. 3 and 4 qualitatively follows the cyclic voltammogram shown in Fig. 2. The change of slope of the discharge curves in the potential range of 0.45–0.5 and 0.1–0.2 V (cell voltage in the symmetric cell containing both identical electrodes) is probably due to the Faradaic processes represented by A (0.3 V versus SCE) and B (−0.3 V versus SCE) in the voltammetric curve (see Fig. 2). These redox peaks, although not very sharp in the voltammogram due to very large double-layer currents of the Pb/Ru pyrochlore electrode represent the Faradaic processes involving surface ruthenium atoms [13]. The possibility of Pb in these redox processes cannot be ruled out. In

situ spectroscopic study may help to clarify the situation. These Faradaic reactions involving the electron transfer reaction give rise to higher pseudocapacitance and hence high energy density. The shift of the potential for the change of slope at higher discharge currents (Fig. 4) is not very clear, but is probably related to the cell resistance.

It is evident from this figure that about 30 F/g of capacitance can be obtained from an electrode consisting of 50 wt.% $Pb_2Ru_2O_{6.5}$+50 wt.% carbon even at current densities as high as 500 mA/cm^2. This translates to about 56 F/g of capacitance, when normalized to the weight of the Pb/Ru pyrochlore oxide only. It is also important to carry out the specialized tests, such as constant-power discharge under various power profiles levels, in order to evaluate the viability of the Pb/Ru pyrochlore capacitors in hybrid vehicle systems made from a combination of a battery and a capacitor. Typical discharge curves of the lead–ruthenate capacitor at various power levels are shown in Fig. 5. The voltage–time profile in the constant-power discharge does not produce a linear curve, as shown in Fig. 5. This is
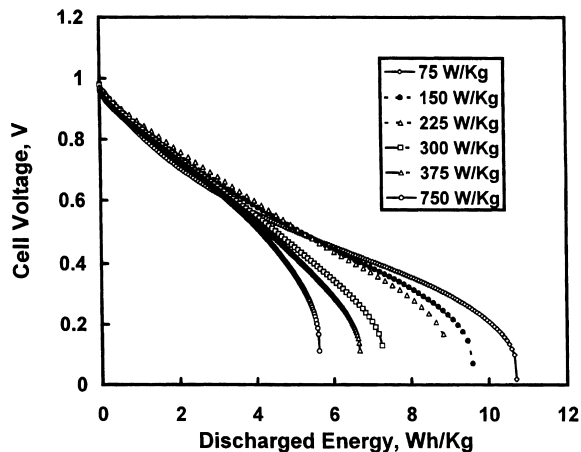

Fig. 5. Discharge voltage vs. discharged energy curves of the 2016 type laboratory-scale $Pb_2Ru_2O_{6.5}$ capacitor at various power levels.
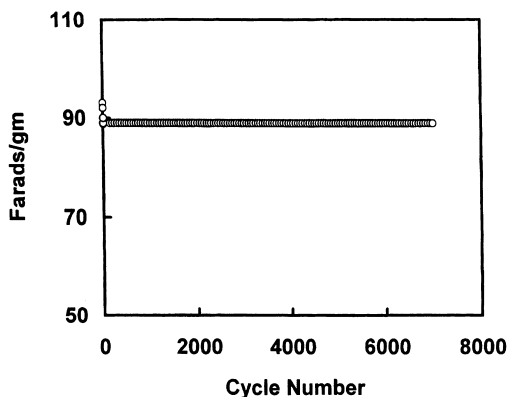
Fig. 6. The capacitance of the $Pb_2Ru_2O_{6.5}$ capacitor as a function of cycle numbers, the capacitor was discharged at 100 mA/cm^2 at room temperature.

because the current during the power discharge increases continuously depending on the voltage in order to maintain a constant power level. It is also clear from this figure that the performance of the capacitor decreases as the power level increases. However, these prototype laboratory-scale cells produce over 5 W h/kg specific energy even at 750 W/kg power level based on the weights of the active electrode materials (carbon and Pb/Ru pyrochlore oxide), electrolyte, and the separator. If normalized to the weight of the Pb/Ru pyrochlore alone, this would translate to a specific energy of about 9.5 W h/kg when discharged at a power level of 750 W/kg. These cells were also tested at 100 mA/cm^2 for more than 6000 cycles (Fig. 6) to investigate the performance variation as a function of cycle number. The initial drop in the capacitance is due to the earlier power discharge tests. It is clear from this figure that there is negligible or no loss in the cell capacitance even after 6000 cycles.

Fig. 7 is a plot showing the power and energy performance of the capacitors fabricated with 50 wt.% $Pb_2Ru_2O_{6.5}$ and 50 wt.% XC-72 carbon. The values for the energy and power
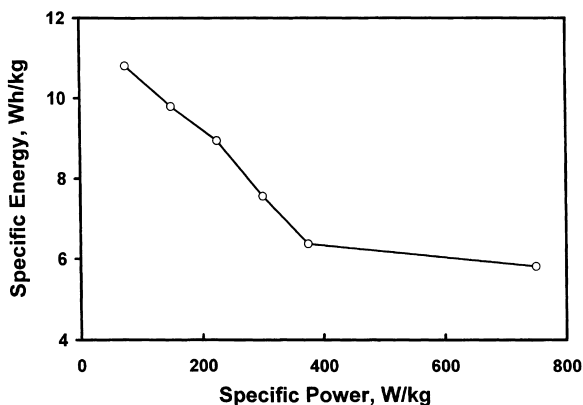

Fig. 7. A plot showing the energy and power performance of the $Pb_2Ru_2O_{6.5}$ laboratory-scale capacitors. The energy density numbers used in this plot were obtained from constant power discharge of the $Pb_2Ru_2O_{6.5}$ capacitor.

densities in this figure are based on the results of the constant-power discharge carried out on these cells. Although, these prototype coin cell devices were not fully optimized, these devices built on the concept of pseudocapacitance exhibited an excellent performance under constant-power discharge. Improvement of energy performance can be achieved, if a higher composition of Pb/Ru pyrochlore was used to fabricate the electrode. The particle size and BET surface area of the oxide powder are all very sensitive to the synthesizing condition and heat treatment process. Optimization of these parameters of the electrode preparation process still offers significant room for performance improvement. The high performance of the Pb/Ru capacitors under a realistic power discharge is comparable to those of the RuO_2 based capacitors [14] due to similar characteristics, such as high surface area, availability of several surface redox processes, and high electronic conductivity (RuO_2 [15]: 3.5×10^{-5} Ω cm, Pb/Ru pyrochlore [11]: 3×10^{-4} Ω cm) of these oxides.

The high performance of these capacitors based on Pb/Ru pyrochlore is attractive from both technical and cost viewpoints. This is because the general chemical composition of the Pb/Ru pyrochlore ($Pb_2[Ru_{2-x}Pb_x]O_{7-y}$), involving two metals provides an opportunity to develop low-cost materials by reducing the amount of Ru. The amount of the expensive metal Ru can be substantially reduced by increasing the Pb content in the formula using $Pb_2[Pb_xRu_{1-x}]O_{6.5}$. In addition, the molecular formula of the pyrochlore $A_2[Ru_{2-x}A_x]O_{7-y}$ also provides an opportunity to substitute other elements in the A sites as long as the ionic radii are appropriate and charge neutrality is maintained. Consequently, a number of different Pb/Ru pyrochlores containing Ru can be developed.

4. Conclusions

It has been demonstrated that electrochemical capacitors fabricated with the lead ruthenate pyrochlore $Pb_2Ru_2O_{6.5}$ electrodes exhibit high pseudocapacitance, and hence improved specific energy. The capacitors built with these electrodes also show an excellent performance under constant-power discharge producing a specific energy of more than 5 W h/kg at 750 W/kg power level. The Pb/Ru pyrochlore could offer significant saving in materials cost compared to pure noble metal oxides.

Acknowledgements

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