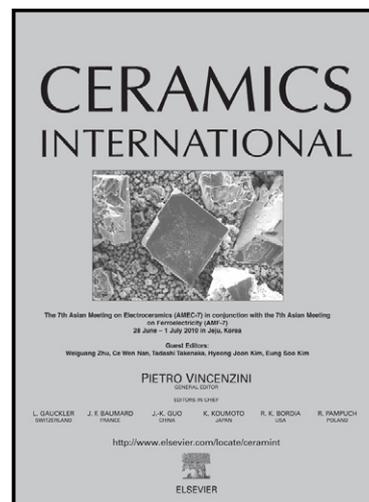


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Calcium-based Nanosized Mixed Metal Oxides for Supercapacitor Application

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Abstract

The nanosized mixed metal oxides ($\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3) have been synthesized and their electrochemical performance as supercapacitor electrodes have been evaluated. All of them show good pseudocapacitance in KOH electrolyte with specific capacitance of 563, 384 and 275 F g^{-1} for $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 , respectively. The charge kinetics of $\text{Ca}_3\text{Co}_2\text{O}_6$ is further evaluated by electrochemical impedance spectroscopy and the results show the low resistivity of $\text{Ca}_3\text{Co}_2\text{O}_6$ and its charge kinetic shows little variation after long continuous cycling. The present study signifies the successful application of nanosized mixed metal oxides as supercapacitor electrode.

Keywords: Calcium-based mixed metal oxides; Pseudocapacitance; Electrochemistry; Impedance; Supercapacitor.

1. Introduction

The development of high energy density supercapacitor is one of the critical requirements for high energy demanding devices such as electric vehicle. The most direct way of energy density improvement is achieved by maximizing the specific capacitance of a supercapacitor electrode. In this context, metal oxides with excellent pseudocapacitance could significantly improve the energy density. Hydrated ruthenium oxide is a remarkable metal oxide with very high specific capacitance of 1585 F g^{-1} [1]. However, the toxicity and high cost dampened the commercial application of the material. Research studies have been going on to find a cheap yet environmental friendly material to replace hydrated ruthenium oxide as supercapacitor electrode. Non-noble metal oxides such as, cobalt oxide, manganese oxide and copper oxide had been reported as the promising materials for supercapacitor electrode [2-8]. Apart from pure metal oxides, mixed metal oxides were reported to be the good supercapacitor electrode [9-11].

To the best of our knowledge, the application of calcium-based mixed metal oxides as supercapacitor electrode has not been reported. Our previous work reported the synthesis of calcium-metal oxides as heat and corrosion resistant pigments [12, 13]. The current work is motivated by the presence of transition metals (Co, Mn and Cu) in our samples, which possess various oxidation states that contribute to pseudocapacitance.

2. Experimental procedures

2.1. Samples preparation and characterization

The nanosized mixed metals oxide $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 materials have been prepared by solid-state calcination and co-precipitation routes. Detailed preparation procedure had been reported in our previously published paper [12, 13]. Phase compositions of the mixed metal oxides were obtained from the data of the X-ray diffractograms (XRD) using X-ray diffraction analysis (Bruker/D8). Cu $K\alpha$ radiation target of wavelength 0.154 nm was employed in the 2θ range

from 10° to 80° at room temperature. The sample morphology was studied by a scanning electron microscope (SEM, JEOL/JSM-T 330A) with an acceleration voltage of 30 kV.

2.2. Electrode preparation and electrochemical testing

The electrode for electrochemical characterization were made by mix up the active material (80 wt.%) with carbon black (15 wt.) and polyvinylidene fluoride (5 wt.%). The mixture was stirred overnight, brush coated on nickel foam (Goodfellow) and dried at 60 °C for 30 min. After drying, the electrode was uni-axially pressed (5 tons) and a microbalance was used to determine the weight of the active material. The active material covered 1 cm² of the nickel foam surface with the loading mass varied from 4 mg to 8 mg. The electrochemical measurements were conducted with a 3-electrode configuration system: working electrode (sample), reference electrode (Ag/AgCl (3 M KCl)) and counter electrode (Pt wire). The data were collected using an electrochemical workstation (Autolab/PGSTAT M101) equipped with frequency response analyzer. Cyclic voltammetry tests were carried out in the potential range between 0 to 0.5 V vs. Ag/AgCl with scan rates ranged from 5 mV s⁻¹ to 100 mV s⁻¹. Charge-discharge galvanostatic tests were conducted at different current densities (0.25 - 1 A g⁻¹). Impedance measurements were collected in the frequency range from 50 kHz to 0.01 Hz, at open circuit potential (OCP) with a.c. amplitude of 10 mV. All electrochemical measurements were carried out in 5 M KOH solution as the electrolyte. All the reported specific capacitance values were normalized against the weight of the active material.

3. Results and discussion

3.1. Phase identification and morphology

Figure 1 shows the X-ray diffraction (XRD) patterns of the Ca₃Co₂O₆, CaMnO₃ and Ca₂CuO₃ samples. It reveals the formation of perovskite structures for all three samples. All main XRD peaks are assigned to the calcium copper oxide (Ca₂CuO₃) phase (JCPDS Card # 84-1970), tricalcium dicobalt oxide phase (Ca₃Co₂O₆, JCPDS Card # 89-0630) and calcium manganese oxide (CaMnO₃) phase (JCPDS Card # 50-1746), respectively. The left insets represent the SEM images of the corresponding mixed metals oxides. The Ca₃Co₂O₆ precipitated in the form of deformed polyhedron

crystals. The size of the crystals ranged from nanometer (~ 50 nm) to micrometer (~ 1 μm). The SEM image of CaMnO_3 shows porous spherical-like particles which were aggregated of small particles and each particle was in the nano size. The SEM image of Ca_2CuO_3 reveals the formation of compact coalescence platelet structures. The width of these platelets was in the range of about 20 nm.

3.2. Cyclic voltammetry

Figure 2a shows the representative CV curves for $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 electrodes at 25 mV s^{-1} , in 5 M KOH electrolyte. It can be clearly seen that all mixed metal oxides exhibit pseudocapacitance behavior by having redox peaks within the potential window of 0 to 0.5 V. $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 electrodes show the oxidation and reduction peaks at 0.32/0.22 V, 0.31/0.1420 V and 0.34/0.21 V, respectively. Since calcium is the alkaline earth metal which does not have multiple valency state, the redox reactions for the mixed metal oxides could be attributed to the transition metals (Co, Mn and Cu) that possess multiple valency states and their redox peak potential are very close to the previously reported values [4, 6, 14]. The specific capacitance values were calculated from the CV curve by integrating the area under the curve and their variations as a function of scan rate are presented in Figure 2b. All mixed metal oxides demonstrate similar specific capacitance trend where the values are decreasing with increasing scan rate. This could be associated with the diffusion rate of electrolyte ions. The highest specific capacitance value is attained on $\text{Ca}_3\text{Co}_2\text{O}_6$ (563 F g^{-1}), as compared to those obtained on CaMnO_3 (384 F g^{-1}) and Ca_2CuO_3 (275 F g^{-1}) electrodes at 5 mV s^{-1} . This could be associated to the high capacitance behavior of cobalt oxides material [3, 15]. The relationship of redox current density and scan rate are summarized in Figure 2c and 2d. A linear relation between current and square root of scan rate could be observed for anodic and cathodic peaks of the mixed metal oxides, indicating the diffusion-controlled redox reaction. Similar observation has been obtained for other reported metal oxides [4, 11]. CV test has been conducted on nickel foam to investigate the contribution of nickel foam towards specific capacitance. CV curve of nickel foam is presented in Figure 2a and it only shows low value of specific capacitance (2.1 F g^{-1} at 25 mV s^{-1}). It is consistent with the literature to highlight the negligible capacitive contribution from the nickel foam [16].

3.3. Galvanostatic charge-discharge

Figure 3a shows the representative galvanostatic charge-discharge curves for mixed metal oxides at 0.25 A g^{-1} . The nonlinearity in all discharge curves suggests the pseudocapacitance behavior of these materials resulting from the redox reactions, as suggested from CV results. All discharge curves show insignificant iR drop, suggesting suitability of mixed metal oxides as supercapacitor electrode. The specific capacitance values were obtained from the discharge curve and they were calculated as 314, 227 and 144 F g^{-1} at 0.25 A g^{-1} for $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 electrodes, respectively. Similar as CV observation, the highest specific capacitance is attained on $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode, possibly due to the high theoretical specific capacitance of cobalt oxide [15] and the polyhedral crystals structure as shown in the SEM image. Furthermore, the incorporation of calcium into the $\text{Ca}_3\text{Co}_2\text{O}_6$ framework enhances the specific capacitance as compared to that obtained from other reported cobalt oxides [2, 17].

3.4. Electrochemical impedance spectroscopy

The charge kinetics of mixed metal oxides were further evaluated by electrochemical impedance spectroscopy (EIS) and they are presented as *Nyquist* plots in Figure 3b. In *Nyquist* plots, near 90° vertical line at low frequency region can be observed for all mixed metal oxides, indicating the good capacitive behavior of the materials. Figure 3b inset (top) shows the equivalent circuit fitting for all mixed metal oxides and the parameters are tabulated in Table 1. Out of three mixed metal oxides, $\text{Ca}_3\text{Co}_2\text{O}_6$ shows lowest bulk solution resistance (R_s) as well as charge transfer resistance (R_{ct}), probably due to the polyhedron crystal. The electrochemical active surface area (S_E) was calculated as reported elsewhere [2]. The calculated values of S_E were computed to be 997.9, 341.9 and $216.1 \text{ m}^2 \text{ g}^{-1}$ for $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 , respectively. These are in good agreement with the specific capacitance values, where $\text{Ca}_3\text{Co}_2\text{O}_6$ shows the highest electrochemical active surface area which provide the highest specific capacitance value among other investigated mixed metal oxides. All electrochemical analyses demonstrate that $\text{Ca}_3\text{Co}_2\text{O}_6$ is the most suitable mixed metal oxide for supercapacitor application, and thus further investigation is carried out on this material.

Figures 3c and 3d show the capacitance real (C') and imaginary (C'') parts for $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of frequency, respectively. Potential is applied to investigate its charge kinetics at different potential condition. It can be clearly seen that the C' reaches optimum at 0.25 V as potential beyond 0.25 V is producing similar C' value at low frequency. The C'' relationship with frequency in Figure 3d is used to calculate the relaxation time constant ($\tau = 1/f_0$) where f_0 is the corresponding frequency for maximum peak. τ is defined as the minimum time required to discharge all of the energy from the sample with an efficiency greater than 50%. τ is found to be increased with increasing of applied potential (1.22, 2.29, 3.13 and 3.13 s at 0.1, 0.15, 0.25 and 0.3 V, respectively) and reaches its maximum at 0.25 V. Though τ is higher at higher applied potential, the τ is still maintained at a reasonable value at 0.25 V, as compared to other reported τ for metal oxide such as $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ (1.98 s) [18].

3.5. Electrochemical stability

Cycling stability is a crucial element for long term application of supercapacitor. Figure 4a shows the capacitance retention (left y axis) and Coulumbic efficiency (right y axis) of $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode for 700 continuous cycling at 1 A g^{-1} . It can be noticed that $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode shows high capacitance retention of 96% and high Coulumbic efficiency of 83% after 700 continuous cycling. Such high capacitance retention suggests that the $\text{Ca}_3\text{Co}_2\text{O}_6$ is a good electrode material for long term supercapacitor application. This is much higher than that reported for for Co_3O_4 thin film which shows only 66% after 500 cycles [2] and Co_3O_4 crater-like microspheres which shows only about 74% after 500 cycles [16]. Figure 4b shows the *Nyquist* plots for $\text{Ca}_3\text{Co}_2\text{O}_6$ before and after 700 continuous cycling. Insignificant change is observed, indicating high stability of the $\text{Ca}_3\text{Co}_2\text{O}_6$.

4. Conclusions

Mixed metals oxides of $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 show high specific capacitance of 563, 384 and 275 F g^{-1} at scan rate of 5 mV s^{-1} , respectively. The incorporation of calcium in the metal oxide structure enhances the charge storage ability whilst maintaining the low resistivity and high electrochemical active area. Calcium based cobalt oxide ($\text{Ca}_3\text{Co}_2\text{O}_6$) exhibits the best performance and further confirmed to have good charge kinetics under different applied potential and superior cycling stability.

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Graphical Abstract:

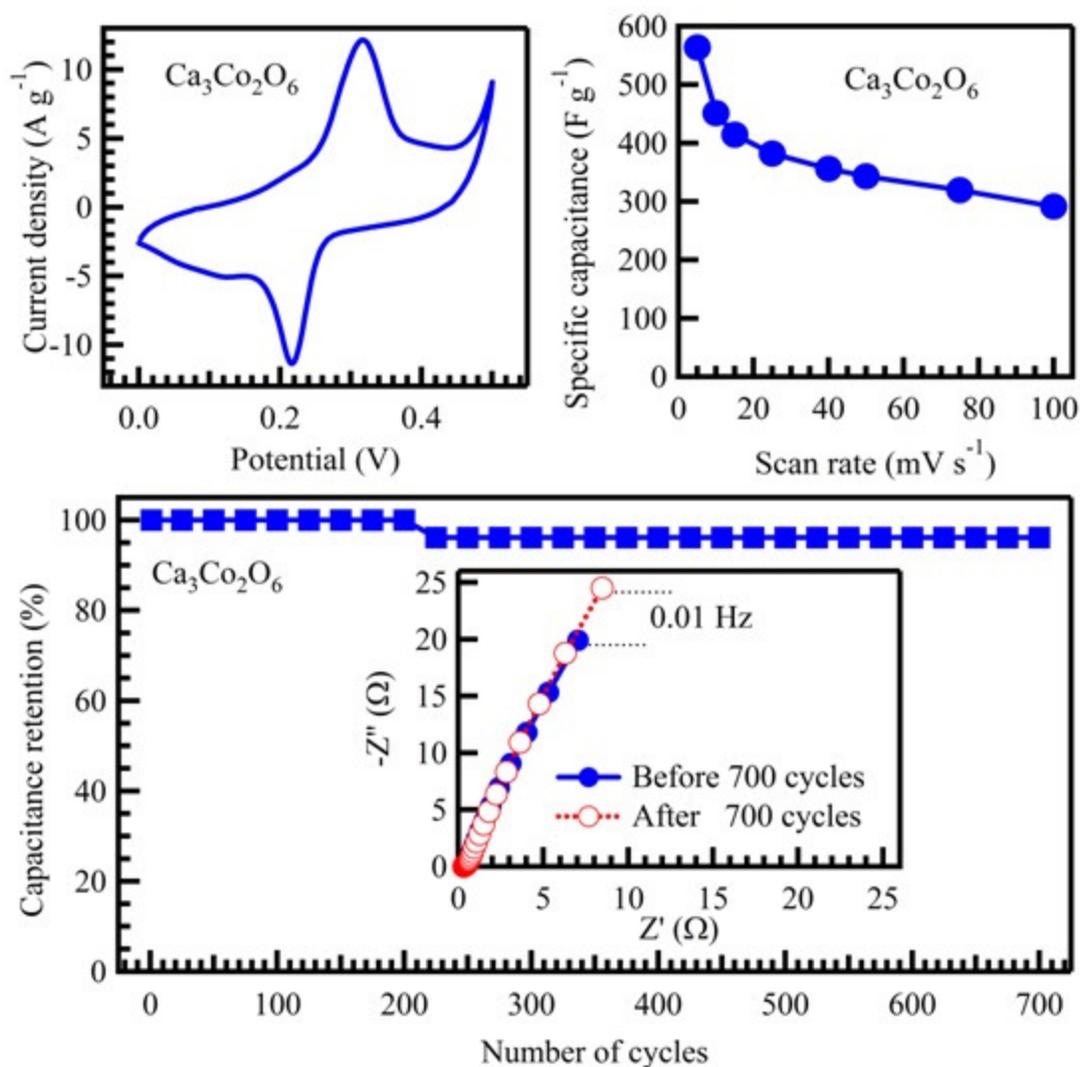


Figure 1. XRD patterns of $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 . Insets show the SEM images for the corresponding samples.

Figure 2. (a) Cyclic voltammetry curves at 25 mV s^{-1} , (b) specific capacitance as a function of scan rate; (c) anodic and (d) cathodic peaks current as a function of square root of scan rate for the $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 electrodes.

Figure 3. (a) Galvanostatic charge-discharge curves at 0.25 A g^{-1} and (b) *Nyquist* plots for $\text{Ca}_3\text{Co}_2\text{O}_6$, CaMnO_3 and Ca_2CuO_3 electrodes (insets are the magnified view of *Nyquist* plots at high frequency region and the equivalent circuit); (c) real and (d) imaginary parts of the capacitance as a function of the frequency at different applied voltages for $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode.

Figure 4. (a) Cycling stability (left vs. bottom) and Coulombic efficiency (right vs. bottom); (b) *Nyquist* plots before and after 700 complete charge-discharge continuous tests (inset is the magnified view at high-frequency region of *Nyquist* plots) for $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode.

Table 1. Fiting parameters of the complex impedance experimental data.

	<i>R_s</i> (Ω)	<i>R_{ct}</i> (Ω)	<i>C</i> (<i>mF</i>)	<i>CPE</i> (<i>mF</i>)	<i>W</i> (Ω)	<i>S_E</i> ($m^2 g^{-1}$)
Ca ₃ Co ₂ O ₆	0.293	0.117	47.33	531.57	0.579	997.9
CaMnO ₃	0.326	0.233	3.50	370.10	0.478	341.9
Ca ₂ CuO ₃	0.423	0.552	1.59	305.47	0.097	216.1

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List of Figures:

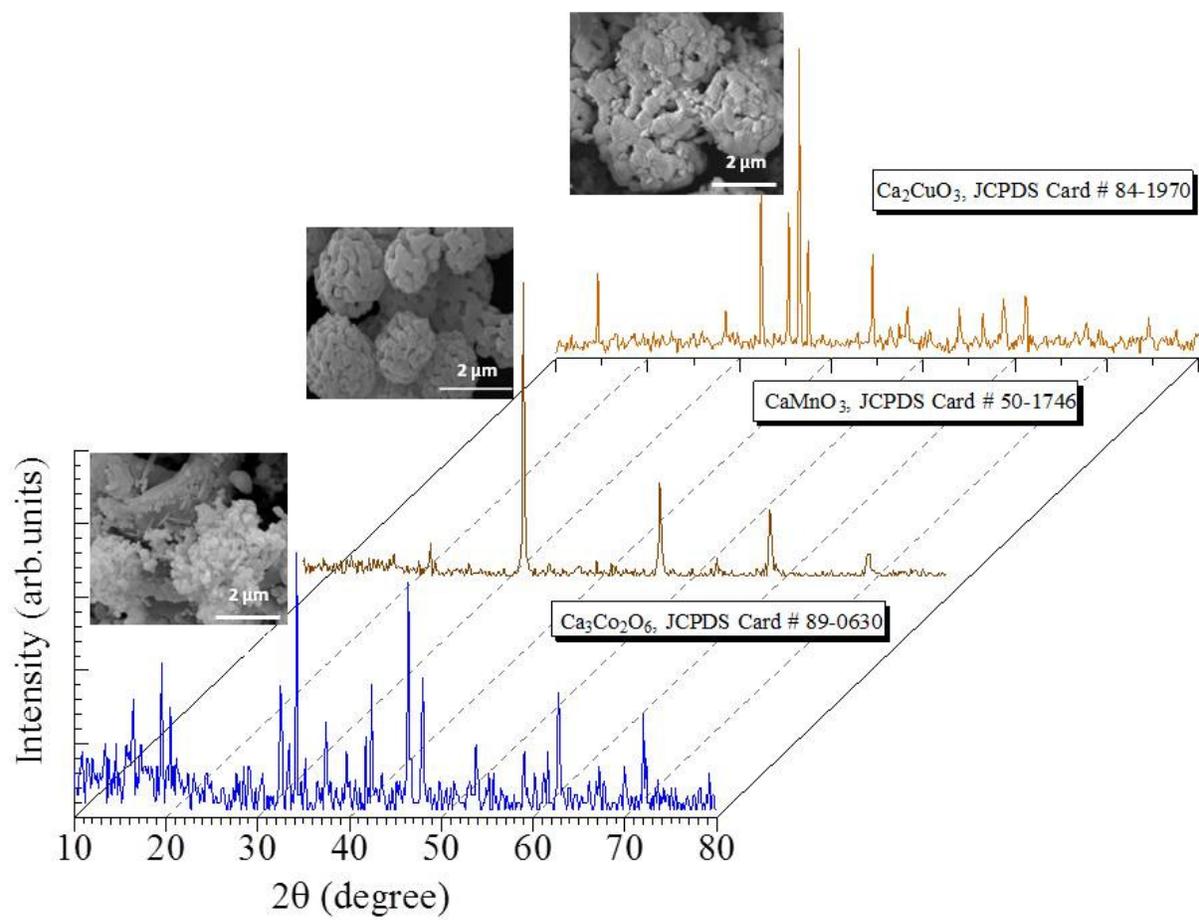


Figure 1

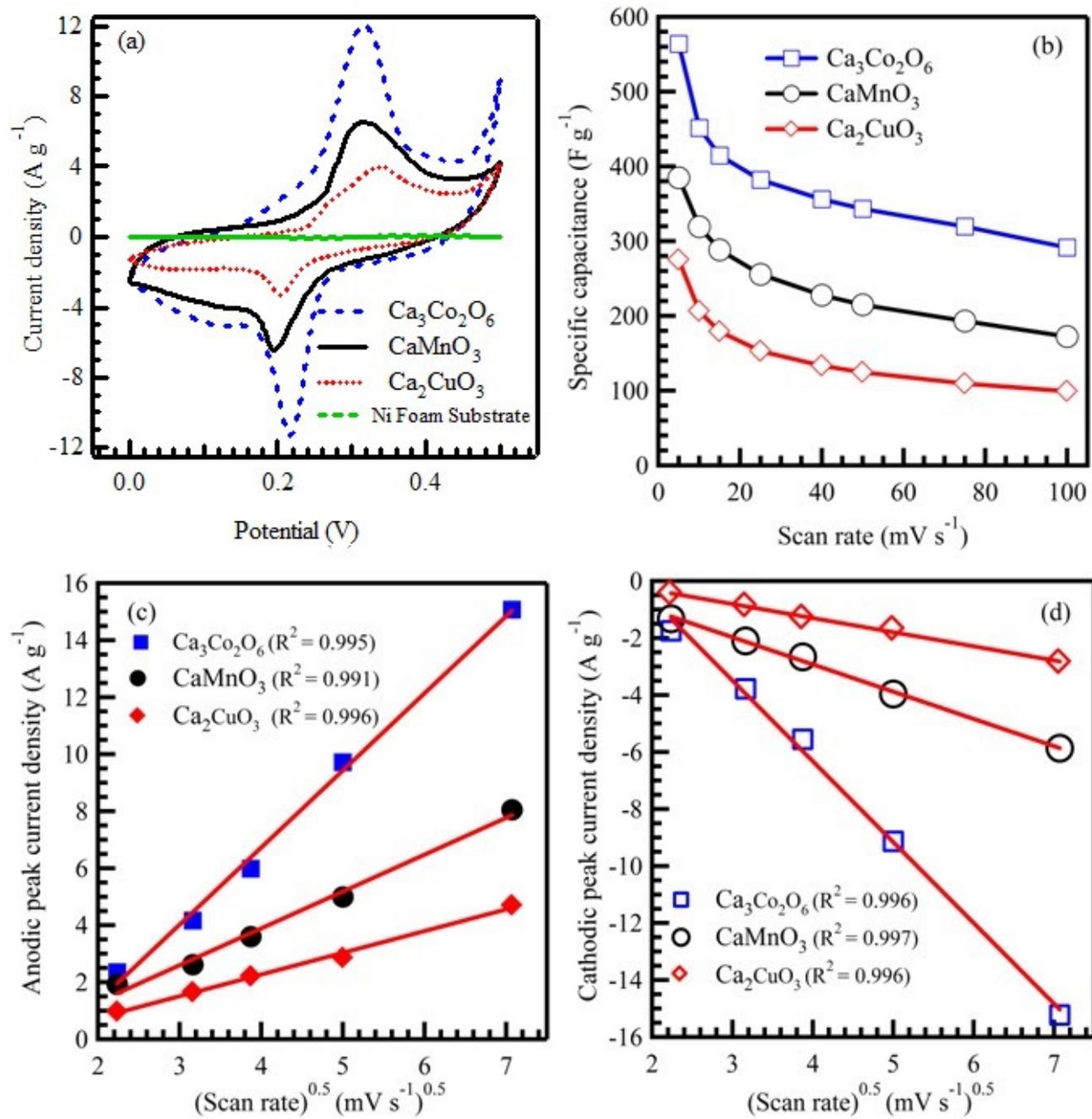


Figure 2

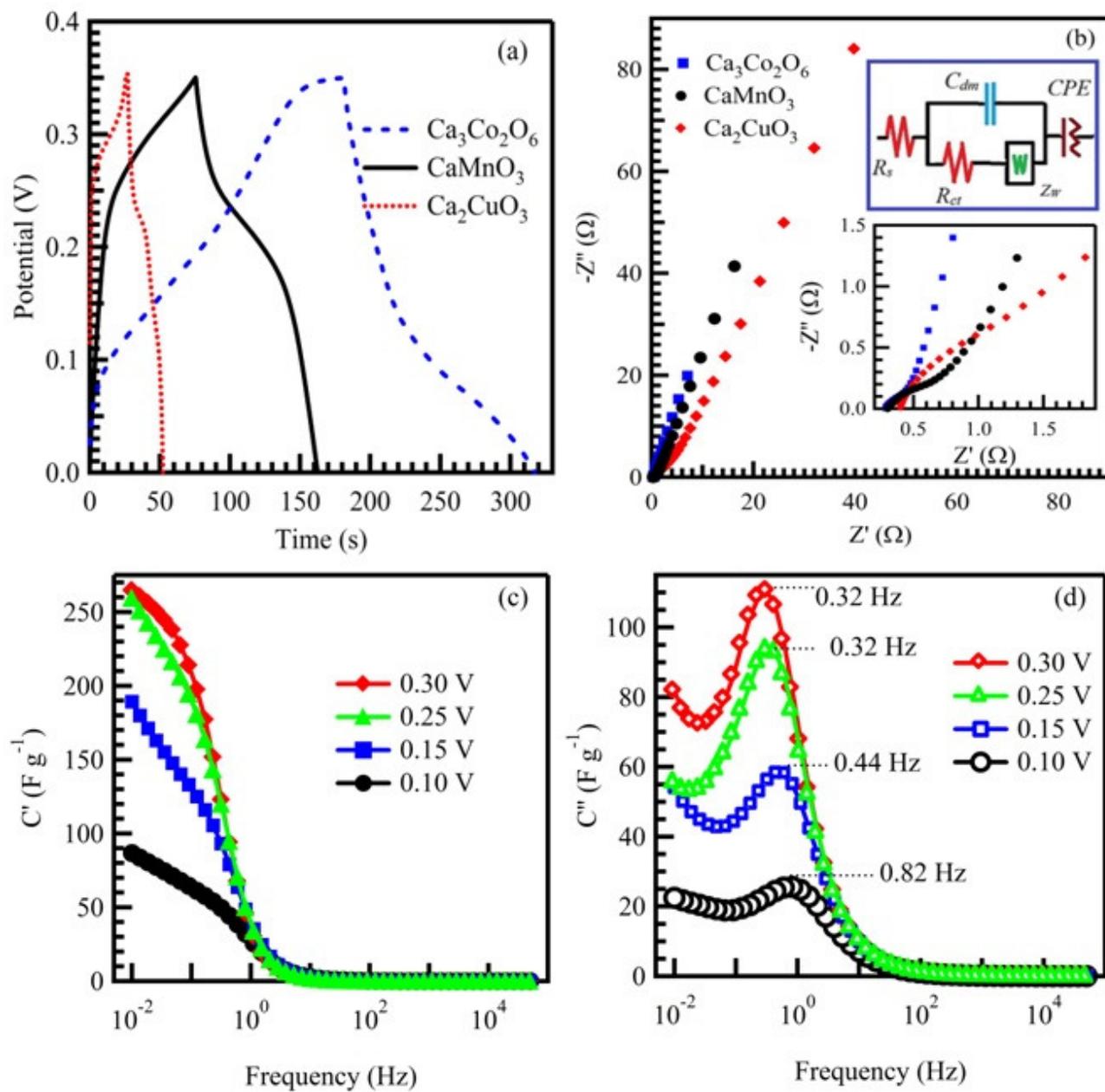


Figure 3

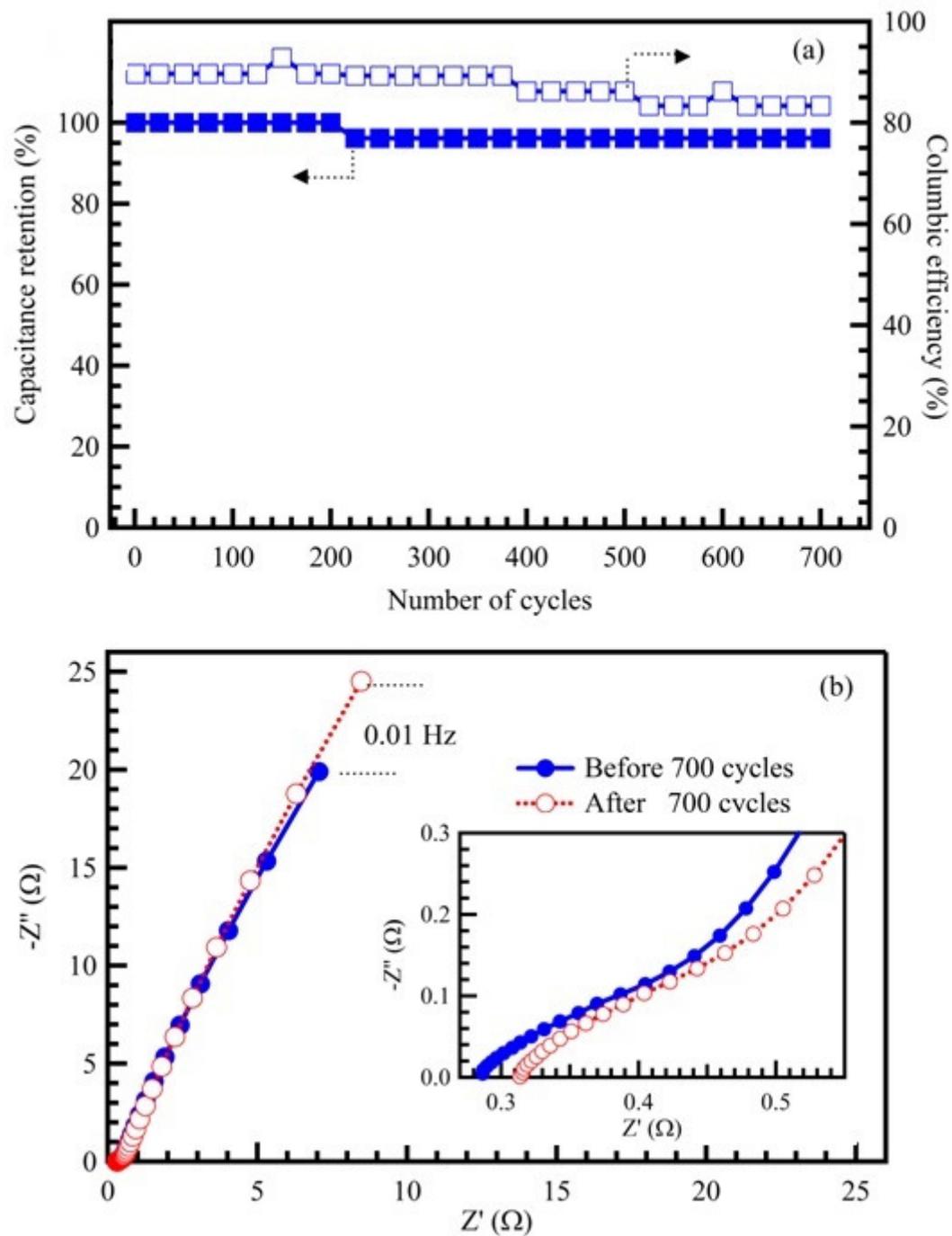


Figure 4

References

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