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CV ANALYSIS OF MANGANESE DOPED COBALT OXIDE THIN FILM ELECTRODES FOR SUPERCAPACITOR APPLICATION

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ABSTRACT

Manganese doped Cobalt oxide thin films were deposited on steel substrate by sol-gel spin coat method and investigated the impact of doping on electrochemical behaviour. Cyclic Voltammetry technique was used for the electrochemical characterizations of supercapacitor cells fabricated using the Mn doped Co_3O_4 thin films as their electrodes. The characterization of the doped electrodes showed a notable effect of the Mn concentration on electrochemical properties and consistently found that with increase in Mn concentration performance of supercapacitor goes on improved, accordingly 1%Mn doped electrode exhibited higher specific capacitance 675F/g at 10mV/s scan rate and good cyclic stability compared to other electrodes with different doping concentrations.

KEYWORDS

Doping, Cyclic Voltammetry, Scan rate, Stability and Supercapacitor.

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INTRODUCTION

The Electrochemical supercapacitors (ESs) are ideal for energy storage that undergoes frequent charge and discharge cycles at high current and short duration. These are considered important energy efficiency devices for rapid energy storage and delivery. Among the advantages of ESs are high power density, environmentally friendly, long cycle life, high efficiency, wide range of operating temperatures, environmental friendliness and safety. ESs also serves as a bridging function for the power/energy gap of traditional dielectric capacitors. These characteristics have made ESs very competitive for applications in electric hybrid vehicles, digital communication devices such as mobile phones, digital cameras, electrical tools, pulse laser technique, uninterruptible power supplies and storage of the energy generated by solar cells[1-3].

Co_3O_4 thin film and series of Mn incorporated Co_3O_4 thin films deposited by sol-gel spin coat method and investigated the influence of doping concentrations of Mn in Cobalt such as 0.001% to 1% on electrochemical properties. The deposited samples were denoted by different codes such as, S1, S2, S3, S4, S5, S6, S7 and S8throughout the paper. Where S1=0%Mn, S2=0.001%Mn, S3=0.005%Mn, S4=0.01%Mn, S5=0.05%Mn, S6=0.1%Mn, S7=0.5%Mn and S8=1%Mn doping in cobalt. There are many electrochemical techniques for the characterization of supercapacitor exist, in the present work, cyclic voltammetry (CV) is used for the characterization of thin film electrodes. The capacitive behaviour of Co_3O_4 and Mn doped Co_3O_4 electrodes have been studied.

Cyclic Voltammetry Analysis

Voltammetry is basically referred to as technique with the common characteristics that the potential of the working electrode is controlled and the resulting current flow is measured. The cyclic voltammogram gives us information on the possible redox reactions of the system, including the Faradaic insertion and extraction reaction, electrode processes, the determination of thermodynamics and kinetics of electron transfer at the electrode/electrolyte interface. The technique involves sweeping the electrode potential between two predetermined values at a known sweep rate[4]. In the present study, several sweep rates in the range from 10 to 100 mV/s were used to study scan rate effect on performance of electrodes and scan rate of 500mV/s was used to test the stability of electrodes.

EFFECT OF SCAN RATE

The cyclic voltammetry study is carried out with Co_3O_4 thin film electrode and Mn doped Co_3O_4 thin film electrode as working electrodes, platinum wire as counter electrode and SCE as a reference electrode in 0.1M KOH electrolyte. Figure No.1 shows the CV curves of Co_3O_4 (S1) electrode and Mn doped Co_3O_4 (S2 to S8) electrodes. Scan rate is varied from 10 to 100mV/s such as 10mV/s, 20mV/s, 40mV/s, 60mV/s, 80mV/s and 100mV/s in the potential window ranging from -1.3V to 0.65V.

From the figures, it is verified that potential window as well as current associated with the CV curve increases with increase in scan rate. Which indicates that voltammetric current is directly proportional to the scan rates of CV and this is an good indication of supercapacitive behaviour[5-7].

From the CV curves, it is observed that the reduction and oxidation peaks are visible. This indicates that the electrochemical capacitance of the electrodes mainly results from pseudo capacitance. It is also observed that in comparison with doped films, Co_3O_4 film showed small current and small potential window. In contrast, doped films have high potential window, large current and good reversible redox activity. The calculated values of specific capacitance (SC) with respect to Mn doping concentrations for different scan rates 10mV to 100 mV/s are plotted in the Figure No.2. All the electrodes exhibited a common trend of decreasing specific capacitance values against an increasing scan rate. It is well known that for very low scan rates, the specific capacitance values are higher because the ions have a much longer time to penetrate and reside in the electrode pores and form electric double layers, which are needed to generate higher capacitance.

As evidenced from Figure No.2, for lower Mn concentrations (electrodes S2 to S6) there is no much change in the values of SC with variable scan rates. It may be due to the fact that at lower content of Mn incorporation, Co species sustain the redox transition. The charge and mass transfer resistance do not decrease (IR drop) suddenly. At higher content of Mn incorporation (electrodes S7 and S8), SC value increase rapidly. Because at higher %Mn incorporation the charge and mass transfer resistance of Mn/Co species decrease. We can also observe as the Mn doping concentration increases specific capacitance increases from 492 to 675F/g at 10mV/s scan rate, 451 to 620F/gat 20mV/s, 371 to 524F/g at 40mV/s, 327 to 465F/g at 60mV/s, 287 to 424F/g at 80mV/s, and 265 to 383F/g at 100mV/s.

This is due to increase in Mn ion concentration which increases the electrical conductivity of the films. Here electrode S8 showed better SC for all scan rates as compared to others.

Electrode S8 showed large area under curve and high value of current as evidenced from CV leading to maximum value of SC, it may be due to capacitive favorable phase of Mn: CO_3O_4 formed at that incorporation leading to optimal Mn incorporation and formation of good porous nature of the sample as reported in our earlier research article[8]. The interconnected crystallites of both Co_3O_4 and MnO_2 may create many micro pores, which help in electrolyte transport and provide large surface area for charge transport reaction for easy ionic intercalation between species leading to the increase in SC value of S8.

Stability Study

Retaining of specific capacitance for long cycles at higher scan rate operation condition is essential for practical applicability of a supercapacitor. Figure No.3 shows CV plots of S1, S3, S6 and S8 electrodes in 0.1 M KOH at higher scan rate 500mV/sec for 1st and 1000th cycles.

Figure No.4 shows the overall stability result, which indicates that S8 electrode behaves reversibly as an excellent supercapacitor material for a large number of potential cycles. The Co_3O_4 revealed the cyclic stability up to 66% over 1000 cycles. It indicates that the material behaves reversibly as a good capacitor material for a large number of potential cycles. Wang et al have reported the value of cyclic stability for Co_3O_4 nanowires up to 90% over 500 potential cycles[9].

After Mn incorporation stability of the electrodes were improved. Compared to other electrodes, electrode S8 (1% Mn) exhibited good stability of nearly 80%. As evidenced from Figure No.3 (d), there are no major changes between CV’s and the total area/charges enclosed by both curves are probably similar to each other illustrating the stable nature of electrode in the energy storage application. The specific capacitance values are decreased by a comparably small amount with number of cycles may be due to the loss of active material caused by the dissolution or detachment, during the early charging and discharging cycles in the electrolyte.

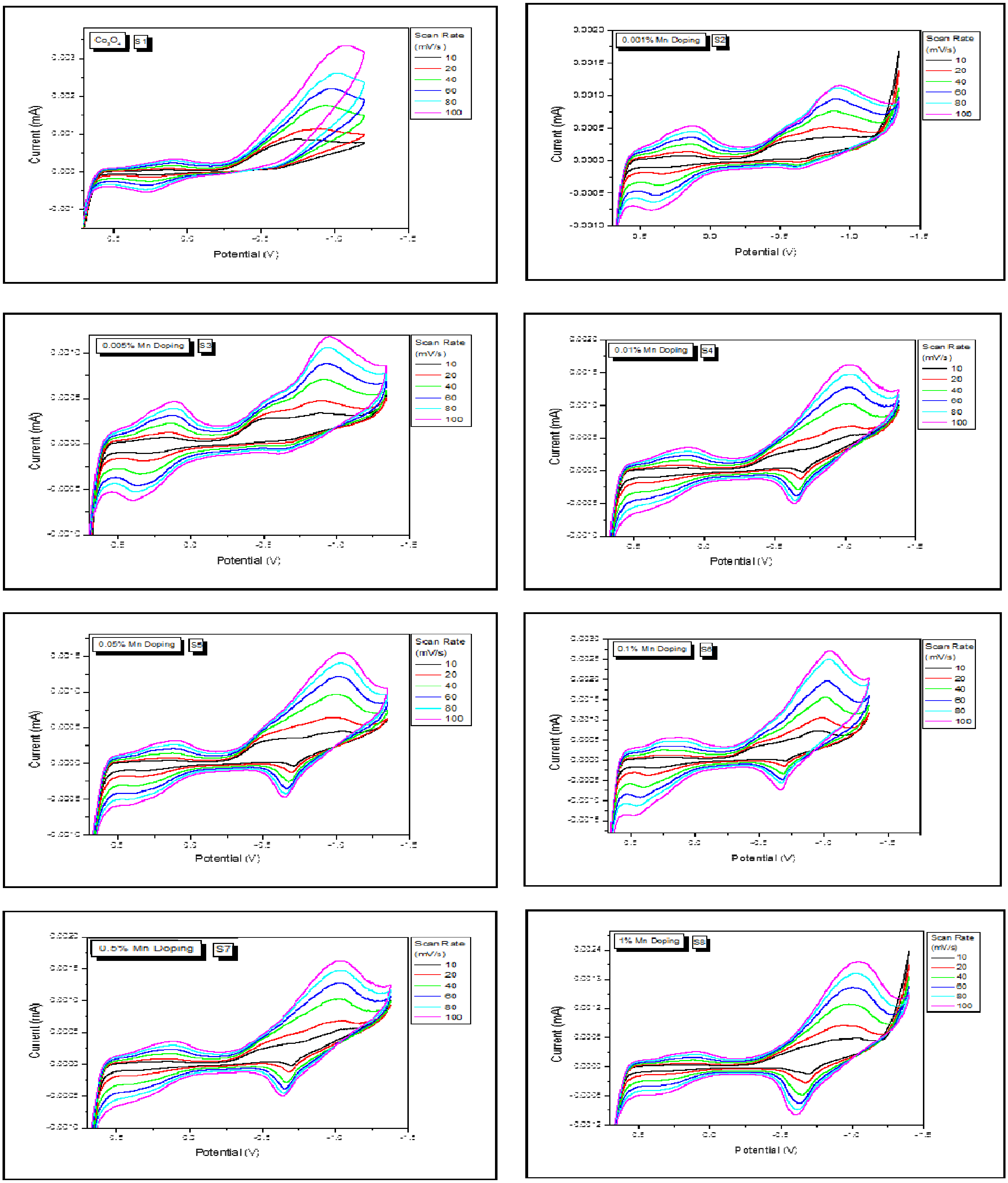

Figure No.1: Cyclic voltammograms of thin film electrodes from S1 to S8

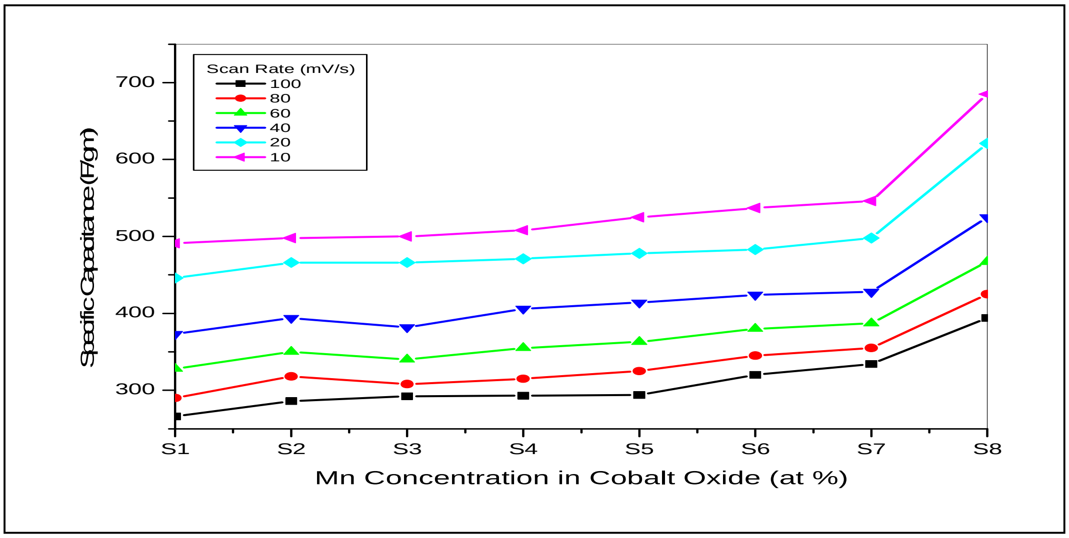

Figure No.2: Graph of Specific capacitance with Mn concentration at different scan rates

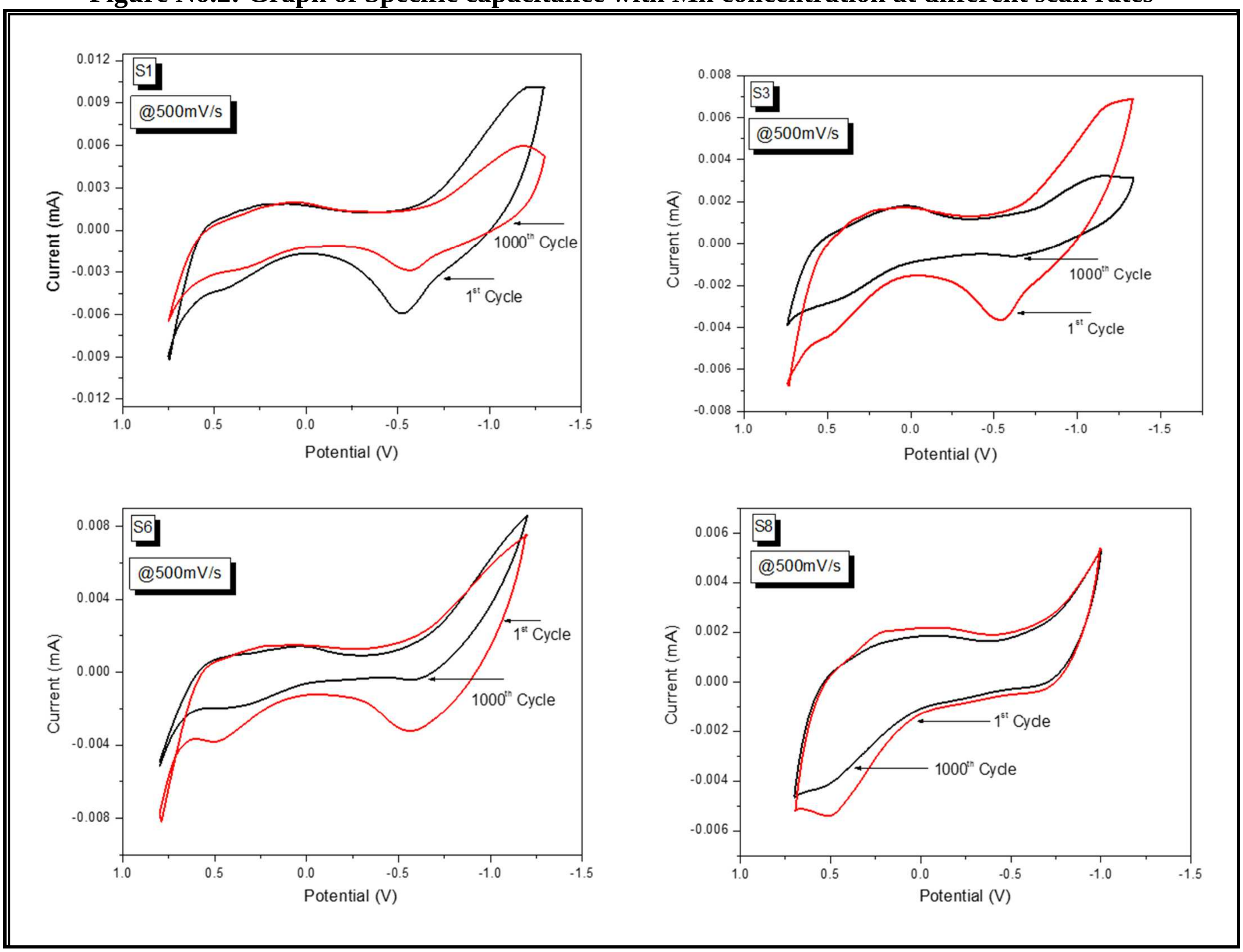

Figure No.3: CV curves of S1, S3, S6 and S8 electrodes for 1st and 1000th cycle at 500mV/s scan rate

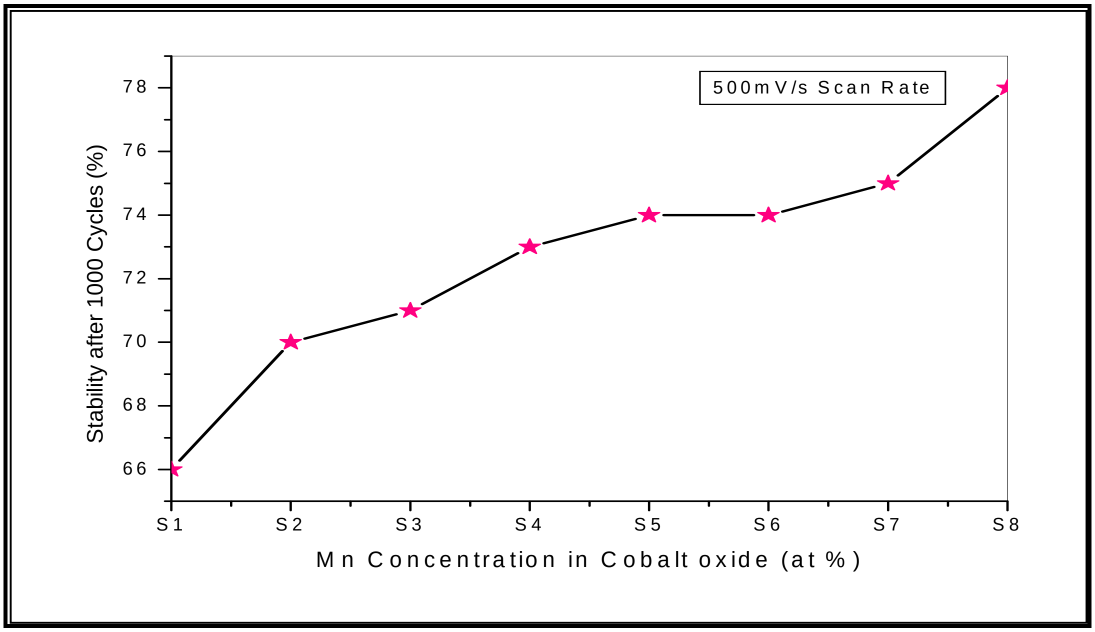

Figure No.4: Cyclic stability of all electrodes for 1000 cycles at 500mV/s scan rate

CONCLUSION

Characterization by CV methods consistently found that increase in Mn concentration improved the electrochemical properties of the electrodes. The electrode with 1% Mn exhibited better specific capacitance and cyclic stability compared to other doped electrodes. The specific current of the cyclic voltammograms varies linearly with scan rates in the range of 10mV/s to 100mV/s, demonstrating a high power characteristic for all the electrodes. The specific capacitance obtained for S8 electrode is 675 F/g at 10 mV/s scan rate still retaining a considerable specific capacitance of 383F/g at high scan rate of 100mV/s. It showed a high cyclic stability of about 80% over 1000 cycles. In comparison with pure Co_3O_4electrode, manganese doped oxide material showed better supercapacitive performance, among which electrode S8 can be considered as a promising candidate for superacpacitor materials.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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