MnO/Mn_2O_3 Aerogels as Effective Materials for Supercapacitor Applications

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1. Experimental

1.1 Materials

All the chemicals required for the experiment such as manganese nitrate ($Mn(NO_3)_2.4H_2O$, 99%), sodium borohydride ($NaBH_4$, 99%), sodium sulfate (Na_2SO_4, 99%), and potassium hydroxide (KOH, 99%) were purchased from Sigma Aldrich. Battery cathode grade Nickel foam with 1000 mm length, 300 mm width and 1.6 mm thickness, were purchased from Sigma Aldrich. Acetone and ethanol were purchased from Alfa Aesar. The nitrogen gas cylinder was purchased from a local dealer (South Korea). All sol-gel and electrochemistry experiments were performed with deionized water, and the temperature was maintained at 25 °C unless otherwise specified.

1.2 Preparation of Mn_{AGL} and Mn_{AGL}@200, Mn_{AGL}@400 and Mn_{AGL}@550

The procedure to prepare the transition metal AGLs(manganese) was adopted from an earlier synthesis procedure [1]. In a typical synthesis, $Mn(NO_3)_2.4H_2O$ was completely dissolved in a mixture of 25 ml ETOH + 75 ml deionized (DI) water (total volume: 100 ml). Nitrogen gas was bubbled through the cobalt salt solution for 25 min. Subsequently, a 100 ml of 0.5 M $NaBH_4$ ethanolic solution was prepared by sonicating the $NaBH_4$ in ethanol and placing it in a standard flask. The $NaBH_4$ solution was then slowly added dropwise to the manganese salt solution. Unlike the case with noble metal hydro and alcogels, the color of the solution changed to black in a few seconds, indicating the formation of the Mn hydrogel. As a result of hydrogen formed from the $NaBH_4$ solution many bubbles floated to the top of the beaker. The whole reaction was then allowed to proceed for another 15 min. Next, the manganese hydrogel which was formed as a precipitate was washed 5-6 times with a solution of DI water and ethanol. The black hydrogel obtained was dispersed in DI water until the precipitate was completely immersed. The manganese hydrogels were freeze-dried for two days. Hence obtained manganese powder was named as Mn_{AGL} and stored in a desiccator for further use. Subsequently, some of the as-formed Mn_{AGL} were annealed in air at 200°, 400° and 550° C at a heating rate of 10 °C/min for 2 h to form annealed manganese AGLs and stored in a desiccator until further use.

1.3 Characterizations

The structural, physical and morphological properties of the as-formed AGLs were analyzed using measurement techniques, such as Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and high-resolution scanning electron microscopy (HR-SEM). All electrochemical studies, including electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) were performed using an Autolab PGSTAT302N (Metrohm, Netherlands). For all the electrochemical measurements, an electrolyte solution of 3M KOH was used. The working electrode used for capacitor studies was aerogel modified Ni foam (size: 1 cm × 1 cm; loading: ~2 mg), whereas the reference electrode was a silver-silver chloride electrode (Ag/AgCl). In a three-electrode arrangement, the Pt foil was used as the counter electrode (BASi, USA). The working electrodes were prepared by mixing the Mn_{AGL} or Mn_{AGL}@200 or Mn_{AGL}@400 or Mn_{AGL}@550 (85%), 10 wt % of carbon black, and 5 wt % of PVDF (poly(vinylidene fluoride)), N-methyl pyrrolidone (NMP) as a mixing solvent to obtain a slurry. The slurry was pressed onto a nickel foam and dried at 60 °C for 24 h in a vacuum oven. The following softwares like OriginPro 2018, X'Pert HighScore Plus(3.0.0) Almelo, The Netherlands and Casa XPS Version 2.3.26PR1.0 were used in the manuscript for the characterization studies.

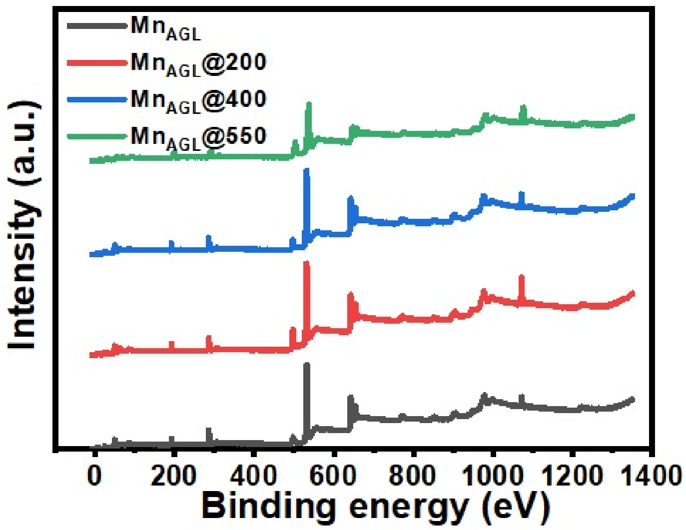

Fig S1. XPS survey of Mn_{AGL}, Mn_{AGL}@200, Mn_{AGL}@400 and Mn_{AGL}@550 aerogel samples.

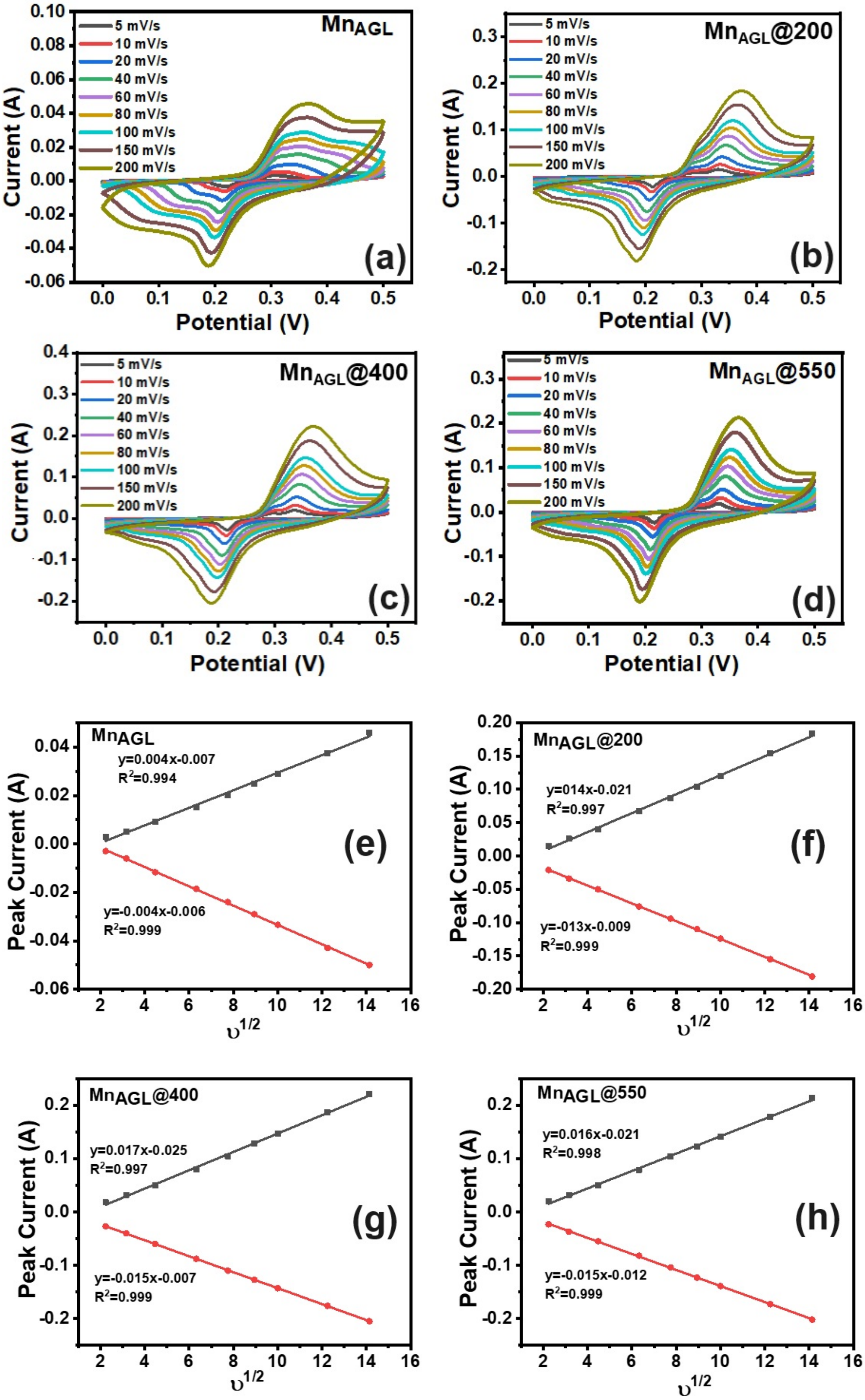
Mn$_{AGL}$
(a)
Mn$_{AGL}$@200
(b)
Mn$_{AGL}$@400
(c)
Mn$_{AGL}$@550
(d)
5 mV/s
10 mV/s
20 mV/s
40 mV/s
60 mV/s
80 mV/s
100 mV/s
150 mV/s
200 mV/s
Current (A)
Potential (V)
Mn$_{AGL}$
y=0.004x-0.007
R^2=0.994
y=-0.004x-0.006
R^2=0.999
(e)
Mn$_{AGL}$@200
y=014x-0.021
R^2=0.997
y=-013x-0.009
R^2=0.999
(f)
Mn$_{AGL}$@400
y=0.017x-0.025
R^2=0.997
y=-0.015x-0.007
R^2=0.999
(g)
Mn$_{AGL}$@550
y=0.016x-0.021
R^2=0.998
y=-0.015x-0.012
R^2=0.999
(h)
Peak Current (A)
$\upsilon^{1/2}$

Fig S2. (a–d) CV's for Mn_{AGL}, Mn_{AGL}@200, Mn_{AGL}@400 and Mn_{AGL}@550 aerogel samples at scan rates from 5-200 mV/s and their corresponding (e–h) square root of scan rate vs. peak current plot.

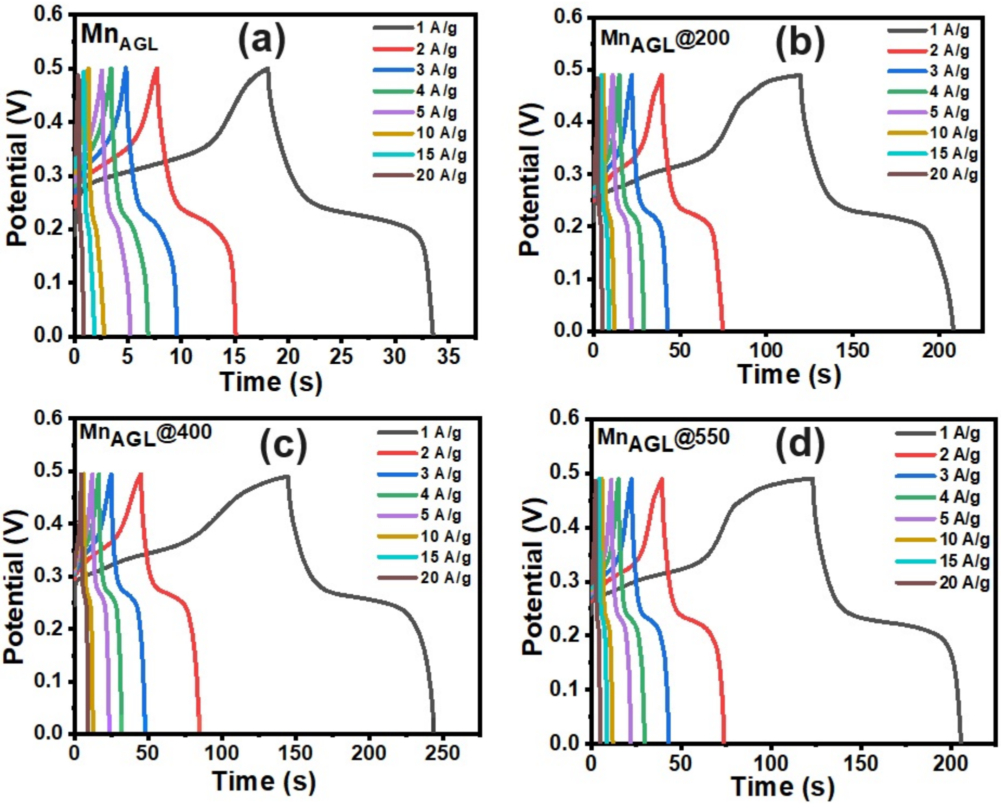

Fig S3. (a–d) GCD graphs for Mn_{AGL}, Mn_{AGL}@200, Mn_{AGL}@400 and Mn_{AGL}@550 aerogel samples at various current densities.

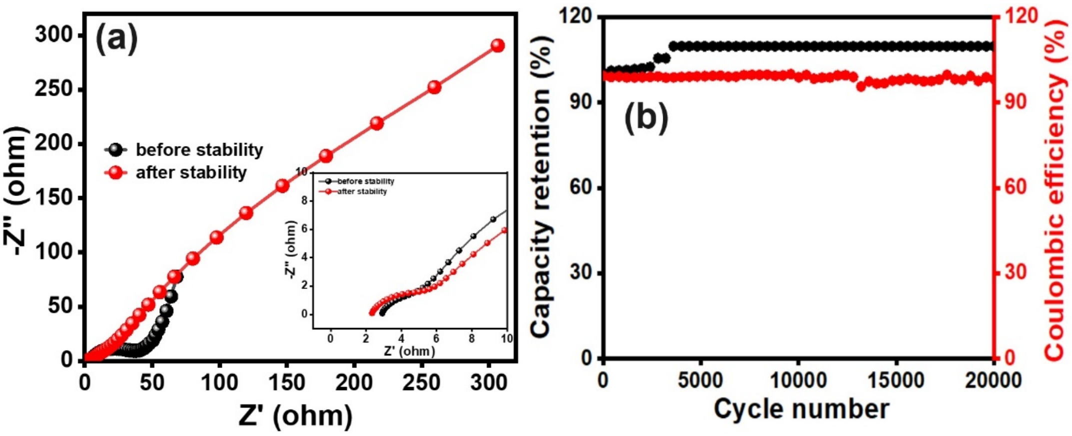

Fig S4. (a) EIS graphs for Mn_{AGL}@400 before and after cycling stability(inset: enlarged view) and (b) Cycling stability indicating capacity retention and Coulombic efficiency for the device using Mn_{AGL}@400//NF aerogel samples and AC//NF electrodes.

References

1. Ramkumar, R.; Rajkumar, C.; Do, H.; Kim, H.; Kim, W.K. A Remarkable Oxygen Vacancy-Rich Rare Earth Aerogel with High Activity towards Electro and Catalytic Reduction of 5-Nitroquinoline. *Journal of Cleaner Production* **2023**, *423*, 138683, doi:10.1016/j.jclepro.2023.138683.