LPM2021 (The 22nd International Symposium on Laser Precision Microfabricaton)

MXene in-plane micro-supercapacitor prepared by laser direct writing

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Wearable Devices

http://www.mumbrella.asia/2013/08/wearable-technology-fad-or-the-future/

Small, Lightweight
Portable, Flexible,
Fashionable

ICT（Information and Communication Technology）

Smart city

http://www.myabcspace.com/wirelesscity/

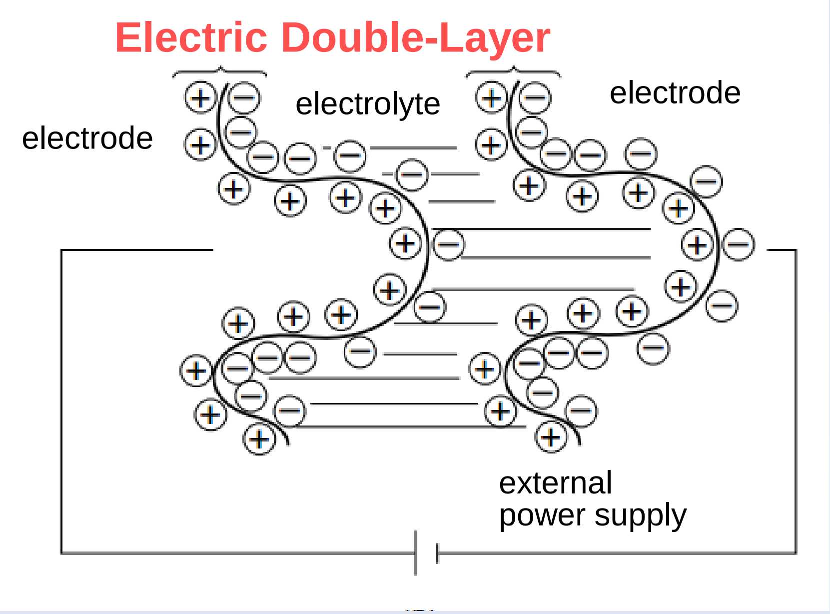
Energy Storage Devices

- Fast chargeability
- Compatibility with wireless charging
- Safety

Various energy storage devices

	Capacitor	Supercapacitor Electric double-layer capacitor (EDLC)	Li ion battery (LIB)
Charge-discharge mechanism	Charge separation	Adsorption-desorption of ions at the electrode interface	Redox reactions of electrode
Charging time	Several seconds	Several-tens seconds	Several hours
Product life	Limitless	Limitless	- 800 times

- Fast chargeability
- Compatibility with wireless charging
- Safety

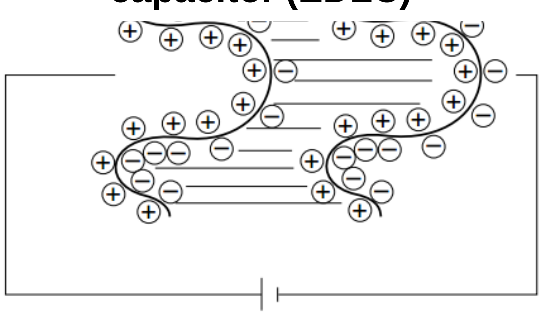


Structure comparison of energy storage devices

In-plane micro-supercapacitor (MSC)

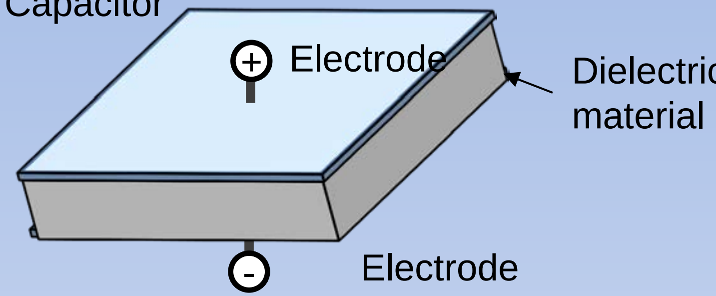
- light weight, thin, flexible
- bending resistance, safety

Electrochemical double layer capacitor (EDLC)

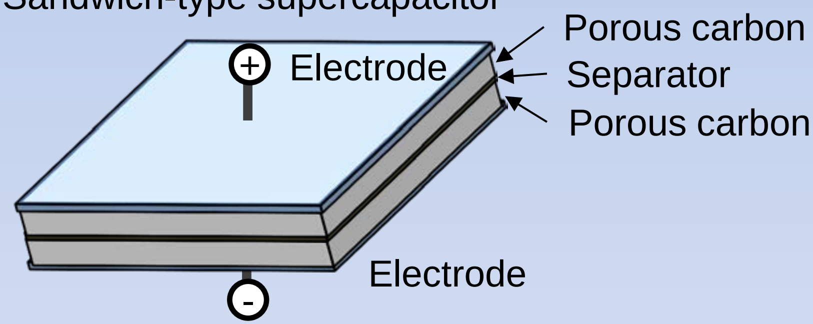


Conventional supercapacitor

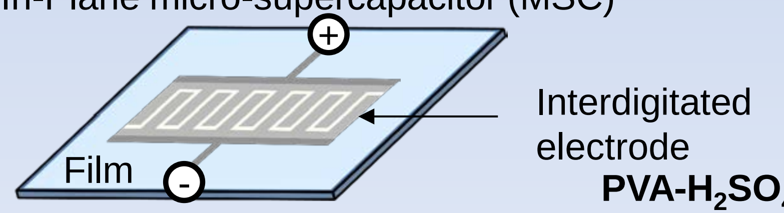
(a) Capacitor



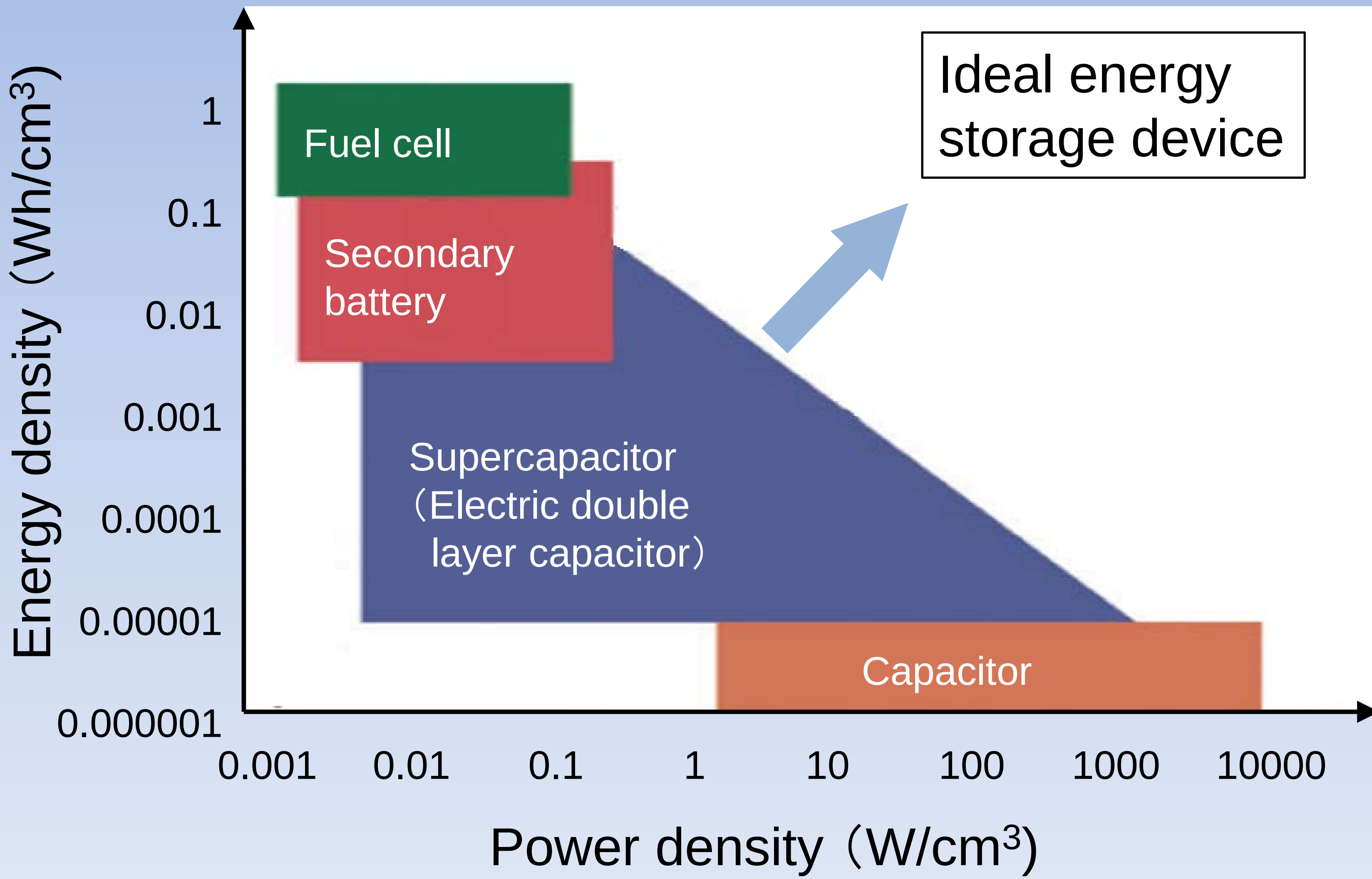
(b) Sandwich-type supercapacitor



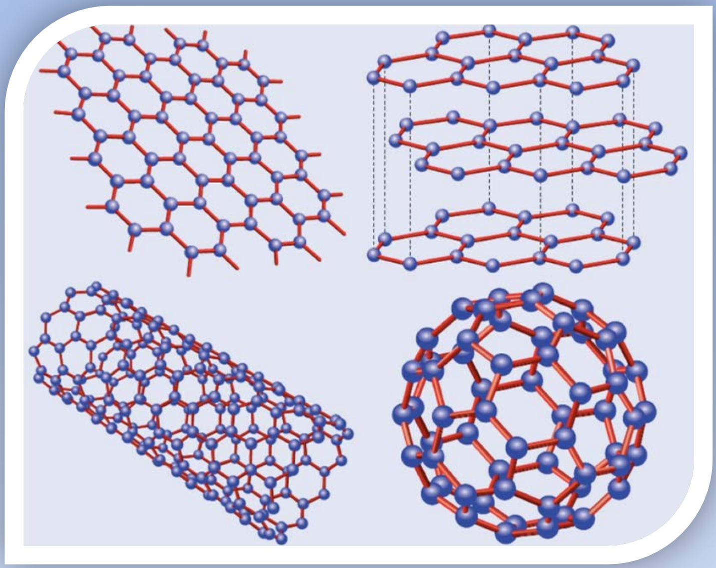
(c) In-Plane micro-supercapacitor (MSC)



Performance comparison of energy storage devices



Materials for MSC



Graphite nanomaterials, graphene, carbon nanotube, etc.

- High specific surface areas
- Electrochemical stability
- High electrical conductivity
- High mechanical tolerance

Good candidates for wearable energy storage device

Further improvements of energy storage device are required in capacitance, energy density, and power density, etc.

New Material for Innovation

New Material for MSC: MXene $Ti_3C_2T_x$

Japan Material Technologies Corporation

Mxene is a new class of two-dimensional materials

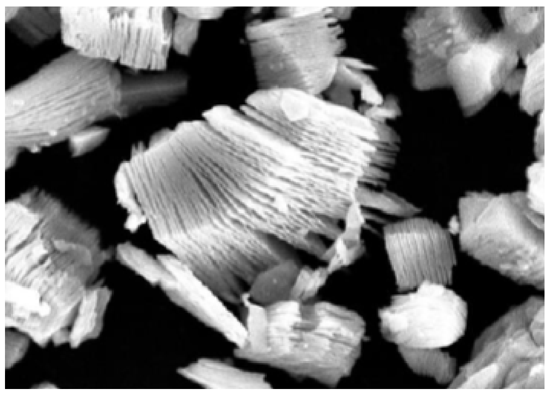
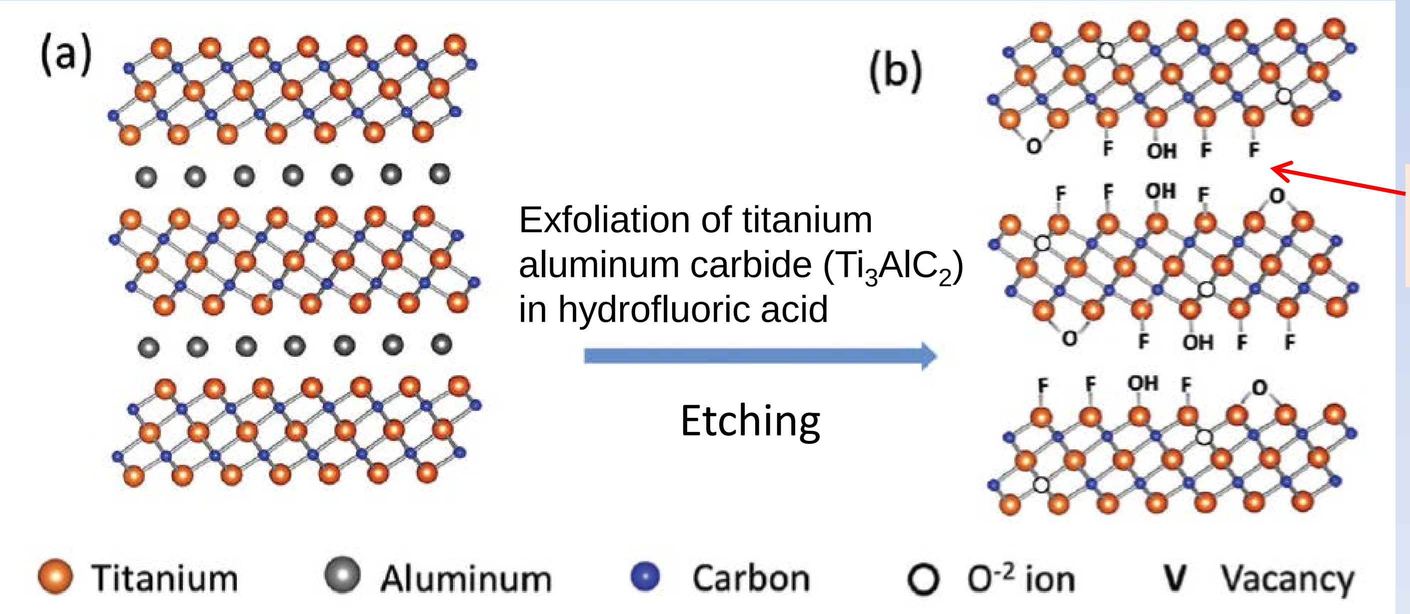


Fig. SEM image of MXene.

MXenes have a general formula $M_{n+1}X_nT_x$, where `M' is a transition metal, X is C and/or N, and Tx represent surface functional groups.

$Ti_3C_2T_x$ T = O, H, F, etc.

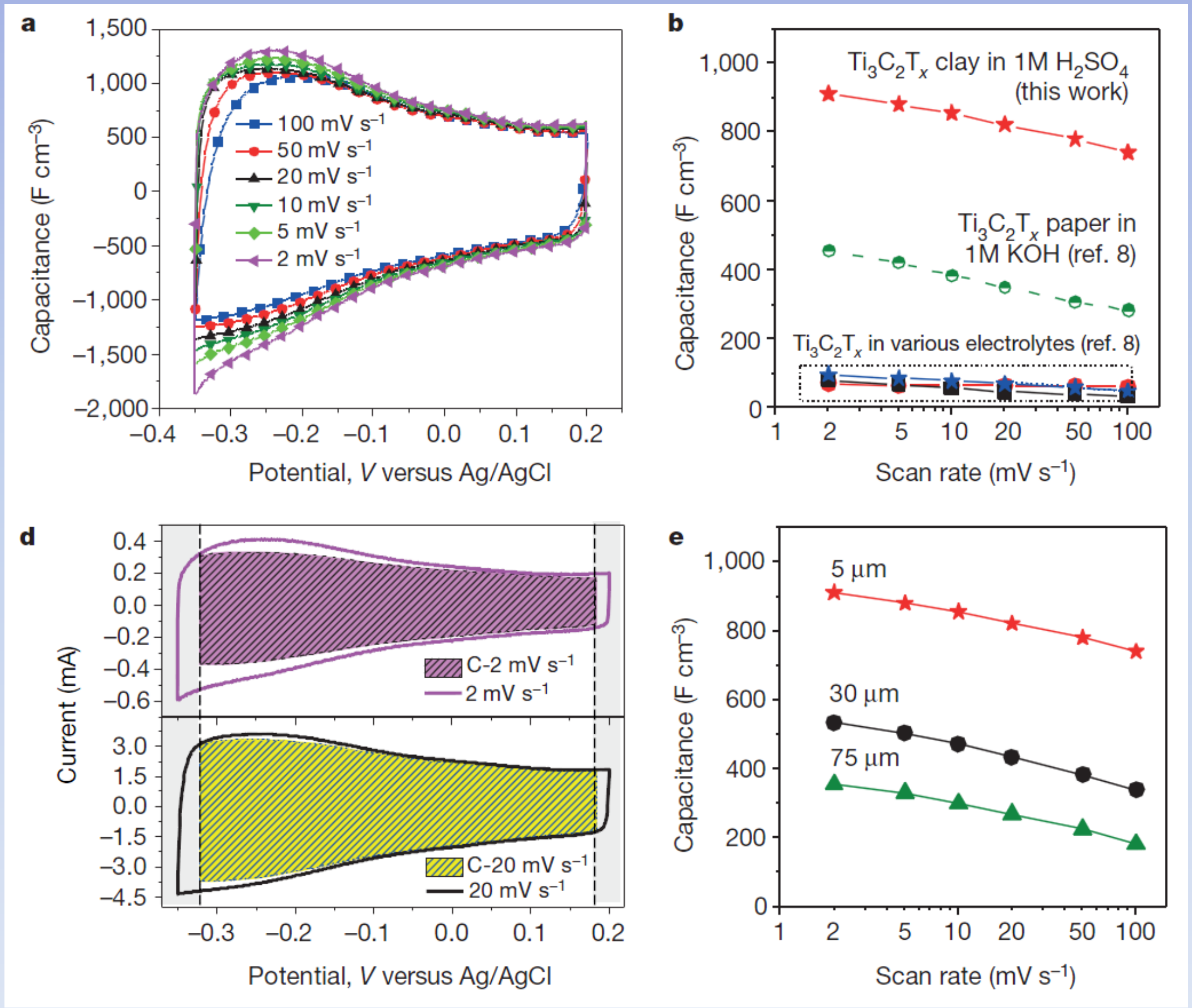
Ref.) M. Naguib et al, *Adv. Mater.*, 2011, **23** , 4248
Tej B. Limbu et al., *J. Mater. Chem. C*, 2020, B, 4722



Hydrophilicity polar groups

MXene supercapacitor in a H_2SO_4 electrolyte solution

Pseudo-capacitive characteristics



Ref.) M. Ghidiuet al., *Nature*, **516,** 7881 (2014)

This work

MXene all-solid in-plane MSC

Preparation of MXene in-plane MSC

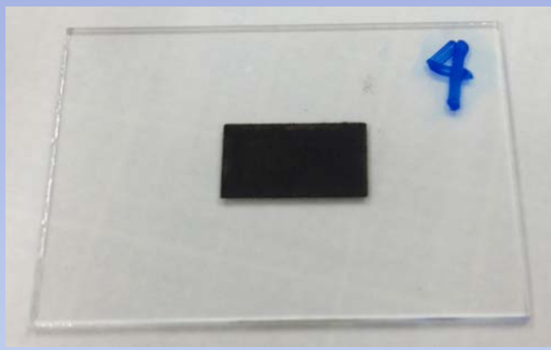
(1) Mixture (1/3 w/w) of Mxene and PA (polyamide) NMP solution (12.8%) was coated on a glass substrate covered by a PI (polyimide) film (50 μm thickness) with a rectangular hole (11.3x6.3 mm).

(2) A MXene/PA (polyamide) composite film was prepared on a glass substrate by peeling off the PI mask film after drying at 110^{o}C.

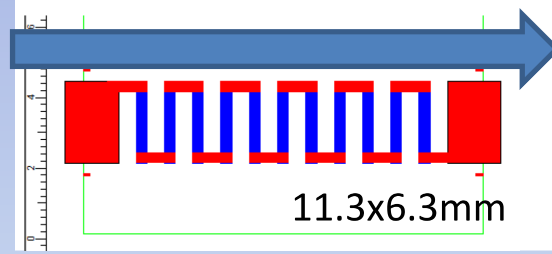
(3) The raster scan of CW 445 nm laser beam on the MXene/PA composite film gave a MXene/laser-induced graphene (LIG) composite film by laser-carbonization of PA binder polymer.

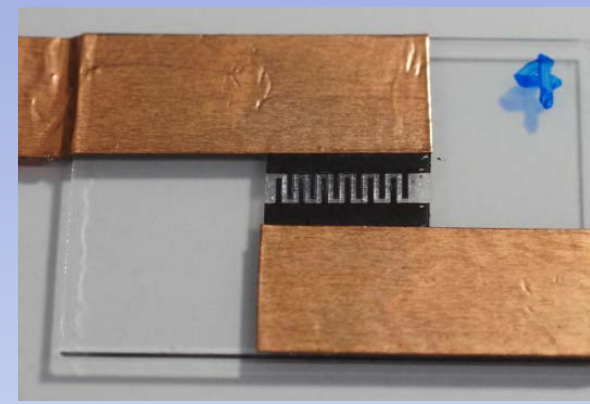
Film	Surface resistivity（Ω/□）
MXene/PA composite film (1/3 w/w) before 445 nm laser annealing	3400
MXene/LIG composite film after 445 nm laser annealing	119

Preparation of MXene in-plane MSC



(4) Laser ablation using a fiber laser (1064 nm) - galvano-scanner system

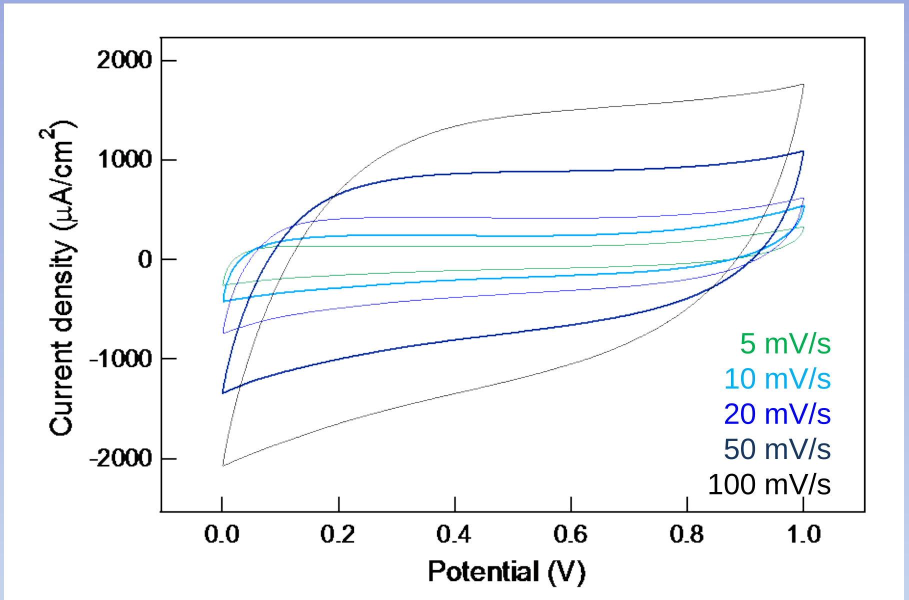




(5) Copper tape electrode terminal were connected to the MXene/PA with a Ag paste and then the connected area was covered by PI tape.

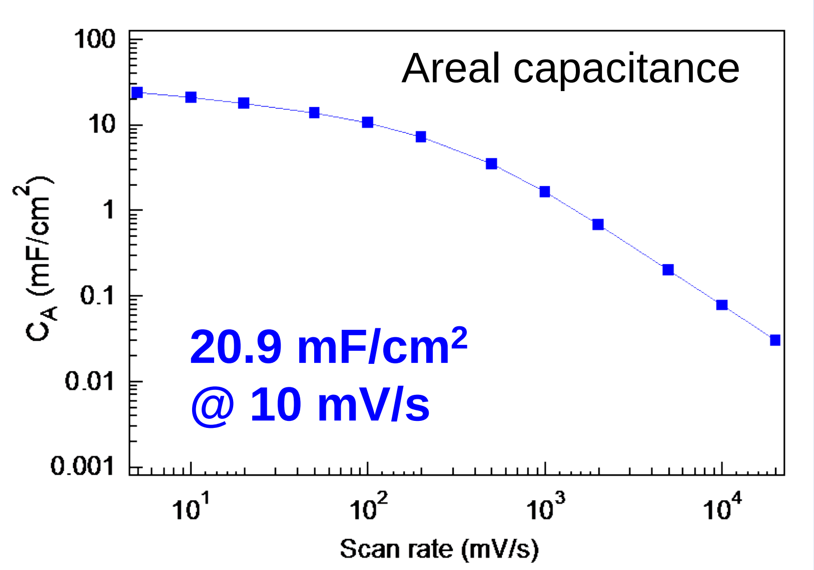
(6) The interdigitated electrode was covered by PVA (polyvinyl alcohol) – H_2SO_4 as a solid electrolyte.

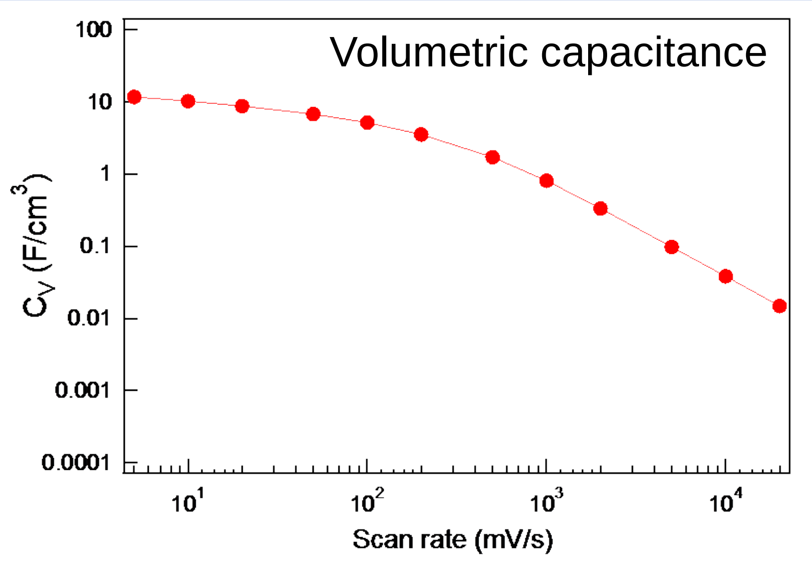
Cyclic voltammograms of MXene/LIG in-plane MSC



- Pseudo-capacitive characteristics of MXene was not clear in the cyclic voltammograms of a MXene/LIG all-solid in-plane MSC.

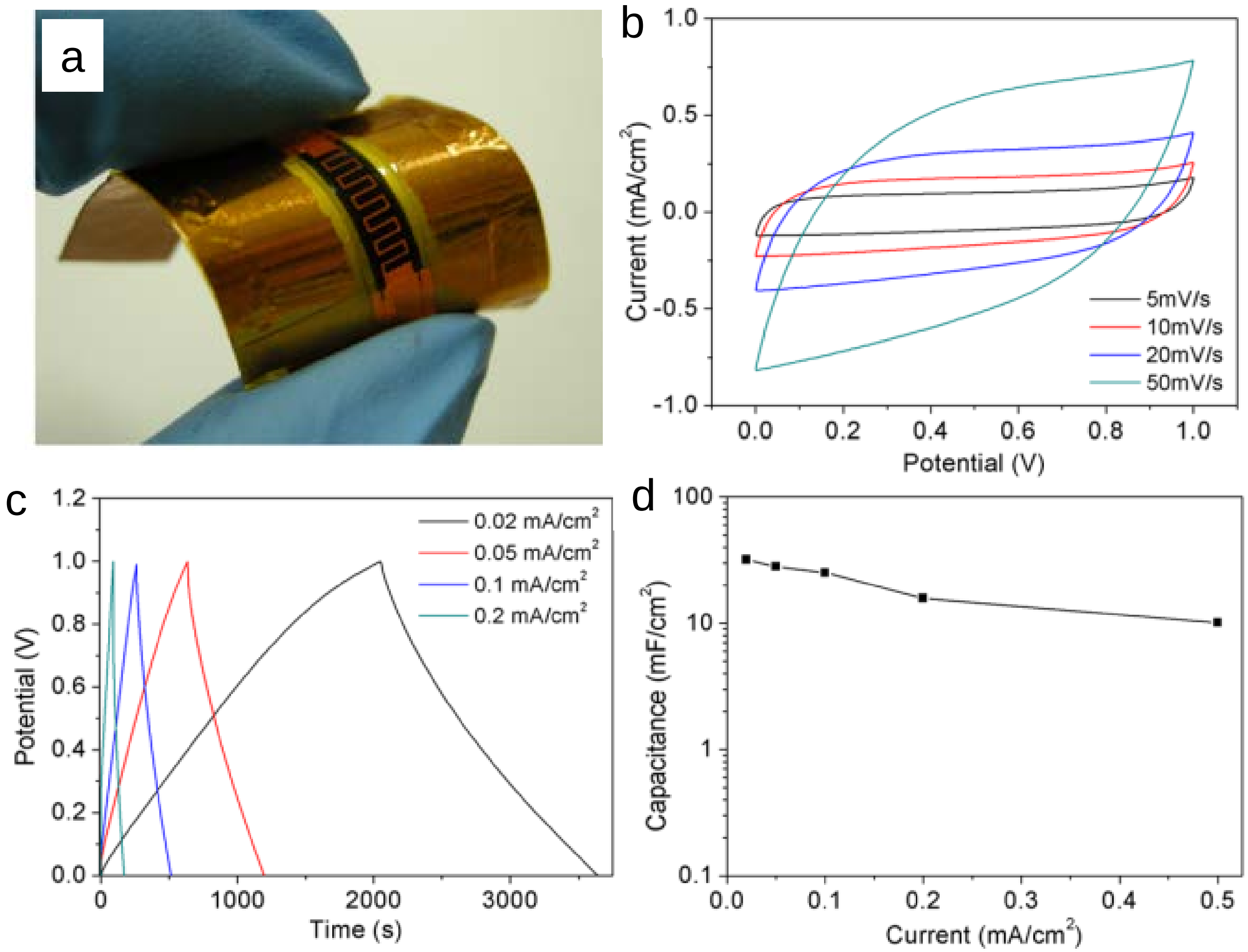
- Laser annealing of PA binder polymer and carbonization caused the change of surface structure of MXene.





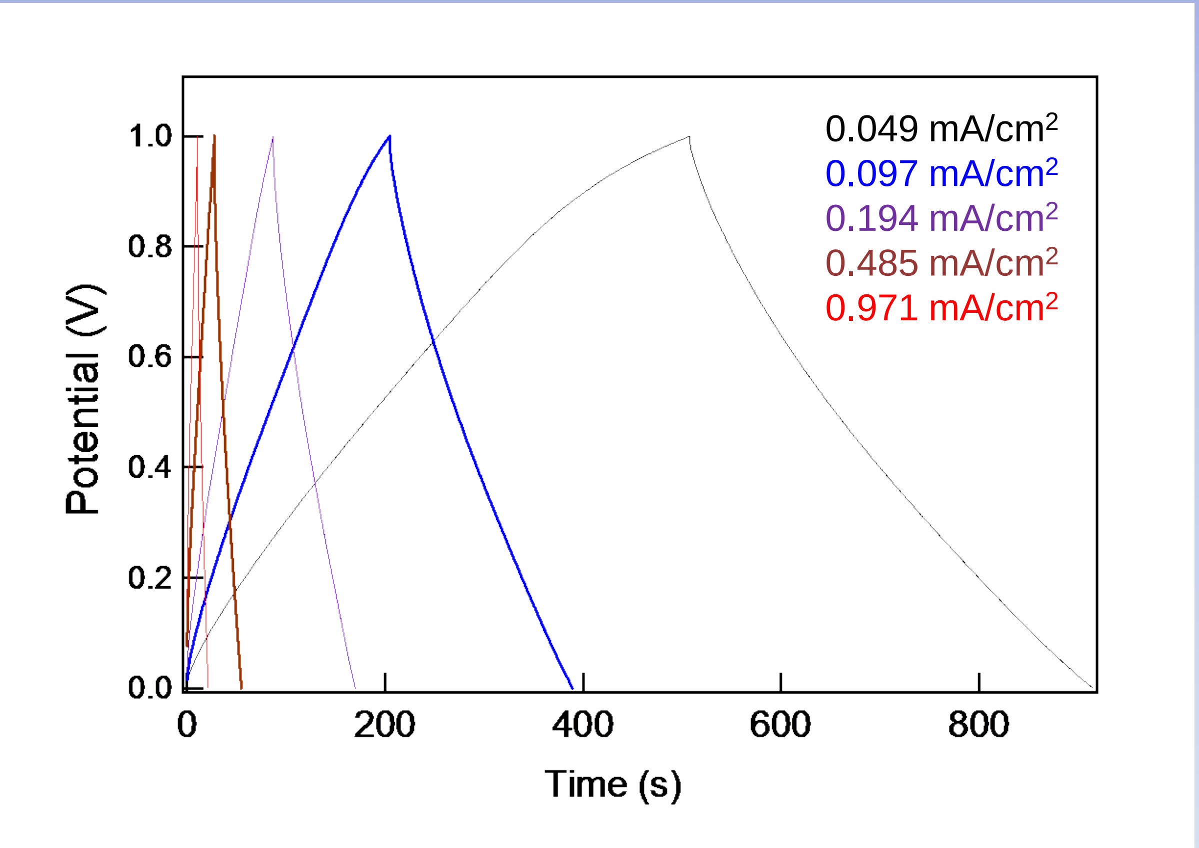
Previous highest laser-induced graphene MSC prepared by laser carbonization of PI film

16.4 mF/cm² @ 10 mV/s

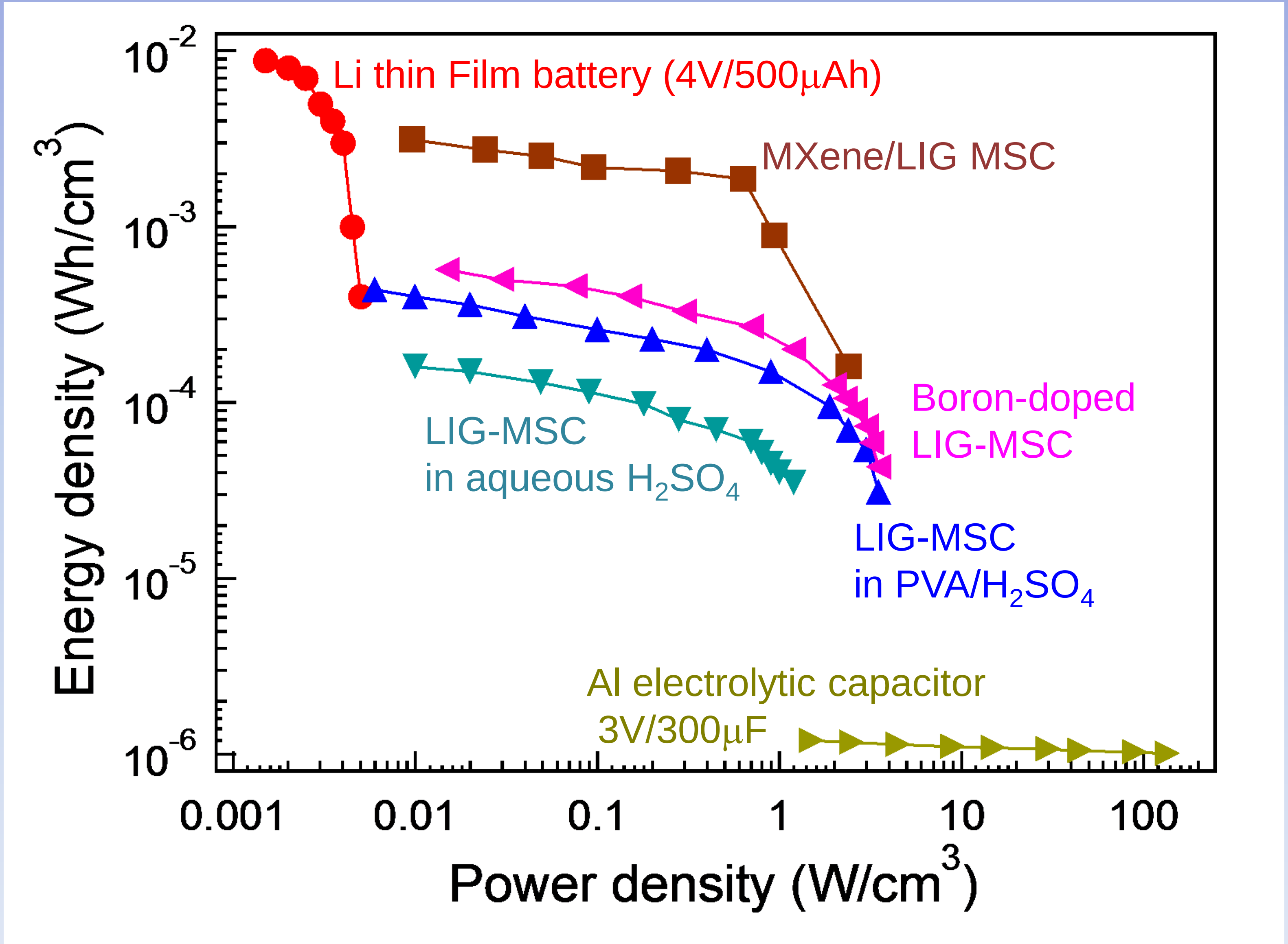


Ref.) J. Cai, C. Lv, A. Watanabe, *Nano Energy*, **30**, 790 (2016).

Galvanostatic charge-discharge (CC) curves of MXene/LIG in-plane MSC

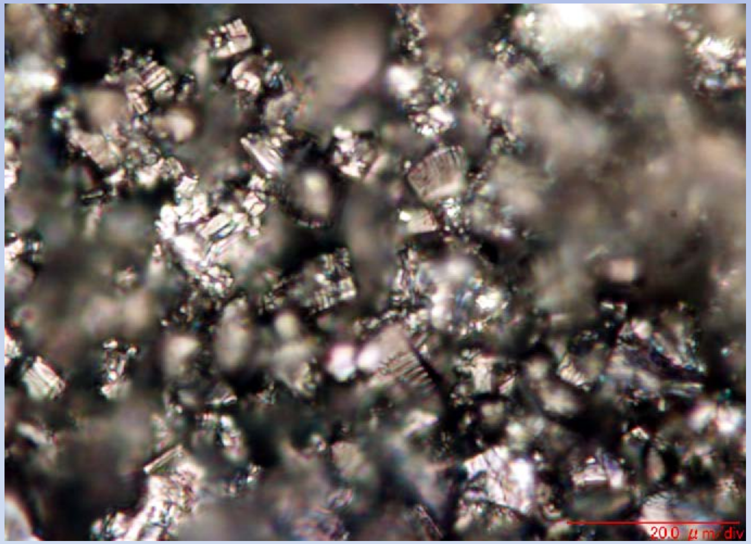


Ragone plots of MXene/LIG in-plane MSC in comparison with other energy storage devices

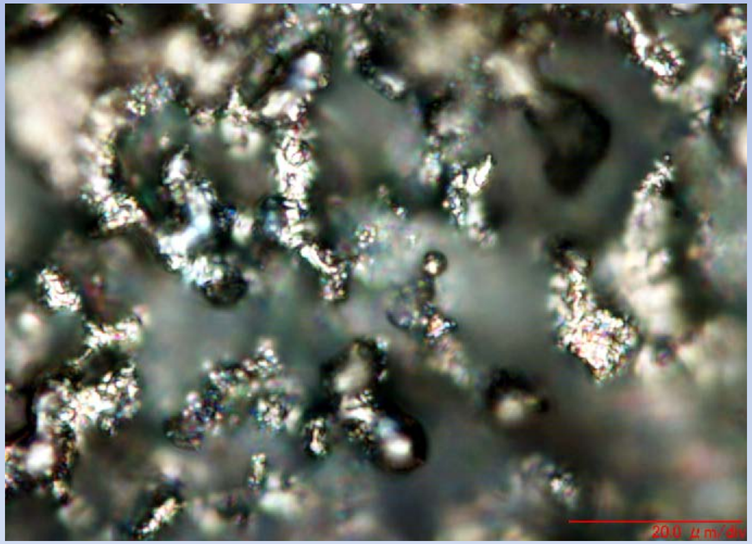


Optical microscope image of MXene/PA composite film

Before laser annealing



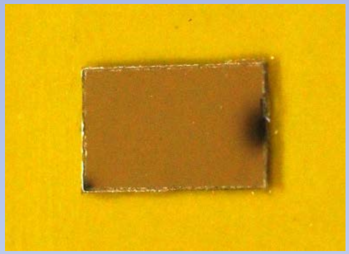
After laser annealing

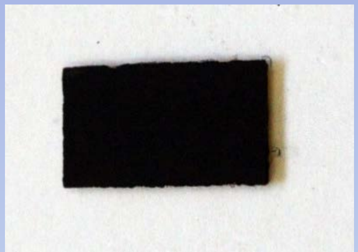


Preparation of MXene/PA/Au in-plane MSC Without laser annealing

(1) Au (120 nm) was sputtered on a glass substrate through a PI mask with a rectangular hole (11.3x6.3 mm).

(2) Mixture of MXene, PA (polyamide, 12.8% NMP sol.), and NMP (2/1/1 weight ratio) was coated on the Au layer (120 nm) through a PI mask.

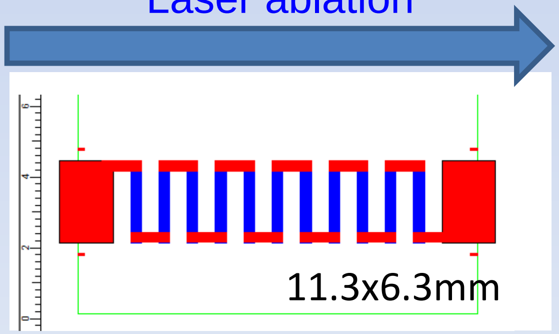


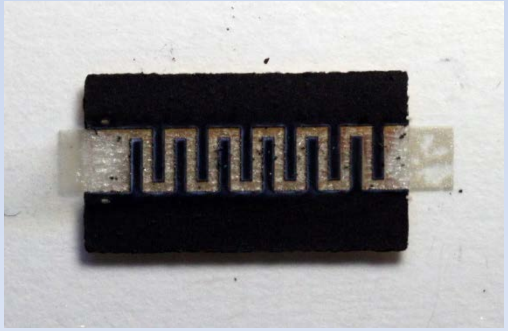


(3) A MXene/PA/Au layered film was prepared on a glass substrate by peeling off the PI mask film after drying at $110^{o}C$.

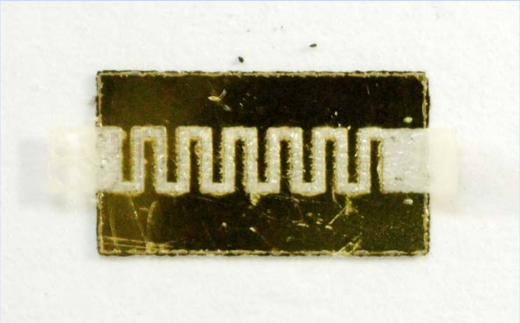
(4) Laser ablation by a fiber laser (1064 nm) - galvano-scanner system

Laser ablation





Front side of Interdigitated electrode (MXene/PA)

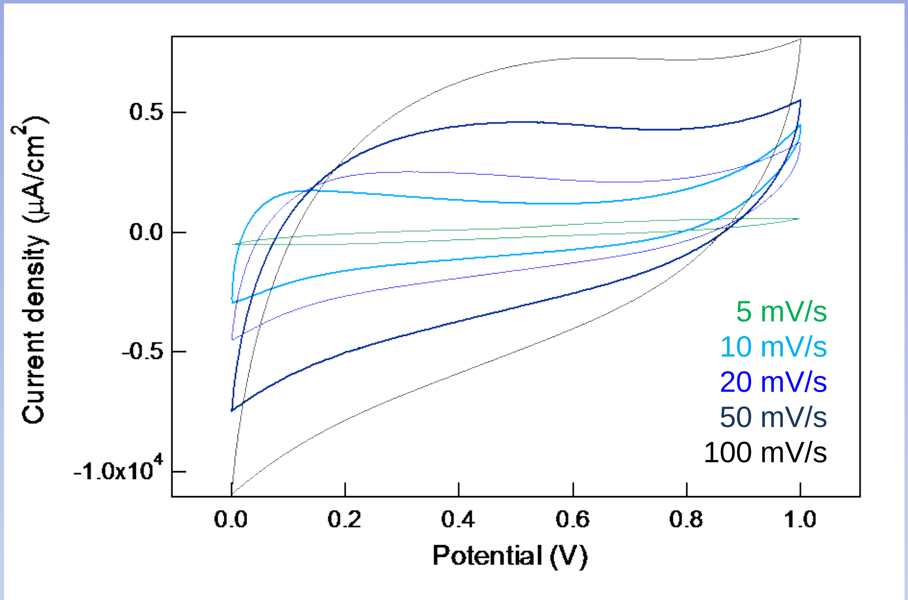


Back side of Interdigitated electrode (Au)

Surface Resistivity

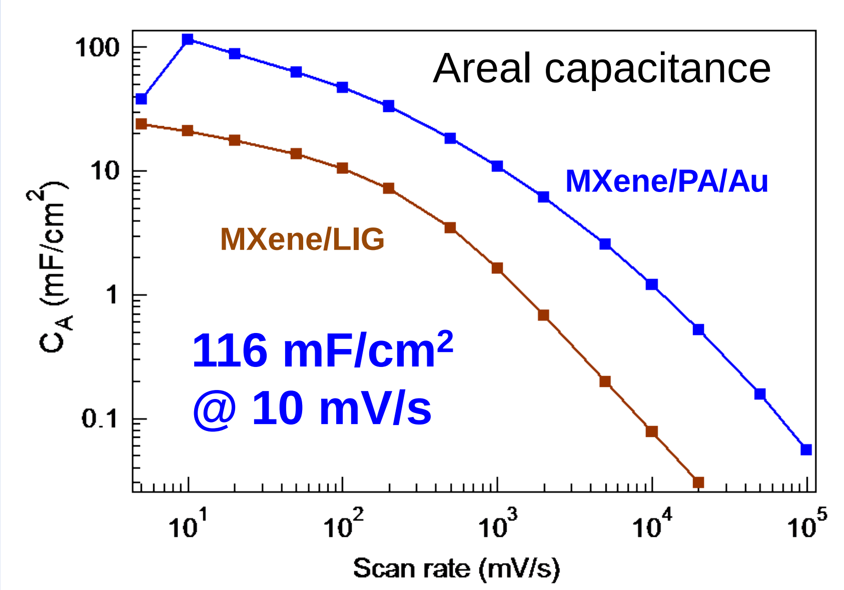
MXene/PA sol. w/w	Laser annealing	Surface resistivity (Ω/□)	Thickness (μm)	Remark
1/3	-	3400	52.0	
1/3	Laser annealing	119	20.4	
1/1	-	535	52.1	
1/1	Laser annealing	1754	21.3	Cracking by laser annealing
2/1	-	1.45	35.1	Au

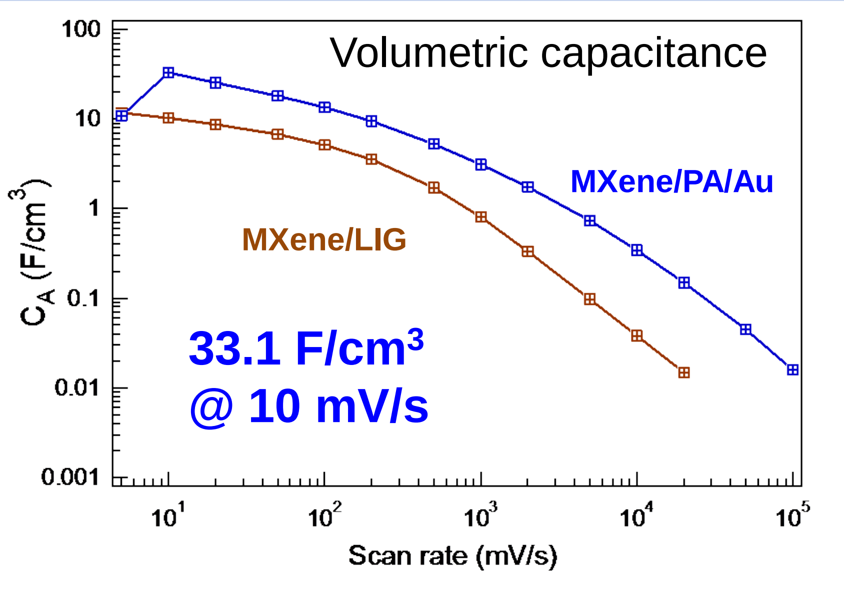
Cyclic voltammograms of MXene/PA/Au in-plane MSC



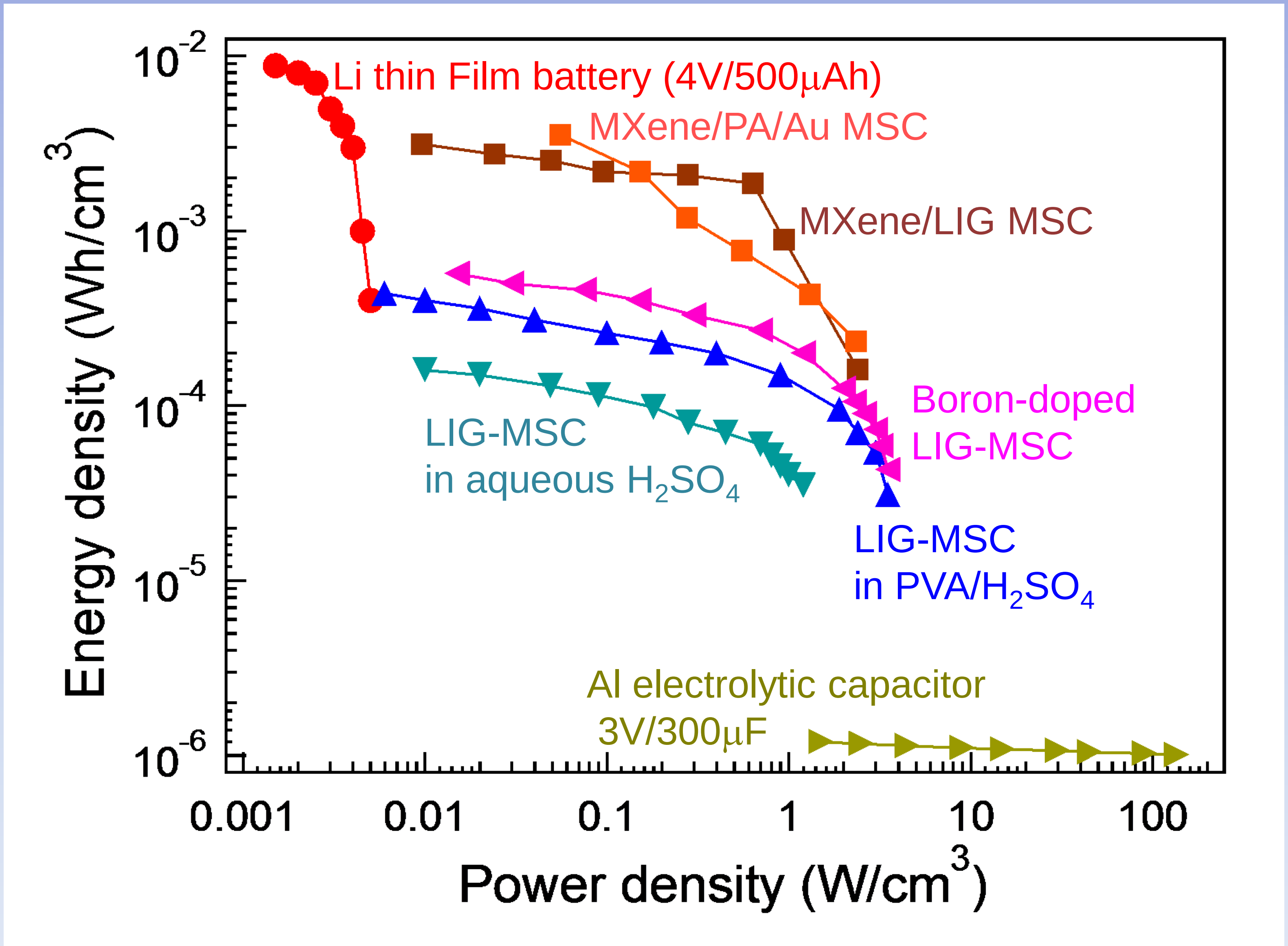
- Pseudo-capacitive characteristics were clear in the cyclic voltammograms of a MXene/PA/Au in-plane MSC.

- The capacitance was 5 times higher than those of MXene/LIG and previous highest laser-induced graphene MSCs.





Ragone plots of MXene/PA/Au in-plane MSC in comparison with other energy storage devices



Summary

- An all-solid-state in-plane micro-surpercapacitor (MSC) was studied by applying laser direct writing method to a MXene-polyamide (PA) composite film.
- The energy density of the MXene/LIG in-plane MSC was remarkably higher than previously reported laser-induced graphene MSCs.
- The capacitance of MXene/PA/Au in-plane MSC was 5 times higher than those of MXene/LIG and previous highest laser-induced graphene MSCs.
- MXene is a potential candidate material for a high performance all-solid MSC.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number JP15H04132, JSPS KAKENHI Grant Number JP19H05356.

Thank you for your attention!