A molten carbonate fuel cell without CO_2 recirculation

Professor Shanwen Tao

School of Engineering, University of Warwick
Department of Chemical Engineering, Monash University

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Types of fuel cells

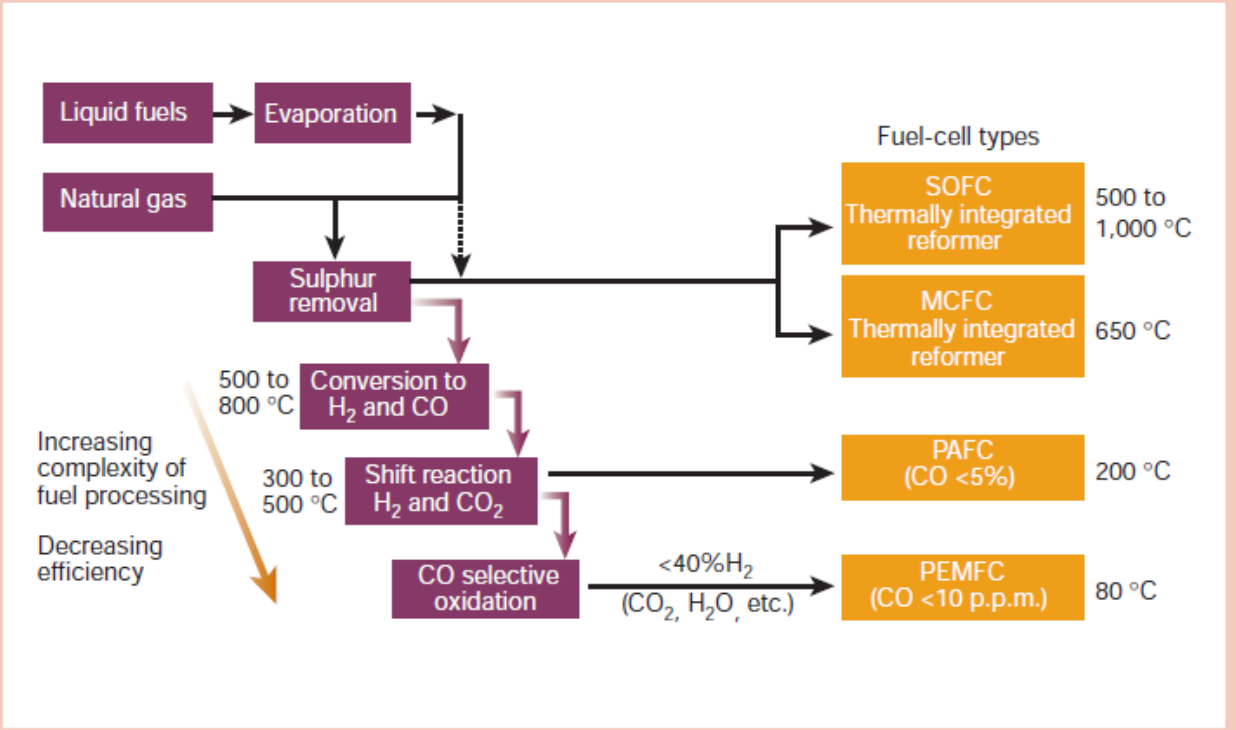
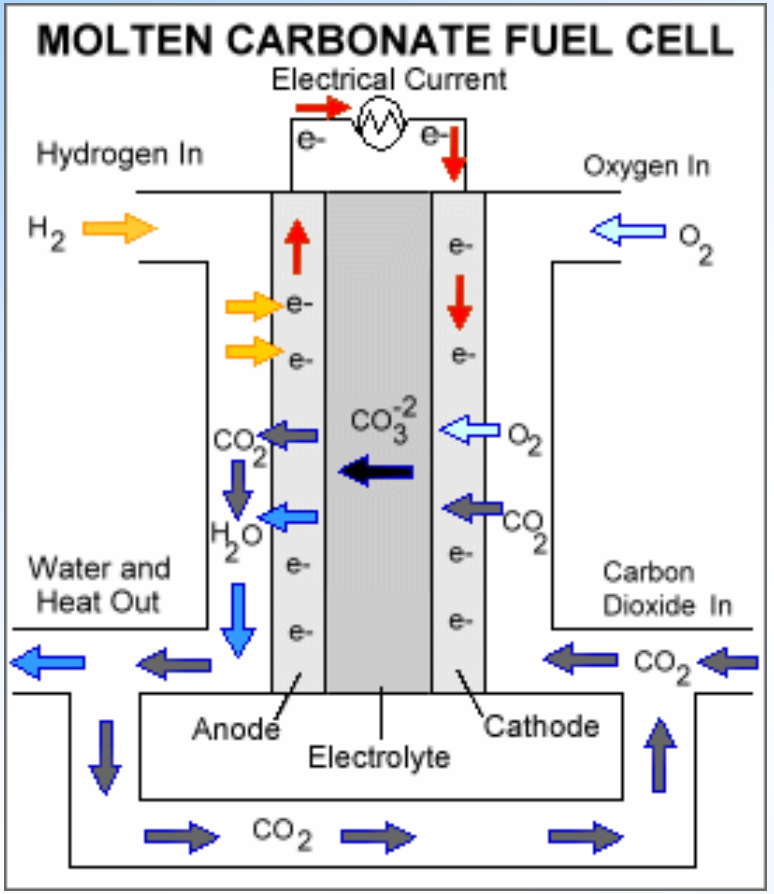


Figure 2 Fuel-cell types and fuel processing. Although selected fuels can be introduced directly into the anode compartment of the high-temperature fuel cells (SOFC and MCFC), better thermal management of the stack can usually be achieved by having separate reformer compartments that are thermally integrated within the stack to produce a mixture of fuel and syngas (H_2 and CO). For the lower-temperature fuel cells (PAFC and PEMFC), external reformers are required. Some of the fuel has to be consumed in these external reformers to maintain the operating temperature. Moreover, dilution of the H_2 fuel reduces performance of the cells, resulting in significant efficiency losses compared with operation on pure H_2. It should be noted that the AFC stack cannot be operated on reformate fuels because of the presence of CO_2 in these gases.

B. Steele, Nature, 414 (2001) 345-352.

Principle of conventional MCFCs



For a MCFC using H_2 as the fuel.

The reaction at cathode is:

$$CO_2 + \frac{1}{2}O_2 + 2e^- \rightarrow CO_3^{2-}$$

The formed $CO_3$2- ions will transport to the anode through the carbonate electrolyte, then react with the fuel. At anode:

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$$

The overall reaction is:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

CO_2 circulation from anode to cathode, was believed to be essential.

Electrode reactions of direct carbon MCFC

Reactions at cathode:

$$CO_2 + 1/2O_2 + 2e^- \rightarrow CO_3^{2-}$$

$$O_2 + e^- \rightarrow O_2^-$$

$$CO_2 + O_2 + 2e^- \rightarrow CO_4^{2-}$$

Reactions at anode:

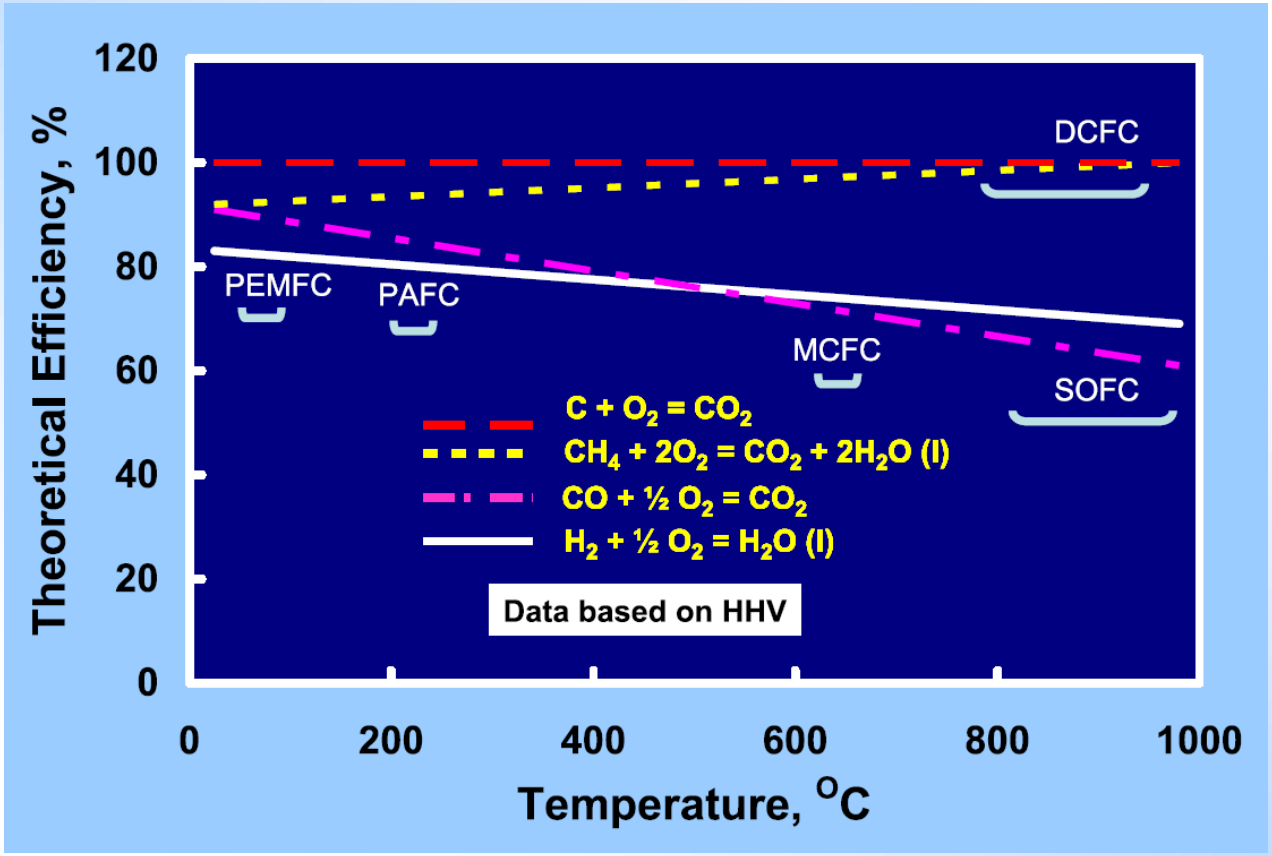
$$C + O_2^- \rightarrow CO_2 + e^-$$

$$C + CO_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-$$

Presence of CO_2 at the cathode is NOT required. On the other hand, CO_2 produced at the anode can dissolve in molten carbonate electrolyte then diffuse to the cathode. Therefore recirculation of CO_2 in MCFC is **NOT** essential.

Why direct carbon fuel cells (DCFCs)



S. Giddey et al., *Progress in Energy and Combustion Science* 38 (2012) 360-399

Direct carbon fuel cells

	Fuel / Anode	Electrolyte	Cathode	T, °C
	Solid graphite rod as fuel & anode $C + 4OH^- = 2H_2O + CO_2 + 4e^-$	Molten Hydroxides OH^- ←	Air as oxidant $O_2 + 2H_2O + 4e^- = 4OH^-$	500 - 600
	Carbon particles as fuel in MC & anode $C + 2CO_3^{2-} = 3CO_2 + 4e^-$	Molten Carbonates CO_3^{2-} ←	Air as oxidant $O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$	800
Concept1	Carbon particles in a fluidised bed $C + 2O^{2-} = CO_2 + 4e^-$	Oxygen ion conducting ceramic electrolyte O^{2-} ←	Air as oxidant $O_2 + 4e^- = 2O^{2-}$	700 – 900
Concept2	Molten tin + C $Sn + 2O^{2-} = SnO_2 + 4e^-$ $SnO_2 + C = Sn + CO_2$		Air as oxidant $O_2 + 4e^- = 2O^{2-}$	
Concept3	Molten salt + C particles $C + 2O^{2-} = CO_2 + 4e^-$		Air as oxidant $O_2 + 4e^- = 2O^{2-}$	

S. Giddey et al., *Progress in Energy and Combustion Science* 38 (2012) 360-399

Challenges on DCFCs

- The challenge for the hydroxide electrolyte is the formation of carbonates inside the electrolyte.
- The main challenges related to Molten Carbonate DCFC are cathode performance loss with time, high cathode polarization, fuel delivery difficulties, corrosion of bipolar metallic plates, shorter cell life. Shorter cell life problem is due to material degradation.
- For DCFCs based on solid oxide electrolyte, availability of materials stable at higher temperatures, degradation of electrode especially in the impurities like sulphur, sealing etc.

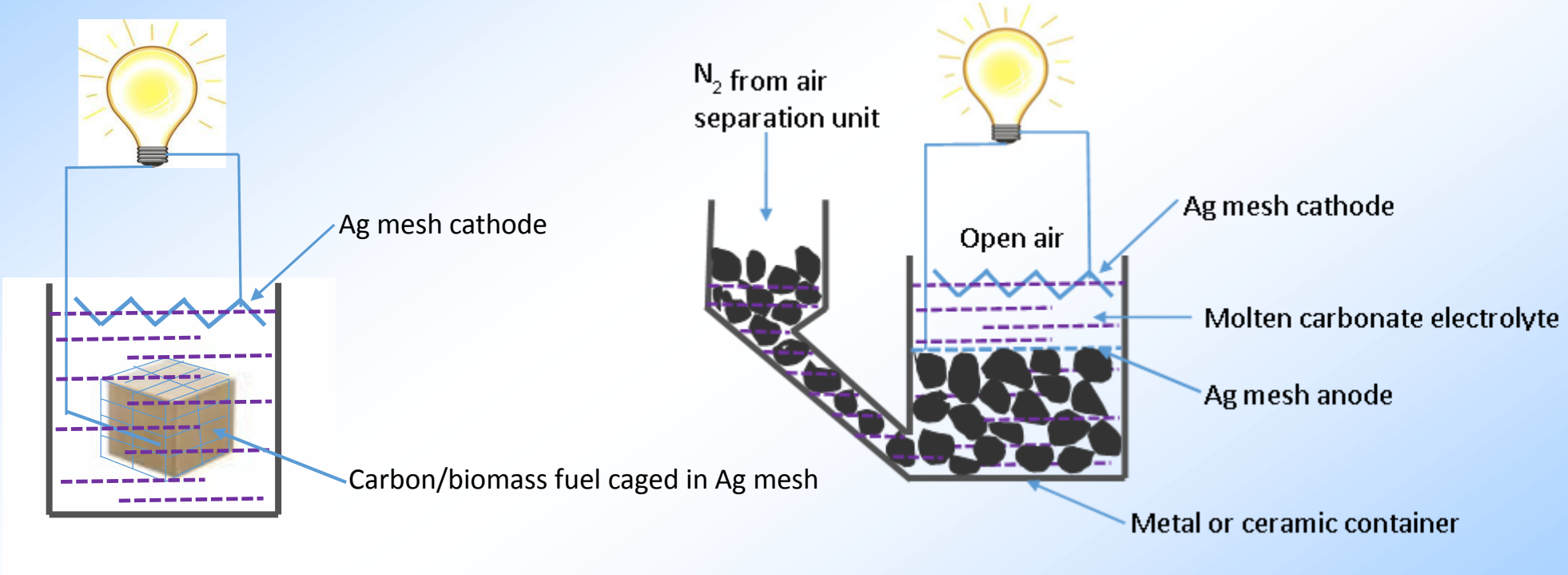
In conclusion, the key challenge is stability of materials for DCFCs.

Biomass – ideal fuels

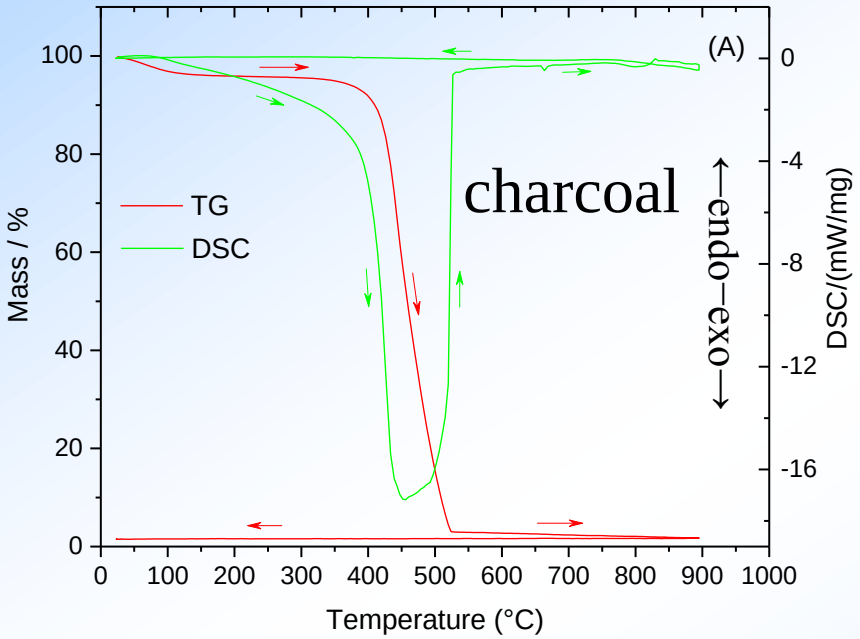
- Nearly carbon neutral, low carbon footprint;
- Renewable;
- Sustainable.

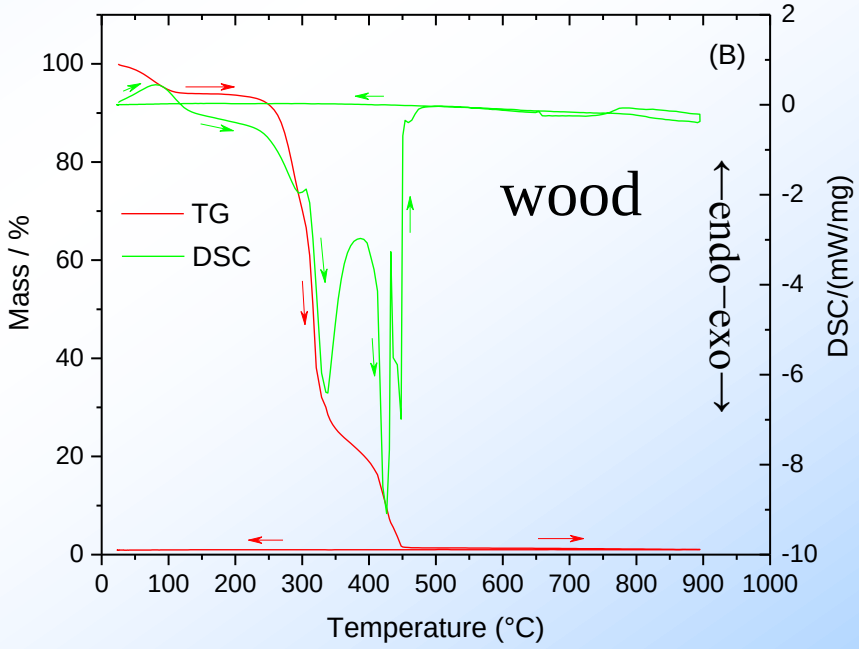
* Global biomass potential is about 200EJ (exajoule, 10^{18} J) (up to 600EJ) which is about one third of world total energy consumption.
* Biomass fuel cell can efficiently generate electricity at low carbon emission.

Direct biomass/carbon fuel cell



TG-DSC analyses of charcoal and wood

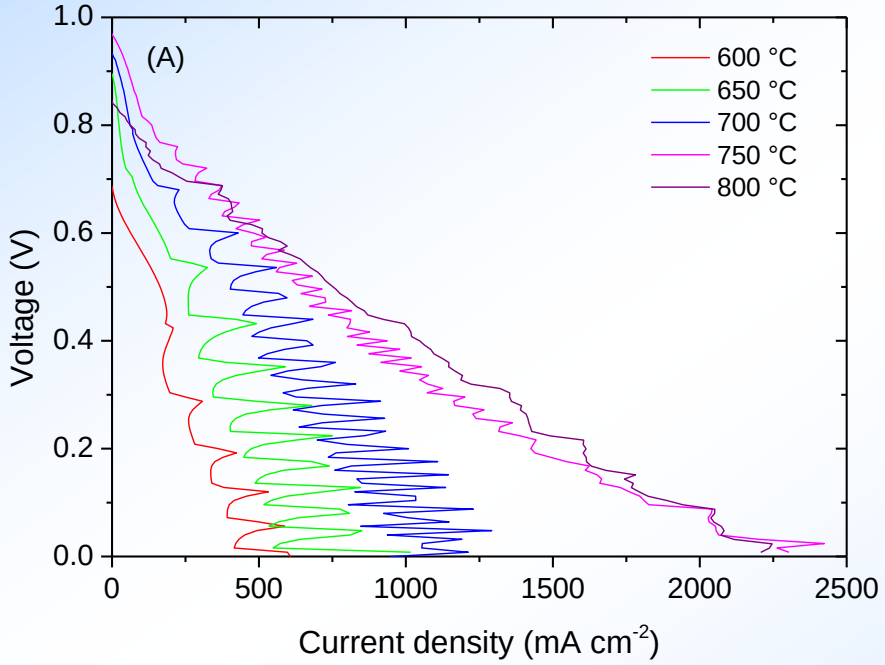


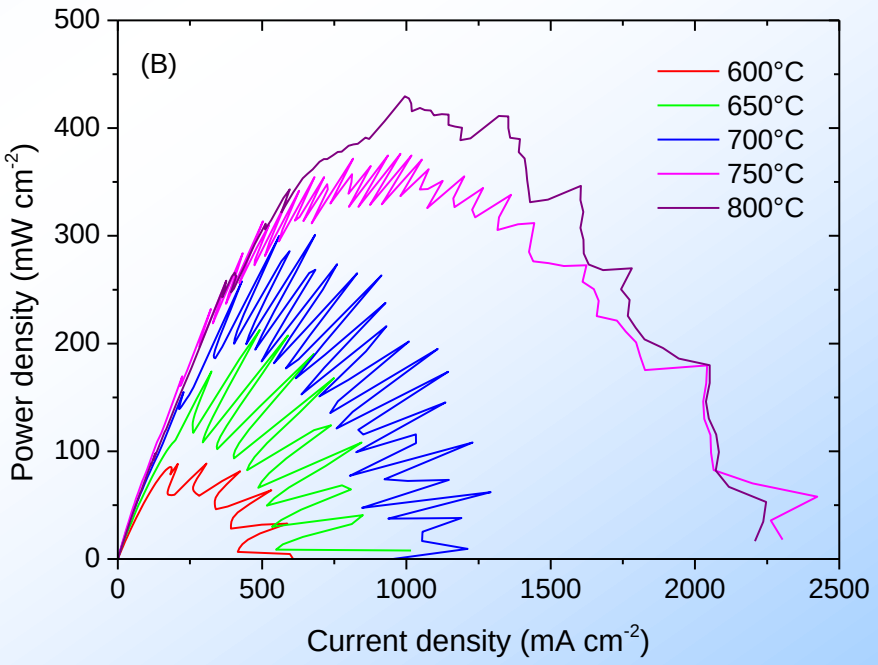


Solid residual 1.47wt%

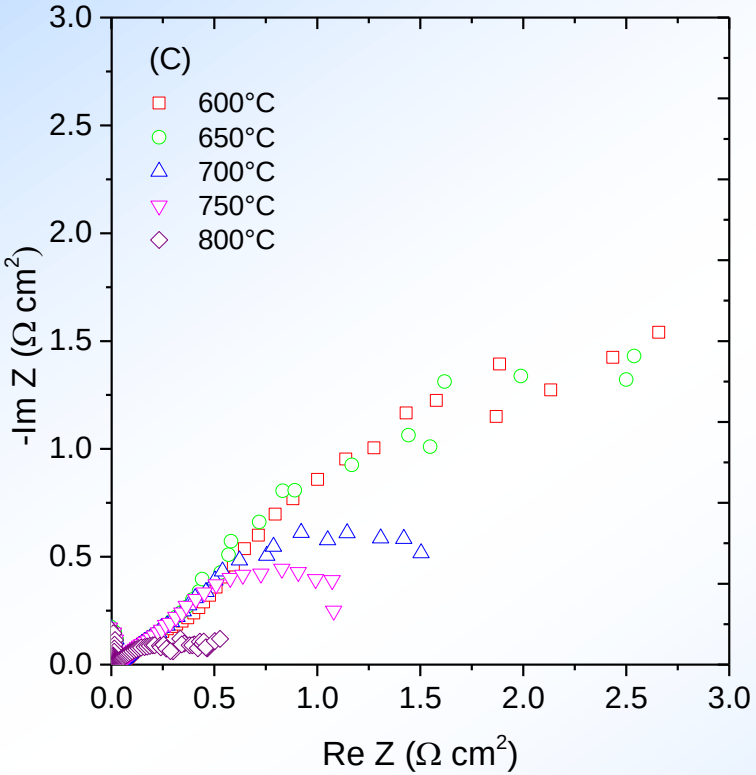
Solid residual 0.90wt%

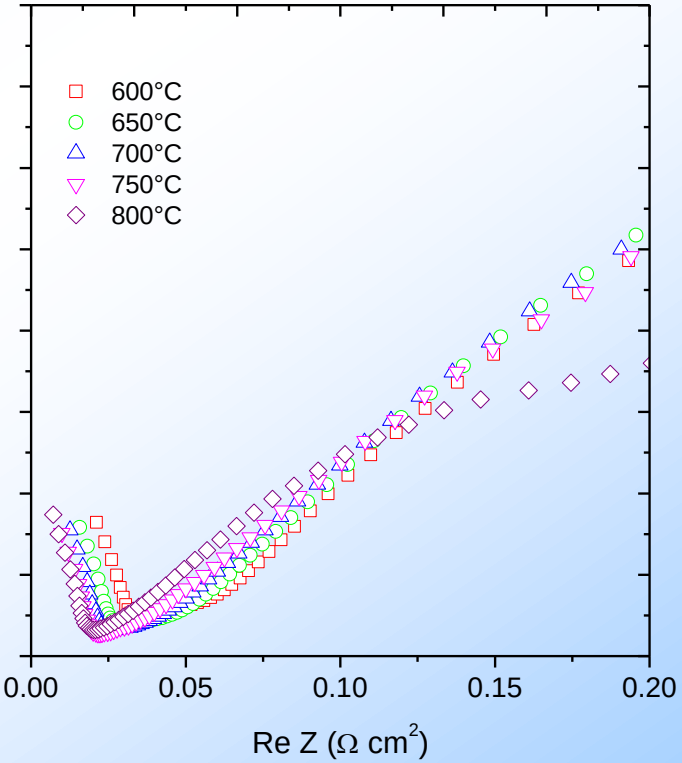
Performance of direct charcoal fuel cell



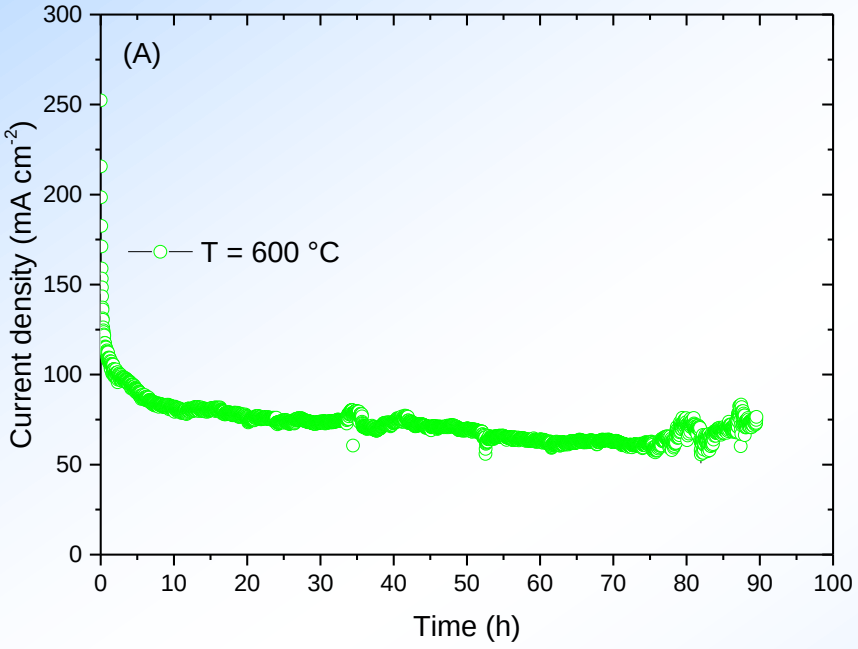


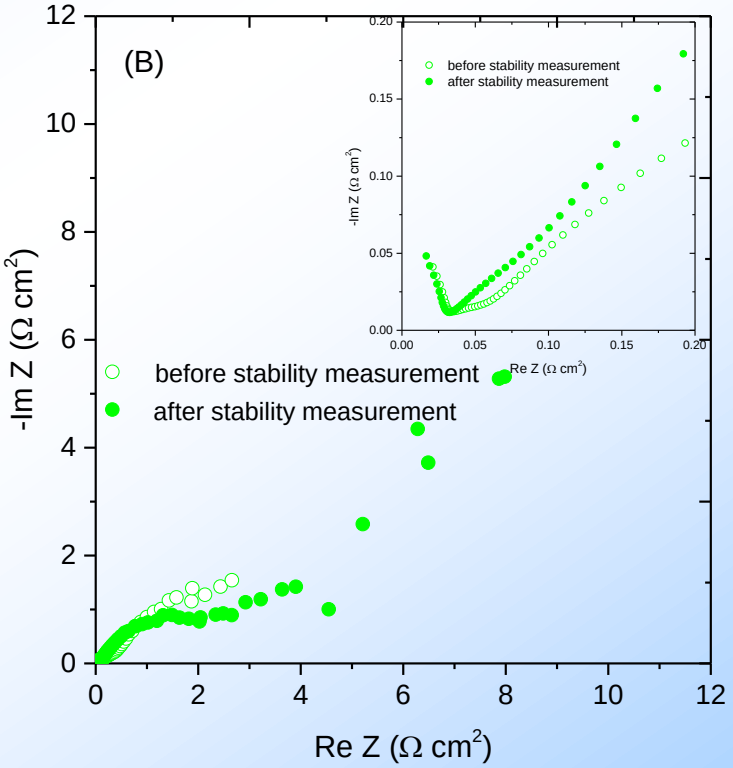
A.c. impedance of direct charcoal fuel cell



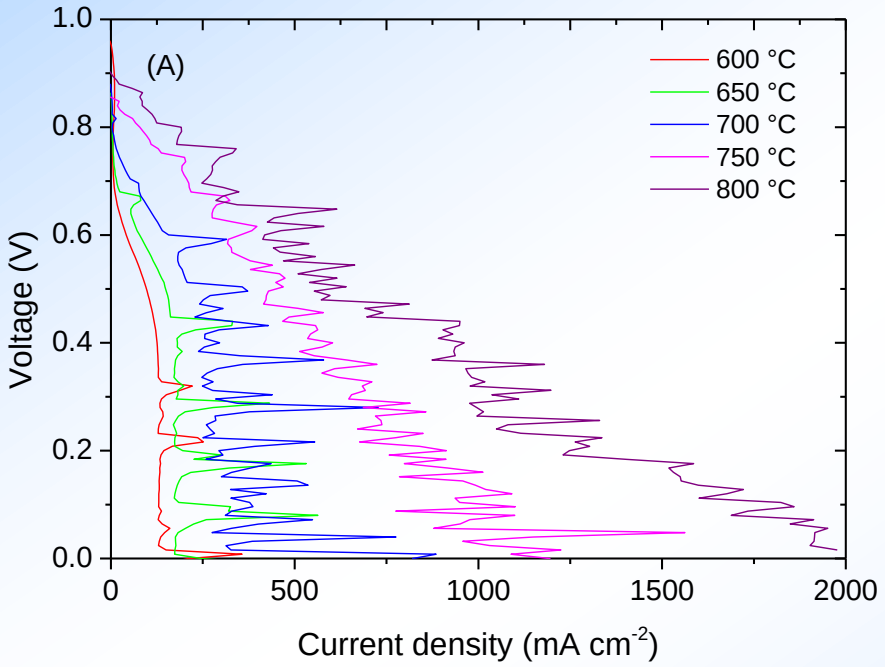


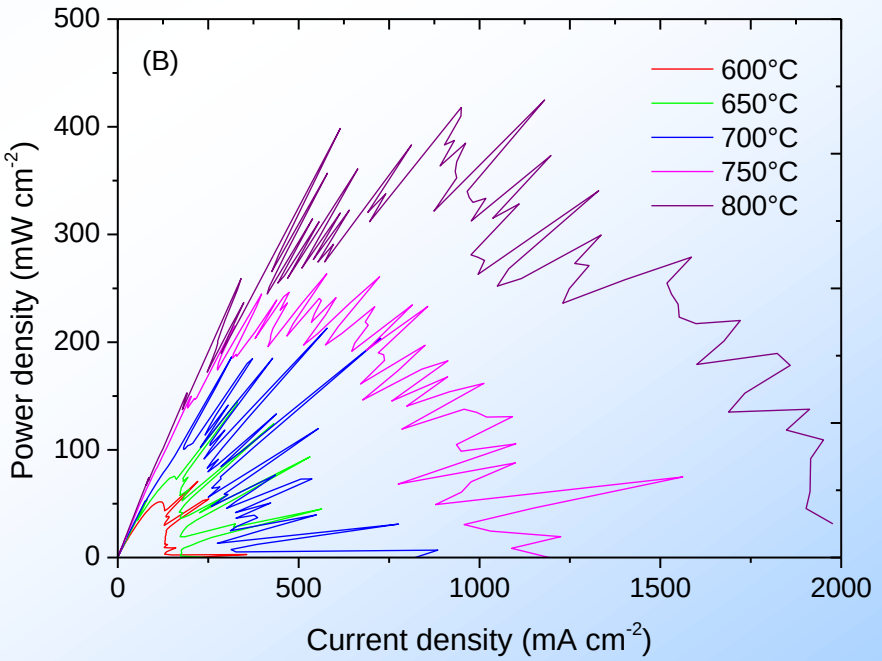
Stability of direct charcoal fuel cell





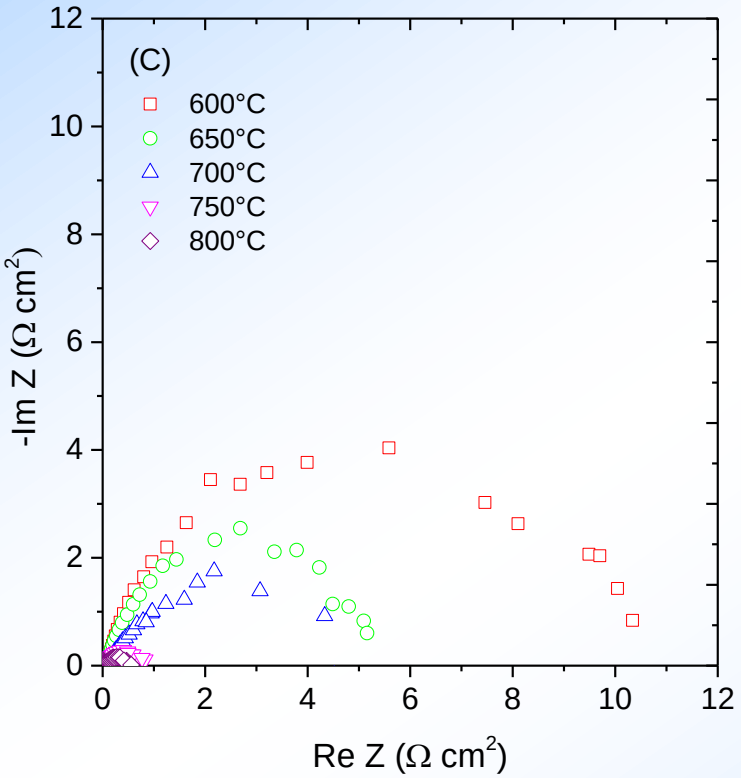
Fuel cell performance of direct wood fuel cell

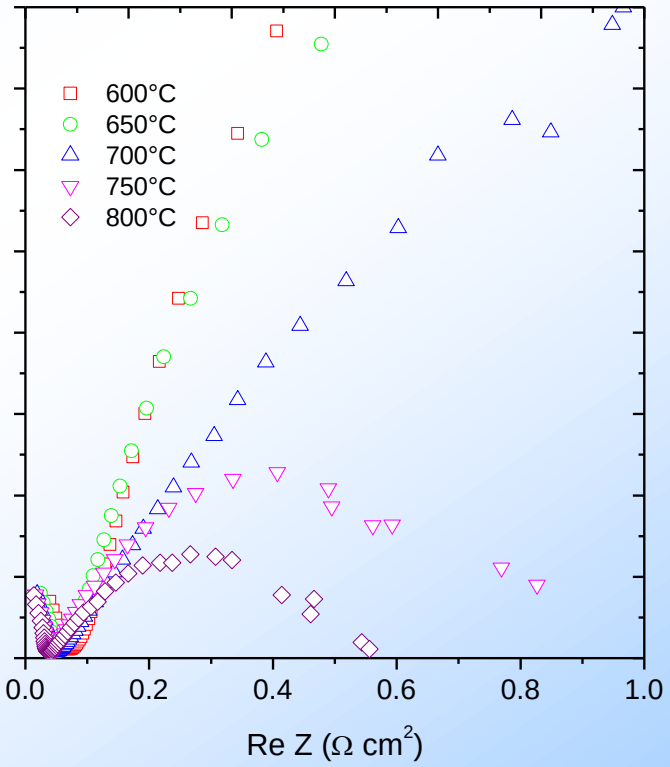




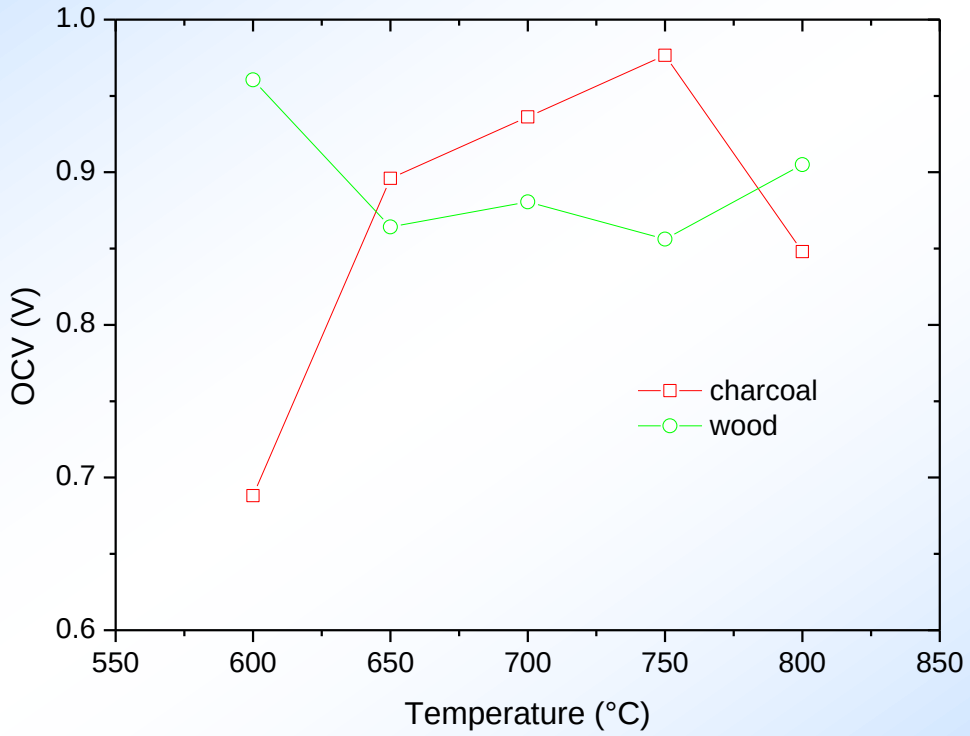
Rong Lan and Shanwen Tao, ***Science Advances***, 2 (2016) e1600772

A.c. impedance of direct wood fuel cell





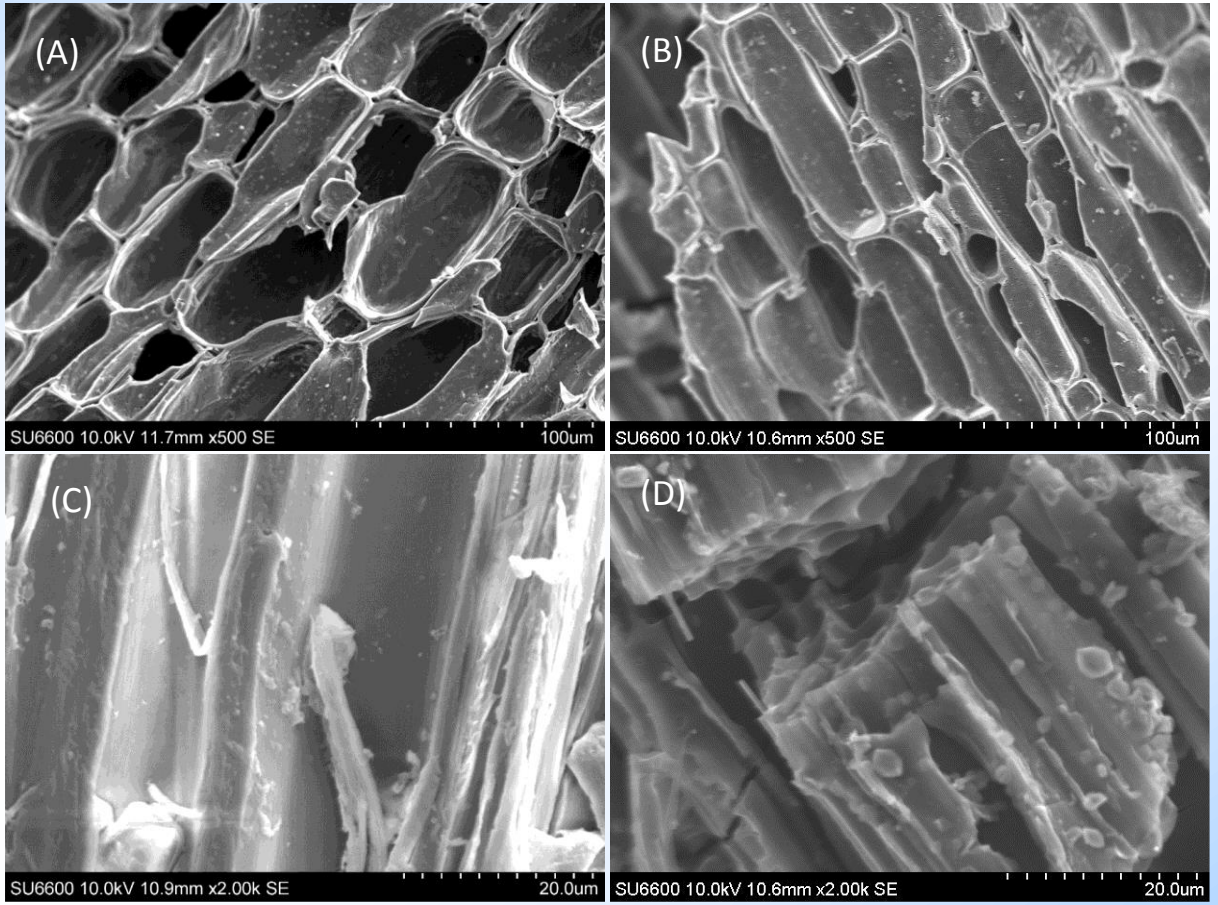
The open circuit voltage of the charcoal and wood fuel cell



Reverse Boudouard reaction (spontaneous at T > 700 °C.

$$C + CO_2 \rightarrow 2CO$$

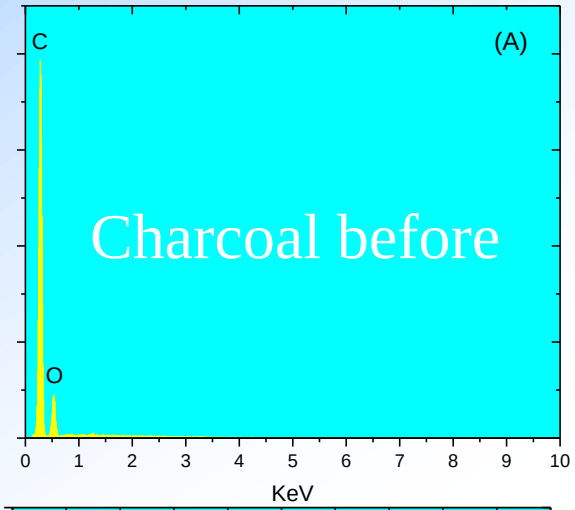
The SEM picture of the charcoal and wood before and after fuel cell measurements

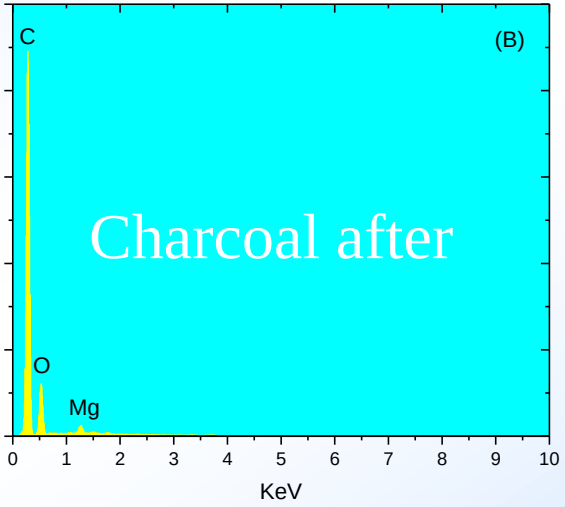


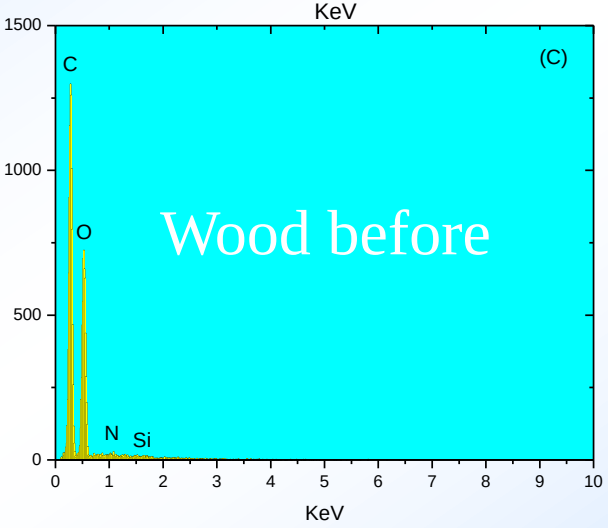
charcoal

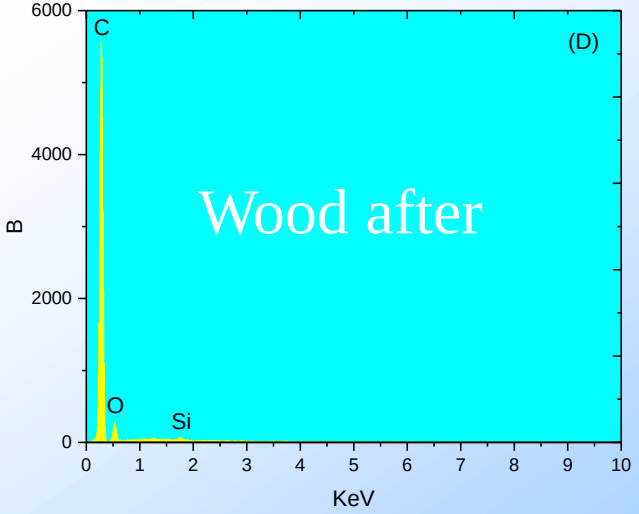
wood

The typical EDS spectra of the charcoal and wood before and after fuel cell measurements









Comparison of reported typical fuel cell performances on using carbon and biomass as the fuel

Electrolyte	Charge carrier	Cathode	Anode	Fuel	Oxidant	Temperature (°C)	Open circuit voltage (V)	Power density (mW cm^{-2})	References
NaOH/KOH 54:46 m/o	OH-	Nickel wound tube	Nickel mesh	activated carbon	O_2/air + H_2O	500	~0.91	~ 38.5	( )
YSZ	O^{2-}	$La_{0.8}Sr_{0.2}MnO_3$+$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	$(Ni_{0.9}$-$Fe_{0.1})$- $Ce_{0.9}Gd_{0.1}O_{2-\delta}$	charcoal	O_2	800	1.0	35	( )
YSZ	O^{2-}	La0.6Sr0.4CoO3-δ	Ni-YSZ	Mixture of pyrolysed fibreboard and Li_2CO_3–K_2CO_3 (62 : 38 mol)	Flowing air	750	1.013	878	( )
38 % Li_2CO_3 + 62 % K_2CO_3	CO_3^{2-}	LiNiOx on stainless steel	Ni-coated stainless steel	soot	Flowing CO_2+O_2 (molar ratio 1:1)	800	~ 1.04	~ 96	( )
32 wt% Li_2CO_3+68wt % K_2CO_3	CO_3^{2-}	Ag sheet	Porous Ni rod	graphite	Flowing CO2+O2 (molar ratio 2:1)	700	~ 1.0	~ 640	( )
Molten $(Li,Na,K)_2CO_3$	CO_3^{2-}(O_2^-)	Ag	Ag	bamboo charcoal	Static air	800	0.97	430	This study
Nafion 212	H+	Pt/C	Carbon paper/carbon nano-tube/enzyme	0.01mM maltodextrin	air	50	~ 0.6	0.8	( )
Nafion 117	H+	Pt/C	Pt/C	Starch processing waste water	air	30	0.49	0.0239	( )
Nafion 117	H+	Pt/C	Carbon clothe (C)	Lignin in $H_3PMo12O40$ solution	Flowing O_2	Room temperature	~0.37	~ 0.55	( )
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$-$(Li,Na)_2CO_3$	O^{2-}/CO_3^{2-}	Lignin+ active carbon $Ce_{0.8}Sm_{0.2}O_{2-\delta}$-$(Li,Na)_2CO_3$	Composite Li/Cu/Ni/Zn oxides	lignin	Flowing air	560	~ 0.74	25	( )
62mol%Li_2CO_3+38mol%K_2CO_3	CO_3^{2-}	Ag	Ag	62mol%Li_2CO_3+38mol%K_2CO_3+5wt% carbon	Flowing CO_2+air	700	0.9	34	( )
Molten $(Li,Na,K)_2CO_3$	CO_3^{2-}(O_2^-)	Ag	Ag	wood	Static air	800	0.9	410	This study

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Thank you for your attention !