

Kraft versus organosolv lignin in a 500 °C molten carbonate fuel cell: volumetric BET surface area and mixed-potential losses in a fuel-structure–performance relationship

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ABSTRACT

Technical lignins are abundant solid carbon fuels, yet their use in molten-carbonate cells has been shown almost only above 700 °C. We operate a molten carbonate lignin fuel cell at 500 °C with a Li–Na–Cs eutectic and a 30:70 O₂/CO₂ cathode feed. Softwood kraft lignin delivered 3.2 mW cm⁻² and a voltage efficiency at P_{max} of 32%, compared with 1.5 mW cm⁻² and 15% for hardwood organosolv lignin (Nernst potential 0.99 V at 773 K). Both cells opened 455–595 mV below this potential. The deficit cannot be explained by carbon activity and is consistent with a mixed anode potential set by fuel–melt–collector contact. Volumetric BET surface area differs by a factor of 3.8 and tracks power, whereas gravimetric BET areas differ by only 36%. Wetted interfacial area per unit anode volume — packing density, pore accessibility and surface polarity — therefore appears to be the more informative descriptor. Reported values are voltage efficiencies only; fuel utilisation and faradaic efficiency were not measured.

NOMENCLATURE

Latin symbols are listed alphabetically, followed by Greek symbols and subscripts. Dimensional symbols are given with SI units. Dimensionless quantities are identified as such.

NOMENCLATURE

a	activity, dimensionless
b	apparent Tafel slope, mV decade ⁻¹
E	reversible cell voltage, V
E°	standard reversible cell voltage, V
F	Faraday constant, C mol ⁻¹
HHV	higher heating value, MJ kg ⁻¹
i	current density, mA cm ⁻²
i ₀	apparent exchange current density, mA cm ⁻²
n	apparent electron number, dimensionless
p	partial pressure (relative to the standard state), dimensionless
R	gas constant, J mol ⁻¹ K ⁻¹
T	temperature, K

Greek symbols

α	charge-transfer coefficient, dimensionless
η	overpotential, mV

Subscripts

anode	anode compartment
cathode	cathode compartment
max	at maximum power

1. INTRODUCTION

The transition to low-carbon energy systems requires technologies capable of converting renewable solid fuels into electricity at high efficiency. Direct carbon fuel cells (DCFCs) are attractive in this respect because the electrochemical oxidation of solid carbon is not subject to the Carnot limitation, giving theoretical efficiencies above 80% [1,2]. The overall reaction $C + O_2 \rightarrow CO_2$ proceeds with an entropy change close to zero, so that the reversible voltage is almost independent of temperature and the theoretical fuel-to-electricity efficiency approaches unity, a property that no gas-fed fuel cell shares [3,4]. Practical devices nevertheless fall well short of that limit, and for a reason common to every DCFC configuration: a solid fuel cannot be delivered to the reaction site by convection or diffusion, so the anodic rate is governed by the extent and the quality of the contact between the carbon particle, the electrolyte and the current collector rather than by the intrinsic kinetics of carbon oxidation [5,6].

Three device families have been developed around this constraint — molten hydroxide cells, molten carbonate cells, and solid-oxide or hybrid carbonate/solid-oxide cells — each trading electrolyte conductivity, fuel contact and materials stability against one another [3,4,7,8]. The reaction pathway itself remains debated. Direct multi-electron oxidation of solid carbon competes with a two-step route in which the Boudouard equilibrium $C + CO_2 \rightleftharpoons 2CO$ first gasifies the fuel and the carbon monoxide so produced is oxidised electrochemically; the relative weight of the two contributions depends on temperature, on CO_2 partial pressure and on the presence of gasification catalysts [6,9,10]. Because the Boudouard reaction becomes kinetically slow below about 700 °C, cells operated at intermediate temperature are expected to rely more heavily on the direct pathway, which places an even greater premium on fuel–electrolyte contact.

Among DCFC variants, molten carbonate systems are of particular interest because the liquid electrolyte provides high ionic conductivity and, unlike solid-oxide configurations, wets the fuel particles to create a three-dimensional reaction interface rather than a two-dimensional solid–solid contact [3,7]. The same melt chemistry underpins a broader family of energy technologies — carbonate fuel cells for simultaneous power generation, CO_2 capture and hydrogen production [16,17], molten carbonate electrolysis, and high-temperature thermal storage — so that the physical chemistry of these melts is comparatively mature and directly transferable [13].

The principal drawback of conventional molten carbonate operation is the 650–850 °C temperature window, in which corrosion of structural components and electrolyte volatilisation become severe [11,12]. Degradation affects the porous matrix that retains the melt [11], the metallic bipolar plates and current collectors [12,14], and the nickel electrodes themselves, whose tolerance to sulfur and to other fuel contaminants is very limited [18,19]. Lowering the operating temperature while retaining a fully liquid electrolyte is therefore a central design objective. Because the liquidus of an alkali carbonate melt is fixed by its composition, this is

achieved by moving away from the conventional Li–Na and Li–K binaries towards ternary and caesium-containing

eutectics, whose melting points lie well below 500 °C [13]; the thermal stability of such melts is moreover substantially greater under a CO_2 -containing atmosphere than under inert gas [15]. This is the design route followed in the present work.

Lignin is the second most abundant natural polymer and is generated at more than 50 million tonnes per year, overwhelmingly as a by-product of kraft pulping [20,21]. It contains more than 60 wt % carbon and has a heating value of 23–27 MJ kg⁻¹ [20,22], yet the great majority is still burned for process heat inside the mill and only a small percentage reaches any higher-value market; recent supply assessments identify kraft lignin in particular as the technical lignin with by far the largest accessible volume [23,24].

The two industrially dominant technical lignins differ systematically. Kraft lignin retains 1–3 wt % sulfur and is recovered from softwood by an alkaline sulfide process, whereas organosolv lignin is essentially sulfur-free, is recovered from hardwood by solvent extraction, and is richer in oxygenated functionality [25–27]. Comparative characterisation studies show that recovery chemistry and botanical origin together determine molecular weight, polydispersity, degree of condensation and hydroxyl speciation, and that these properties vary far more between lignin types than the elemental composition does [26,27]. Quantitative ³¹P NMR after phosphorylation has become the standard tool for resolving the aliphatic, syringyl, guaiacyl, p-hydroxyphenyl and carboxylic hydroxyl populations that distinguish them [29], while the third major commercial lignin, lignosulfonate, is more strongly ionised and markedly more hydrophilic than either [28]. Lignin has been examined extensively as a precursor for electrochemical energy materials — battery carbons, supercapacitor carbons and electrocatalyst supports [30,31] — and as a feedstock for thermochemical conversion to fuels and aromatics [32]. The consequences of these structural differences for lignin used as the fuel itself in a carbonate melt have not, however, been established.

Direct conversion of lignin has been reported in three distinct device classes [33]. Low-temperature aqueous flow cells reach high power densities, 160 to 270 mW cm⁻², but require engineered electrocatalysts, liquid electrolytes and redox mediators, and they yield depolymerisation products rather than complete oxidation [34,35]; a related photo-assisted concept uses polyoxometalates as both photocatalyst and charge carrier [36]. High-temperature molten carbonate and hybrid cells operate on solid fuel and achieve 100–900 mW cm⁻², but only at 700–850 °C [37,38]. Comparable performance has been obtained in this second class with a wide range of solid biogenic fuels — wood char, corn-cob biochar, carbonaceous residues from steelmaking, exhausted olive pomace and sorted organic waste — and reviews of biochar as a DCFC fuel consistently identify pyrolysis conditions, ash chemistry and surface texture as the controlling variables [39–41,43–45]; direct carbon solid-oxide cells fed with catalyst-loaded activated carbon reach 373 mW cm⁻² at 850 °C [42]. A

third class, intermediate-temperature electrolyzers in which lignin or raw biomass is oxidised at the anode so as to produce hydrogen at the cathode, is the closest electrochemical use of lignin to the present work in terms of temperature, although not in terms of product [47–49]; kraft black liquor itself is electrochemically active under such conditions [50], and the field has recently been reviewed [51].

The single closest comparator to the present work is that of Bohn Lima et al., who obtained 12 mW cm⁻² with kraft lignin blended with activated carbon in a carbonate–ceria composite at 560 °C, and who concluded from their own kraft-versus-lignosulfonate comparison that lignin hydrophilicity was the critical variable [46]. No study has yet operated a solid-lignin-fuelled molten carbonate cell below 560 °C, and none has attempted to relate performance to measured fuel texture.

Where fuel properties have been correlated with DCFC performance, the descriptor almost invariably used is the gravimetric BET surface area, sometimes supplemented by ash content, oxygen surface functionality and degree of graphitisation [5,39,41]. That choice is natural for gas-fed electrodes but is not obviously appropriate here, because the anode of a molten carbonate cell is a fixed volume into which a given mass of powder is packed: what the melt can reach is the interface contained in that volume, not the interface contained in a gram of powder. Two further quantities intervene between the nominal BET area and the electrochemically addressable area. The first is pore accessibility, since a carbonate melt of high surface tension cannot infiltrate the narrowest pores that nitrogen adsorption counts. The second is surface polarity, which controls wetting; quantitative studies of molten carbonate on carbon substrates show that the rate and the final extent of spreading depend strongly on surface chemistry and on the surrounding atmosphere [52,53]. Neither quantity is captured by a gravimetric area, and neither has previously been measured alongside the electrochemical performance of a lignin-fuelled cell. This is the gap that the present work addresses.

We operate an MC-LFC at 500 °C — to our knowledge the lowest reported operating temperature for a solid-lignin-fuelled molten carbonate cell — and compare kraft and organosolv lignin using coupled physico-chemical characterisation and electrochemical diagnostics. The study extends our earlier report of the MC-LFC concept [54], which described a single fuel and a model–experiment correlation, by adding a controlled two-fuel comparison, quantitative ³¹P NMR hydroxyl speciation, nitrogen-adsorption and particle-size analysis, a thermodynamically referenced voltage-loss budget, and the structure–performance relationship that emerges from them.

The work also bears on hydrogen-energy conversion in two ways that motivate its presentation here. First, the Li–Na–Cs carbonate melt used as the electrolyte is the same medium employed for molten carbonate electrolysis and for CO₂-to-syngas and CO₂-to-carbon conversion [55,56], and carbonate fuel cells are themselves being developed as combined CO₂-capture and hydrogen-generation units [16]; the interfacial behaviour characterised here may therefore provide useful insight for carbonate-based hydrogen-carrier routes. Second, direct lignin-to-electricity competes with the indirect route in which lignin is first gasified or reformed to hydrogen and the hydrogen is then converted in a fuel cell, a pathway whose stage efficiencies and economics are now well documented

[57–60]; a comparison of the two on a well-to-electricity basis is developed in Section 3.7.

2. EXPERIMENTAL

2.1 Materials and physico-chemical characterisation

Softwood kraft lignin (sample N38, Canadian pulp mill) and hardwood organosolv lignin (sample N5, biorefinery partner) were used as received without purification, drying or size classification. Elemental composition (C, H, N, O) was determined on a LECO TruSpec Micro analyser and sulfur on a LECO SC632; total organic carbon and the inorganic element inventory were determined independently by combustion analysis and by inductively coupled plasma spectrometry, respectively. Ash content was measured gravimetrically. Higher heating value was calculated from the elemental composition using the modified Dulong relation [61]

$$HHV = 0.3383 C + 1.442 (H - O/8) + 0.0942 S \quad (1)$$

with all compositions in wt %.

Quantitative ³¹P NMR was performed after derivatisation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane on a Varian 500 MHz spectrometer, and hydroxyl contents are reported per C₉ phenylpropane unit. Molecular weight distributions were obtained by gel permeation chromatography. Particle size distributions were measured by nanoparticle tracking analysis and are reported as the mean together with the D10, D50 and D90 percentiles. Specific surface area, pore volume and average pore width were obtained from nitrogen adsorption using the BET and t-plot methods. Apparent (bulk) density was determined by tapped-volume measurement. Solubility in ethanol, used here as a measure of relative lipophilicity, was determined gravimetrically on the soluble fraction. Morphology was examined by scanning electron microscopy (TESCAN VEGA3, secondary-electron mode, 20.0 kV) at 1.00, 3.00 and 6.00 k×.

The carbonate electrolyte (Li₂CO₃:Na₂CO₃:Cs₂CO₃ = 26:35:39 by mass) was characterised by simultaneous thermogravimetry and differential scanning calorimetry (Netzsch STA 449 F3). Thermal analysis was performed under argon. Because carbonate decomposition is atmosphere-dependent, the observed melting temperature (≈415 °C) constitutes a lower bound. Under the CO₂-containing cathode atmosphere used in the cell, phase behaviour may differ from that measured under argon; accordingly, the 415 °C melting endotherm is used only as evidence that molten-electrolyte operation at 500 °C is plausible.

2.2 Cell assembly and electrochemical testing

Anodes were prepared by impregnating porous nickel foam (40% porosity, 2 mm thick, geometric area 2.0 cm²) with a lignin–ethanol slurry (lignin loading ≈ 50 mg cm⁻², corresponding to a total fuel mass of ≈ 100 mg per anode). The slurry was prepared at a concentration of 200 mg mL⁻¹ and the impregnated foam was dried at 50 °C for 2 h. Cathodes

consisted of the same nickel foam oxidised by flame treatment in air for approximately 30 s to form a surface NiO layer. Single cells were assembled in alumina crucibles. The inter-electrode distance was fixed at ≈ 5 mm. Approximately 8 g of the $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--Cs}_2\text{CO}_3$ (26:35:39 by mass) electrolyte was loaded into the crucible. The anode and cathode compartments were separated by the electrolyte melt itself; the crucible was fitted with a sealed lid equipped with gas inlet/outlet ports and a thin-probe thermocouple. The electrolyte was melted in situ at 500 °C. The anode compartment was continuously purged with argon (flow rate ≈ 20 mL min $^{-1}$) and the cathode compartment was supplied with a 30:70 O_2/CO_2 mixture (flow rate ≈ 30 mL min $^{-1}$) to sustain the cathodic reaction



Electrochemical measurements were performed with a PAR 273A potentiostat in a two-electrode configuration. After 600 s of open-circuit stabilisation, linear-sweep voltammetry was recorded at 1 mV s $^{-1}$ from the open-circuit voltage to 0 V. Power density was computed as the product of current density and cell voltage. Unless otherwise stated, the polarisation curves presented in this work correspond to the average of three independent cell builds ($n = 3$). The cell arrangement is shown in Figure 1.

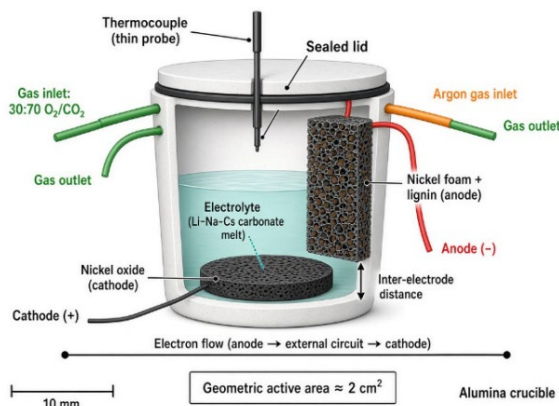


Figure 1. Schematic of the MC-LFC showing the anode and cathode compartments, the argon and 30:70 O_2/CO_2 gas feeds, the sealing arrangement, the inter-electrode distance and the geometric active area.

2.3 Data analysis

The reversible cell voltage was computed from the Nernst expression for the overall reaction $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$,

$$E = E^0 + \left(\frac{RT}{4F} \right) \ln \left[\frac{a_{(\text{C})} \times p_{(\text{O}_2)} \times p_{(\text{CO}_2, \text{cathode})}^2}{p_{(\text{CO}_2, \text{anode})}^3} \right] \quad (3)$$

with $E^0 = 1.025$ V at 773 K obtained from the standard Gibbs energy of formation of CO_2 , $RT/4F = 16.7$ mV, and unit activity assumed for the solid carbon phase. Voltage efficiency is defined throughout as the ratio of the cell voltage at maximum power to this Nernst potential. It is explicitly not an energy efficiency: neither fuel utilisation nor faradaic

efficiency was measured, and no claim of energy efficiency is made anywhere in this work.

Tafel slopes were obtained by linear regression of the activation overpotential against the logarithm of current density over a stated fitting window, and the product of the charge-transfer coefficient and the electron number was computed as

$$\alpha \cdot n = \frac{2.303RT}{Fb} \quad (4)$$

where b is the fitted slope and $2.303 RT/F = 153.4$ mV decade $^{-1}$ at 773 K. Ohmic and concentration contributions were separated from the polarisation curve by the procedure described in Section 3.3. Because no electrochemical impedance data were acquired, the ohmic resistance reported here is a fitted rather than a measured quantity, no iR correction was applied, and — in the absence of a reference electrode — all overpotentials are cell-level quantities that cannot be assigned to the anode or the cathode individually.

3. RESULTS AND DISCUSSION

3.1 Composition and texture of the lignins

Elemental analysis (Table 1) shows that the two lignins are near-identical in bulk composition: both contain 62–65 wt % carbon and have higher heating values within 1.5% of each other (23.48 and 23.84 MJ kg $^{-1}$). Organosolv lignin is the more oxygenated of the two, while kraft lignin retains the sulfur characteristic of its recovery process. The two analytical routes available for sulfur do not agree: combustion analysis returns 0.10 and 1.70 wt % for organosolv and kraft respectively, whereas inductively coupled plasma spectrometry returns 0.038 and 2.13 wt %. Both are reported in Table 1 with their methods identified, and the ICP value is used where the inorganic inventory is discussed. Ash contents are low in both cases (0.00 and 0.65 wt %), confirming that neither fuel carries a significant inorganic burden into the melt.

Table 1. Elemental composition, ash content and higher heating value of the two lignins. Sulfur is reported by both available methods because they do not agree.

Parameter	Organosolv (N5)	Kraft (N38)	Method
C (wt %)	62.40	63.40	LECO TruSpec Micro
Total organic carbon (wt %)	64.00	64.98	combustion / TOC
H (wt %)	6.10	6.30	LECO TruSpec Micro
O (wt %)	31.20	28.40	LECO TruSpec Micro
N (wt %)	0.2	0.2	LECO TruSpec Micro
S (wt %)	0.10	1.70	LECO SC632
S (wt %)	0.038	2.13	ICP
Ash (wt %)	0.00	0.65	gravimetric
Total lignin (mg g $^{-1}$)	936.5	1016.5	acid hydrolysis
HHV (MJ kg $^{-1}$)	23.48	23.84	modified Dulong, Eq. (1)

Notes: compositions in wt % unless stated. The ICP sulfur value is used where the inorganic inventory is discussed.

Quantitative ^{31}P NMR (Table 2) shows that the two lignins carry almost exactly the same total hydroxyl content — 1.507 and 1.517 hydroxyl groups per C_9 unit — but distribute it very differently. Organosolv lignin is richer in aliphatic and syringyl phenolic hydroxyl, the expected hardwood signature, whereas kraft lignin is dominated by guaiacyl phenolic units and carries 2.6 times the carboxylic acid content. This last difference matters for what follows, because carboxylate is the most polar and most readily ionised of the functional groups present and therefore the one most likely to influence wetting by an ionic melt.

Table 2. Hydroxyl-group distribution from quantitative ^{31}P NMR, expressed as hydroxyl groups per C_9 phenylpropane unit.

Group	Organosolv (N5)	Kraft (N38)	Ratio K/O
Aliphatic OH	0.514	0.402	0.78
Total phenolic OH	0.396	0.329	0.83
Syringyl phenolic	0.215	0.074	0.35
Guaiacyl phenolic	0.144	0.318	2.21
p-Hydroxyphenyl phenolic	0.016	0.034	2.10
Condensed phenolic	0.181	0.255	1.41
Uncondensed phenolic	0.376	0.427	1.14
Carboxylic acid	0.040	0.104	2.60
Total OH	1.507	1.517	1.01

The textural data in Table 3 are central to this paper and reveal a pattern that is not visible in the bulk composition. Kraft lignin has a slightly higher gravimetric BET surface area than organosolv lignin (1.686 versus 1.243 $\text{m}^2 \text{g}^{-1}$), a difference of only 36%. Its particles are smaller (mean 141 versus 194 nm) and markedly more uniform, with a D90/D10 span of 1.28 against 2.22. Its pore structure is coarser and more voluminous, with an average pore width of 149 Å against 54 Å and a pore volume 3.7 times larger. Most strikingly, its apparent packing density is 2.8 times higher, 0.635 against 0.224 g mL^{-1} . Finally, kraft lignin is far less soluble in ethanol than organosolv lignin (15.5 against 65.1 wt %), a direct measure of its lower lipophilicity.

Scanning electron microscopy (Figure 2 and Figure 3) is consistent with these numbers: organosolv lignin forms irregular, polydisperse agglomerates of sub-spherical particles, whereas kraft lignin consists of more spherical primary particles organised into short, comparatively homogeneous agglomerates.

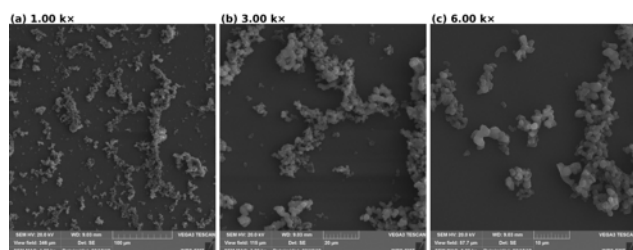


Figure 2. Morphology of organosolv lignin (sample N5) by scanning electron microscopy (TESCAN VEGA3, secondary-

electron mode, 20.0 kV): (a) 1.00 kx, view field 346 μm , scale bar 100 μm ; (b) 3.00 kx, view field 115 μm , scale bar 20 μm ; (c) 6.00 kx, view field 57.7 μm , scale bar 10 μm

Table 3. Textural, physical and molecular properties of the two lignins, with the third characterised lignin (N32) included for reference. The volumetric BET surface area is the product of the BET area and the apparent density.

Property	Organosolv (N5)	Kraft (N38)	Biorefinery (N32)
BET surface area ($\text{m}^2 \text{g}^{-1}$)	1.243	1.686	7.414
t-Plot external area ($\text{m}^2 \text{g}^{-1}$)	0.766	1.730	8.494
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.00167	0.00627	0.03073
Average pore width (Å)	53.9	148.8	165.8
Apparent density (g mL^{-1})	0.224	0.635	0.393
Volumetric BET area ($\text{m}^2 \text{mL}^{-1}$)	0.279	1.070	2.912
Mean particle size (nm)	193.8	140.8	254.9
D10 / D50 / D90 (nm)	127 / 181 / 283	131 / 136 / 168	153 / 239 / 378
Span D90/D10	2.22	1.28	2.47
Soluble in ethanol (wt %)	65.1	15.5	16.8
Mn / Mw (g mol^{-1})	1245 / 4488	2108 / 10989	1469 / 6103
Polydispersity Mw/Mn	3.60	5.21	4.15

Notes: volumetric BET surface area = gravimetric BET area $\times$ apparent packing density. N32 was characterised but not tested electrochemically.

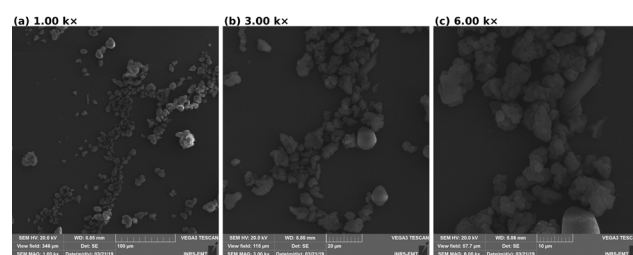


Figure 3. Morphology of kraft lignin by scanning electron microscopy (TESCAN VEGA3, secondary-electron mode, 20.0 kV): (a) 1.00 kx, view field 346 μm , scale bar 100 μm ; (b) 3.00 kx, view field 115 μm , scale bar 20 μm ; (c) 6.00 kx, view field 57.7 μm , scale bar 10 μm .

3.2 Thermal behaviour of the electrolyte

Thermal analysis of the Li–Na–Cs carbonate mixture (Figure 4) shows a mass loss of approximately 7 wt % below 180 °C, from 53.3 to 49.4 mg, attributed to the release of residual moisture and possibly of adsorbed CO_2 and other volatiles. This is followed by a sharp endothermic melting

peak centred near 415 °C with negligible further mass change up to 600 °C. The melting endotherm centred near 415 °C indicates that the electrolyte is expected to be molten at 500 °C, while the operating temperature remains 150–350 °C below the conventional MCFC window.

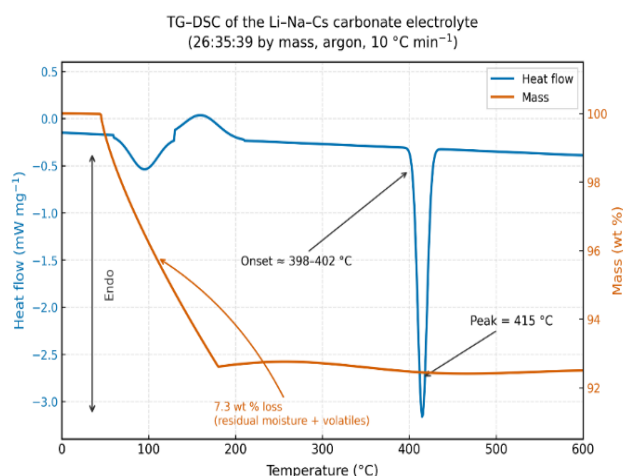
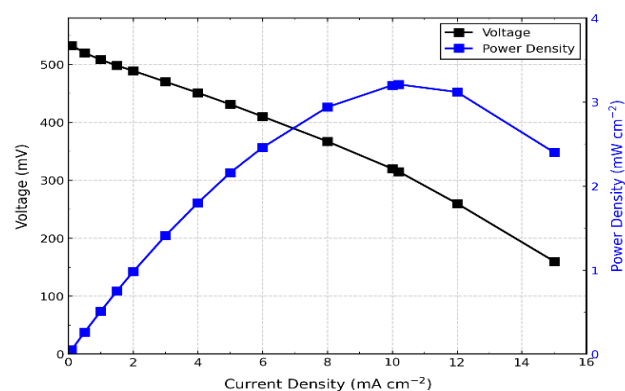


Figure 4. Simultaneous thermogravimetry and differential scanning calorimetry of the Li–Na–Cs carbonate electrolyte (26:35:39 by mass) under argon at 10 °C min^{−1}.

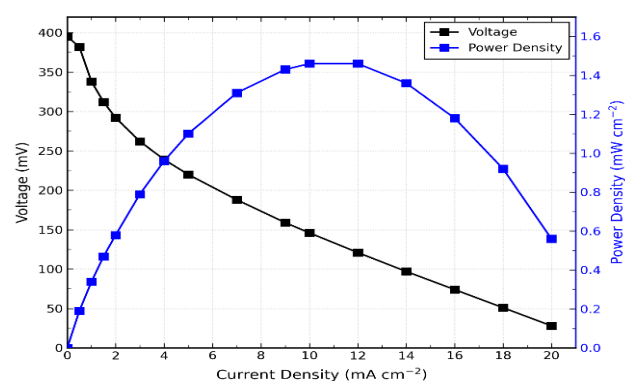
Because the analysis was performed under argon and the cell operates under a CO₂-containing atmosphere, the melting temperature reported here should be regarded as a lower bound on the stability of the melt under operating conditions. Carbonate decomposition is strongly atmosphere-dependent: the equilibrium $M_2CO_3 \rightleftharpoons M_2O + CO_2$ is displaced toward the carbonate in the presence of CO₂. Consequently, alkali carbonate melts exhibit substantially higher thermal stability under CO₂ than under inert gas. Jiang et al., for example, showed that a Li–Na carbonate eutectic displays no measurable mass loss up to 600 °C under CO₂, whereas significant decomposition already occurs at 500 °C under nitrogen [15]. Under the 30:70 O₂/CO₂ cathode atmosphere used in the present cell, significant thermal decomposition of the electrolyte is therefore not expected at the operating temperature of 500 °C.

3.3 Electrochemical performance

Polarisation and power-density curves at 500 °C are shown in Figure 5. Kraft lignin reaches a peak power density of 3.2 mW cm^{−2} at a cell voltage of 315 mV, whereas organosolv lignin delivers 1.5 mW cm^{−2} at 145 mV. The open-circuit voltages differ in the same direction and by a substantial margin, 0.535 V for kraft against 0.395 V for organosolv. Referenced to the Nernst potential of 0.99 V computed in Section 2.3, the voltage efficiencies at maximum power are 32% for kraft lignin and 15% for organosolv lignin. Kraft lignin therefore outperforms organosolv lignin on both metrics; the two do not trade off against one another, and the practical implication is favourable, since the cheaper and vastly more abundant of the two technical lignins is also the better fuel.



(a) Kraft lignin. Open-circuit voltage 535 mV; peak power density 3.2 mW cm^{−2} at 315 mV.



(b) Organosolv lignin. Open-circuit voltage 395 mV; peak power density 1.5 mW cm^{−2} at 145 mV. Both cells reach maximum power near 10 mA cm^{−2}.

Figure 5. Polarisation and power-density curves of the MC-LFC at 500 °C

Tafel analysis of the activation region (Figure 6) yields apparent slopes of 95 mV decade^{−1} for kraft lignin and 135 mV decade^{−1} for organosolv lignin, obtained by linear regression over the interval $\log(i / \text{mA cm}^{-2}) = -0.5$ to 1.05 (1.55 decades). The lower bound of the window corresponds to the onset of the low-overpotential regime, where the Butler–Volmer equation can no longer be approximated by its Tafel limit; the upper bound is set just before the sharp upward deviation that signals the growing influence of mass-transport limitations.

Extrapolation of the linear fits to zero overpotential gives apparent exchange current densities of 0.132 mA cm^{−2} for kraft lignin and 0.415 mA cm^{−2} for organosolv lignin. At the operating temperature of 773 K, $2.303 \text{ RT/F} = 153.4 \text{ mV decade}^{-1}$. The observed slopes therefore correspond, through Eq. (4), to αn values of 1.61 (kraft) and 1.14 (organosolv). Assuming a charge-transfer coefficient $\alpha \approx 0.5$ gives apparent n values of ≈ 3.2 and ≈ 2.3 , respectively. These quantities should not be interpreted as stoichiometric electron numbers: the measurements are cell-level, two-electrode responses without a reference electrode, and the fitted Tafel region may contain contributions from both electrodes. They are therefore used only as apparent kinetic descriptors.

Two points merit emphasis. First, although both regressions exhibit excellent coefficients of determination, the organosolv data in particular display a slight systematic curvature at the

highest current densities inside the fitting window; the reported slopes should therefore be regarded as apparent Tafel slopes. Second, and more importantly for the interpretation of cell performance, organosolv lignin possesses both the higher exchange current density and, within the low-current portion of the curves, comparable or even lower activation overpotentials. Despite these kinetic advantages, it delivers less than half the peak power density of kraft lignin. Consequently, the pronounced difference in overall performance between the two fuels cannot be ascribed primarily to the apparent charge-transfer kinetics; the analysis below shows that it originates predominantly from the open-circuit-voltage difference.

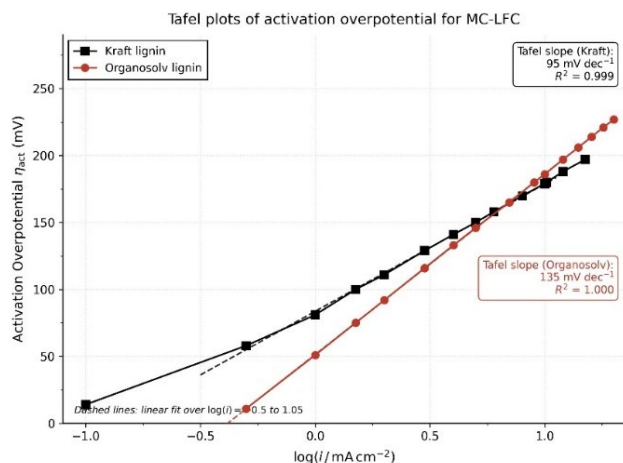


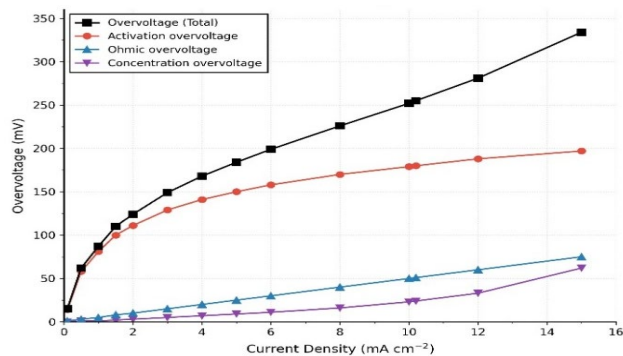
Figure 6. Tafel plots of the activation overpotential for the MC-LFC operated with kraft and organosolv lignin at 500 °C. Dashed lines are linear regressions over $\log(i / \text{mA cm}^{-2}) = -0.5$ to 1.05.

Deconvolution of the total overvoltage into activation, ohmic and concentration components is shown in Figure 7, and the three contributions are compared at 5 mA cm⁻² in Figure 8. Activation overvoltage dominates for both fuels, accounting for 150 mV of a 184 mV total for kraft lignin and 146 mV of a 176 mV total for organosolv lignin, that is, about 82% of the polarisation loss in each case. The ohmic contribution is small and similar for the two cells (25 and 28 mV at 5 mA cm⁻²), and the concentration contribution is negligible below 10 mA cm⁻².

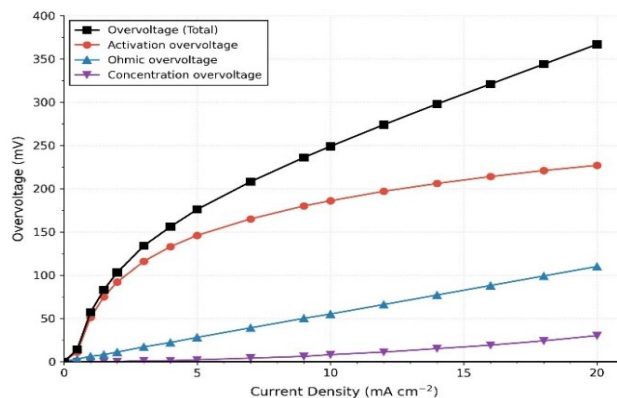
The striking feature of these data is how little the polarisation behaviour depends on the fuel. The total overvoltages at 5 mA cm⁻² differ by 8 mV, the activation components by 4 mV and the ohmic components by 3 mV, and both cells reach maximum power at essentially the same current density, near 10 mA cm⁻². If anything, the marginally lower activation overvoltage and the lower apparent Tafel slope belong to organosolv lignin, the fuel that delivers less than half the power. The performance difference between the two cells therefore does not originate in their polarisation behaviour at all. It originates almost entirely in the open-circuit voltage, which differs by 135 mV, and that is the subject of the following section.

A consistency check should be reported alongside these figures. For organosolv lignin the deconvolution reproduces the measured polarisation curve at every current density: subtracting the total overvoltage of Figure 7b from the open-

circuit voltage of 395 mV returns 290, 219, 146 and 97 mV at 2, 5, 10 and 14 mA cm⁻², against measured values of 290, 220, 145 and 97 mV. For kraft lignin the same operation does not close; consequently, the fitted loss decomposition for the kraft cell should be regarded as indicative rather than quantitatively resolved, and mechanistic conclusions should not depend on the absolute partitioning of its activation, ohmic and concentration terms.



(a) MC-LFC Kraft lignin at 500 °C.



(b) MC-LFC Organosolv lignin at 500 °C.

Figure 7. Deconvolution of the total overvoltage into activation, ohmic and concentration components as a function of current density

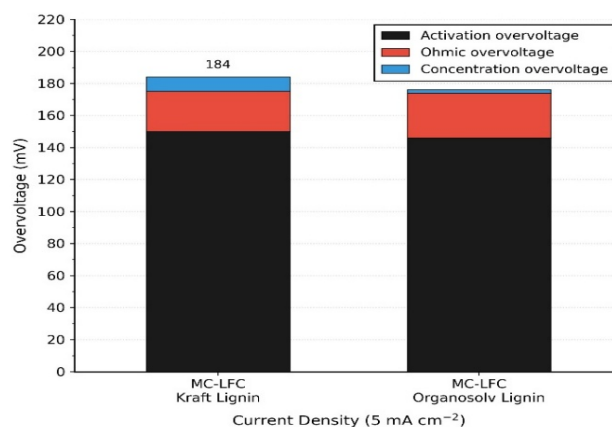


Figure 8. Contributions to the total overvoltage at 5 mA cm⁻² for the MC-LFC operated with kraft and organosolv lignin. Activation overvoltage accounts for 150 of 184 mV (kraft) and 146 of 176 mV (organosolv).

3.4 The open-circuit deficit and the mixed anode potential

The most informative feature of the electrochemical data is not the polarisation behaviour but the open-circuit voltage itself. With a properly fed 30:70 O₂/CO₂ cathode, the Nernst potential of the cell lies between 0.99 and 1.11 V at 773 K, depending on the CO₂ partial pressure at the anode. The measured open-circuit voltages are 0.535 and 0.395 V, so 455 mV and 595 mV respectively are lost before any current is drawn. Since the polarisation losses at maximum power amount to only 215 and 260 mV, the open-circuit deficit is by a wide margin the dominant loss in this cell. Figure 9 presents the complete voltage budget on this basis.

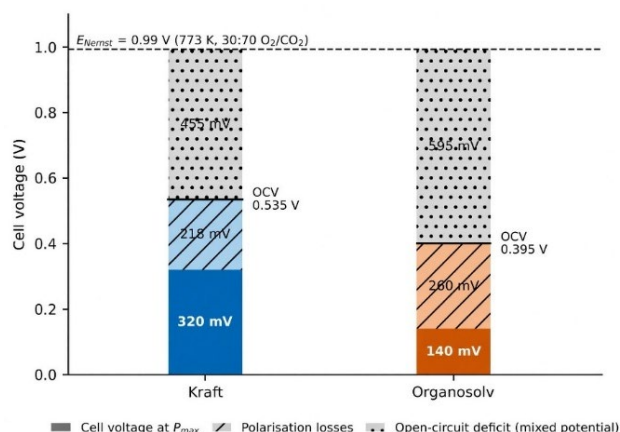


Figure 9. Voltage-loss budget of the MC-LFC at 500 °C, referenced to the Nernst potential of 0.99 V computed for the 30:70 O₂/CO₂ cathode at 773 K. For both fuels the open-circuit deficit exceeds the sum of all polarisation losses at maximum power.

This deficit cannot be attributed to the composition or impurity content of the lignin. Reproducing the kraft open-circuit voltage thermodynamically by lowering the carbon activity alone would require the carbon activity to fall to approximately 1.1×10^{-12} , which is not physically meaningful for a solid carbon phase present in large excess. Nor can it be explained by any alternative equilibrium accessible in this system: at 773 K the partial-oxidation couple $C + \frac{1}{2} O_2 \rightarrow CO$ gives 0.933 V, and even a fully oxidised nickel anode with no fuel participating at all would sit at 0.883 V for the Ni/NiO couple. Every equilibrium potential available to the cell lies at least 340 mV above the measured value. The open-circuit voltage is therefore inconsistent with a simple equilibrium interpretation and supports a mixed-potential interpretation.

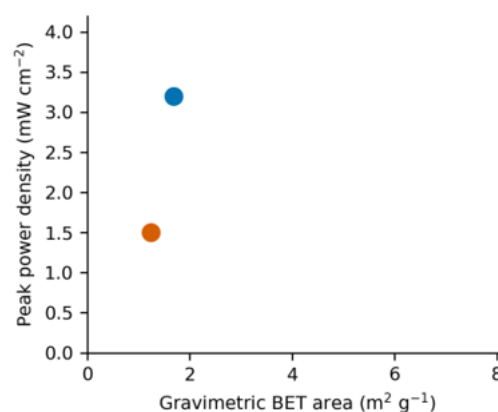
A second observation identifies where that mixed potential originates. The two fuels differ by 135 mV at open circuit despite containing the same carbon content to within 1.5% and having essentially identical heating values. A true equilibrium potential for carbon oxidation cannot depend on which lignin is loaded, because the activity of the solid carbon phase is close to unity in both cases. The fuel-dependent open-circuit voltage therefore supports a kinetically controlled mixed-potential interpretation, potentially linked to the extent and quality of the fuel–melt–collector contact, rather than a simple equilibrium potential.

Two mechanisms can produce such a mixed potential in a matrix-free crucible cell. The first is oxidant crossover between compartments, which would allow direct chemical combustion of lignin at the anode and depress the anode potential; this is a recognised failure mode of matrix-free molten carbonate cells [37]. The second is incomplete triple-phase contact, in which only a fraction of the loaded carbon is electrochemically addressed and parasitic couples contribute to the measured potential. The present data cannot discriminate between them definitively, but they favour the second: crossover would be expected to affect both cells similarly, whereas the observed deficit is strongly fuel-dependent and correlates with the textural descriptors analysed in Section 3.5.

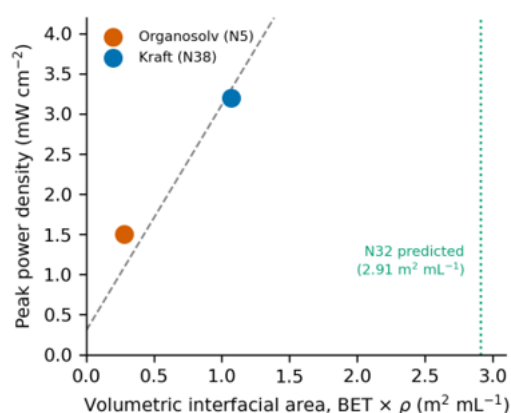
3.5 The fuel structure–performance relationship

The performance difference between the two fuels is a factor of 2.13 in peak power and 1.34 in open-circuit voltage. Neither is explained by bulk composition, since the two lignins differ by less than 2% in carbon content and by less than 1% in total hydroxyl content. Nor is the observed difference proportional to gravimetric BET area: the BET areas differ by only a factor of 1.36, compared with a factor of 2.13 in peak power. With only two electrochemically tested lignins, Figure 10a should be interpreted descriptively rather than as evidence of a statistical relationship.

The resolution follows from the geometry of the electrode. The anode is a fixed volume of nickel foam impregnated with a lignin slurry, so the quantity that governs the available reaction interface is not surface area per unit mass but surface area per unit electrode volume. Weighting the BET area by the apparent packing density gives a volumetric BET surface area of 0.279 m² mL^{−1} for organosolv lignin and 1.070 m² mL^{−1} for kraft lignin, a factor of 3.8. The descriptor reproduces the observed ordering of the two fuels and is physically consistent with the factor of 2.13 difference in power (Figure 10b), although two tested fuels are insufficient to establish a quantitative correlation. Expressed per unit of bed volume, the pore volume differs by a factor of 10.6 in the same direction.



(a) peak power density against gravimetric BET surface area, showing no relationship



(b) peak power density against volumetric BET surface area (BET area weighted by apparent packing density).

Figure 10. Relationship between lignin texture and cell performance, which orders the two fuels correctly. The dotted line marks the volumetric BET surface area of the third characterised lignin (N32), for which the mechanism proposed here predicts substantially higher performance

That the power ratio is smaller than the interfacial-area ratio is itself informative, since it implies that not all of the available interface is electrochemically active. Three independent measurements indicate that the unwetted fraction should be larger for organosolv lignin. First, pore accessibility: the average pore width of organosolv lignin is 54 Å against 149 Å for kraft lignin, and infiltration of molten carbonate into pores of order 5 nm may be less facile than into pores of order 15 nm, so organosolv lignin's accessible area is the more strongly overstated by its BET value. Second, surface polarity: kraft lignin carries 2.6 times the carboxylic acid content and, on the ICP determination, 55 times the sulfur content, both of which raise surface polarity and hence wetting by an ionic melt. Third, lipophilicity: at 65.1 wt % soluble in ethanol against 15.5 wt % for kraft lignin, the higher ethanol solubility of organosolv lignin is consistent with a more lipophilic character. The importance of wetting is consistent with recent quantitative studies of molten-carbonate contact angles on carbon, which show that surface chemistry and atmosphere strongly control the rate and extent of electrolyte spreading [52,53].

One apparent tension must be addressed. If kraft lignin presents 3.8 times the interfacial area per unit anode volume, then at a given geometric current density the true current density on its active surface is correspondingly lower, and its activation overvoltage should be lower by roughly $\ln(3.8)$, or about 48 mV. Figure 8 shows the two activation overvoltages within 4 mV of one another. The most economical explanation is that the activation term measured here is not an anode property. These are two-electrode measurements without a reference electrode, so the activation overvoltage is a cell-level quantity, and the cathode — an identical flame-oxidised NiO electrode in both cells — is common to the two experiments. A charge-transfer process limited at the cathode would produce an activation overvoltage that is almost independent of the fuel, which is what is observed. The Tafel analysis must be interpreted consistently with the fitted slopes: assuming $\alpha \approx 0.5$ gives apparent n values of ≈ 3.2 for kraft and ≈ 2.3 for organosolv, while the apparent

exchange current densities are 0.132 and 0.415 mA cm⁻², respectively. Because these are cell-level two-electrode quantities, they do not identify a stoichiometric electron number or isolate the anode kinetics. The similar activation losses observed for the two fuels are compatible with a substantial contribution from the common NiO cathode, whose reaction, Eq. (2), is a four-electron process, but the present data do not establish cathode limitation. On this more cautious reading, fuel-dependent interfacial effects are implicated primarily in the open-circuit mixed potential, whereas the origin of the polarisation response remains to be resolved with electrode-specific measurements. The interpretation is consistent with all of the present data but it is not established by them; impedance spectroscopy with a reference electrode, or a symmetric-cell measurement, would settle it directly and is the most informative single experiment that could be added to this study.

Taken together, these observations support a working hypothesis in which MC-LFC performance is influenced more strongly by wetted interfacial area per unit anode volume than by gravimetric BET area alone. The relevant interface is expected to depend jointly on packing density, pore accessibility and surface polarity. Kraft lignin is favoured on all three counts, and the same mechanism could contribute to its higher open-circuit voltage, since a larger wetted interface displaces the mixed potential of Section 3.4 towards the thermodynamic value. Sulfur enters this account not as a catalyst but as one of several contributors to surface polarity, which is important because the molten carbonate literature is unambiguous that sulfur poisons nickel anodes at concentrations three orders of magnitude below those present here [19]. We therefore make no claim that sulfur improves interfacial kinetics; post-mortem analysis of the anode would be required to establish what the sulfur actually does.

This account also reproduces an independent result. Bohn Lima et al. compared kraft lignin with lignosulfonate under otherwise identical conditions and found that the more hydrophilic lignosulfonate outperformed kraft by a factor of two, concluding that hydrophilicity was the critical variable [46]. Ordering the three materials by lipophilicity gives lignosulfonate, then kraft, then organosolv, and the power densities follow the same sequence across the two studies. The mechanism proposed here is thus consistent with the only comparable dataset in the literature.

The hypothesis makes a testable prediction. A third technical lignin characterised alongside the two studied here (sample N32, a biorefinery lignin recovered by filtration) has a BET area of 7.41 m² g⁻¹ and a packing density of 0.393 g mL⁻¹, giving a volumetric BET surface area of 2.91 m² mL⁻¹ — 2.7 times that of kraft lignin. If the proposed wetted-volumetric-interface hypothesis is correct, this material would be expected to outperform kraft lignin in the same cell. This is a sharp and readily falsifiable test of the mechanism, and it is the experiment we regard as the highest priority for future work.

3.6 Comparison with other direct carbon fuel cell technologies

Table 4 places the present results alongside the reported performance of other direct carbon and direct lignin systems. The comparison must be made honestly: at 3.2 mW cm⁻² the

present cell is one to two orders of magnitude below high-temperature molten carbonate and hybrid systems, and roughly a factor of four below the closest comparator, the 12 mW cm⁻² obtained by Bohn Lima et al. with kraft lignin at 560 °C [46]. Several factors contribute to that gap: the present fuel was used without blending with activated carbon, the operating temperature is 60 °C lower, the electrode geometry is unoptimised, and — as Section 3.4 establishes — the cell operates far from its thermodynamic potential. It is worth noting that Bohn Lima et al. also report a sub-thermodynamic open-circuit voltage of approximately 0.70 V, so the deficit analysed here is a characteristic of this device class rather than a defect peculiar to the present cell.

Comparison with low-temperature lignin flow cells, which reach 160–270 mW cm⁻² [34,35], is not meaningful on a power-density basis because these are a different device class: they operate in the liquid phase with engineered electrocatalysts or redox mediators and produce depolymerisation products rather than complete oxidation to CO₂. The appropriate axes of comparison are device class, fuel handling and product stream, not peak power.

The defensible claim arising from Table 4 is narrower but genuine. Every other molten carbonate entry in the table operates between 700 and 850 °C. The present work demonstrates operation of a solid-lignin-fuelled molten carbonate cell at 500 °C, the lowest reported for this configuration, and quantifies the loss structure that results. The contribution of this paper is diagnostic and correlative rather than a performance record, and the practical value of the intermediate-temperature approach — reduced corrosion and electrolyte volatilisation — is an expectation supported by the materials literature rather than a result demonstrated here.

Table 4. Benchmarking against reported direct carbon and direct lignin systems. Values are those reported by the original authors.

System	Fuel	T (°C)	P _{max} (mW cm ⁻²)	Ref.
MC-LFC (this work)	Kraft lignin	500	3.2	—
MC-LFC (this work)	Organosolv lignin	500	1.5	—
Hybrid MCFC/SOF C	Kraft lignin + AC	560	12	[46]
Hybrid MCFC/SOF C	Lignosulfonate + AC	560	24	[46]
Matrix-free MCFC	Bamboo charcoal	800	430	[37]
Matrix-free MCFC	Wood	800	410	[37]
Hybrid DCFC	Pyrolysed MDF charcoal	750	878	[38]
Direct carbon SOFC	Ca-loaded activated carbon	850	373	[42]
Lignin flow cell	Industrial lignin, mediator-free	90	160	[34]
Lignin flow cell	Industrial lignin, CoMn-LDH	100	269	[35]

Notes: P_{max} in mW cm⁻². AC = activated carbon. Flow-cell entries are a different device class and are not comparable on a power-density basis.

3.7 Position relative to indirect lignin-to-hydrogen routes

Direct electrochemical conversion of solid lignin competes with the conventional indirect route in which lignin is first gasified or steam-reformed to a hydrogen-rich syngas that is subsequently purified and fed to a low- or intermediate-temperature fuel cell. Typical stage efficiencies reported in the literature allow a first-order well-to-electricity comparison.

Cold-gas efficiency of lignin gasification or fast pyrolysis followed by reforming lies in the range 65–80% [57–59]. Subsequent water-gas-shift, purification and compression consume an additional 10–15% of the chemical energy. A polymer-electrolyte or solid-oxide hydrogen fuel cell then converts the purified H₂ at 45–60% electrical efficiency [58,60]. The product of these stages yields an overall well-to-electricity efficiency of roughly 25–40% under realistic process conditions.

In the present MC-LFC the measured voltage efficiency at peak power is 15–32%, primarily because of the large open-circuit deficit. Reducing that deficit would increase cell voltage and therefore voltage efficiency. However, voltage efficiency is not equivalent to well-to-electricity efficiency: fuel utilisation, faradaic efficiency, parasitic energy demand and durability were not measured here. The present data therefore do not support a quantitative claim that the direct route is competitive with, or superior to, the multi-step gasification–hydrogen pathway. Rather, the comparison identifies open-circuit loss and interfacial engineering as priorities that must be resolved before a rigorous system-level comparison can be made. The shared carbonate-electrolyte physics nevertheless makes these interfacial findings relevant to carbonate-based electrolysis and hydrogen-carrier conversion routes.

3.8 Limitations

Several limitations bound the conclusions drawn above and are stated here explicitly. The comparison is confounded by botanical origin: kraft lignin is derived from softwood and organosolv lignin from hardwood, so pulping chemistry, sulfur content, oxygen content, hydroxyl speciation, molecular weight and morphology all vary together, and the structure–performance relationship of Section 3.5 identifies a correlation supported by a physical mechanism rather than a controlled decoupling. No electrochemical impedance data were acquired, so the ohmic resistance is a fitted quantity, no iR correction was applied, and the separation of loss terms is model-dependent. In the absence of a reference electrode all overpotentials are cell-level and cannot be assigned to a single electrode. No off-gas analysis was performed, so reaction stoichiometry and product selectivity are not confirmed by a coulombic balance; no faradaic efficiency or fuel utilisation is reported, and the efficiencies quoted are voltage efficiencies only. The apparent n values derived from Tafel slopes are cell-level kinetic descriptors and should not be used as direct evidence for a four-electron carbon-oxidation pathway. Measurements were of short duration, so no statement about durability is possible. Although the polarisation curves

represent averages of three independent cell builds ($n = 3$), this sample size is too small to support strong statistical inference; the kraft–organosolv comparison should therefore be interpreted primarily as a reproducible descriptive contrast. In addition, the loss decomposition does not reconstruct the kraft polarisation curve exactly, which further limits quantitative attribution of individual loss terms. Finally, the discrimination between oxidant crossover and incomplete triple-phase contact as the origin of the mixed potential (Section 3.4) is argued from indirect evidence and would require a blank-cell measurement and impedance spectroscopy to settle.

4. CONCLUSIONS

Kraft lignin outperforms organosolv lignin as a solid fuel in a molten carbonate cell operated at 500 °C, delivering 3.2 against 1.5 mW cm⁻² and a voltage efficiency at maximum power of 32% against 15%. The two metrics do not trade off, so the cheaper and more abundant technical lignin is also the better fuel. Apparent Tafel slopes of 95 and 135 mV decade⁻¹ correspond to α n values of 1.61 and 1.14. Because these are cell-level two-electrode measurements, they are treated as apparent kinetic descriptors and do not by themselves establish the electron stoichiometry of lignin oxidation.

The dominant loss in this cell is not polarisation but the open-circuit deficit: with a 30:70 O₂/CO₂ cathode the Nernst potential is 0.99 V, yet the cells open at 0.535 and 0.395 V. No accessible equilibrium and no physically meaningful carbon activity accounts for this, and the deficit is fuel-dependent, which supports a kinetically controlled mixed-potential interpretation rather than a simple thermodynamic-equilibrium interpretation.

The performance difference between the two fuels is not explained by gravimetric surface area, which differs by only 36%, but by the volumetric BET surface area — BET area weighted by packing density — which differs by a factor of 3.8 and follows the power ordering. Pore accessibility, surface polarity and lipophilicity measurements all indicate that the wetted fraction of that interface is additionally smaller for organosolv lignin. For the two fuels tested, the results are therefore consistent with wetted interfacial area per unit anode volume being a more informative performance descriptor than gravimetric surface area alone; validation with additional lignins is required to establish the relationship quantitatively. Three lines of work follow directly. A third lignin already characterised here has a volumetric BET surface area 2.7 times that of kraft lignin and offers a sharp test of the proposed mechanism. Impedance spectroscopy with a blank-cell control would separate the ohmic, charge-transfer and mass-transport contributions and determine whether oxidant crossover contributes to the mixed potential. An off-gas coulombic balance during a galvanostatic hold would determine product selectivity and faradaic efficiency, test whether the net oxidation approaches the expected four-electron pathway to CO₂, and provide the information needed, together with fuel utilisation, to progress from voltage efficiency toward a defensible energy-efficiency assessment. Closing the open-circuit deficit is the single change that would most raise the performance of this cell, and on the present analysis the results suggest that this is primarily an interfacial-engineering rather than a thermodynamic limitation.

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APPENDIX

(1) Appendix. Summary of electrochemical performance of MC-LFC at 500 °C.

Quantity	Kraft	Organosolv
Nernst potential at 773 K (V)	0.99	0.99
Open-circuit voltage (V)	0.535	0.395
Open-circuit deficit (mV)	455	595
Cell voltage at P _{max} (mV)	315	145
Peak power density (mW cm ⁻²)	3.2	1.5
Polarisation loss at P _{max} (mV)	215	260
Total overvoltage at 5 mA cm ⁻² (mV)	184	176
Activation component (mV)	150	146
Ohmic component (mV)	25	28
Concentration component (mV)	9	2
Apparent Tafel slope (mV decade ⁻¹)	95	135
Tafel fit R ² (4 points, 1.55 decades)	0.999	1.000
Apparent i ₀ (mA cm ⁻²)	0.132	0.415
α _n	1.61	1.14
n at α = 0.5	3.2	2.3
Voltage efficiency at P _{max} (%)	32	15

Notes: voltage efficiency is the cell voltage at maximum power divided by the Nernst potential. It is not an energy efficiency.