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# Electronic Supplementary Information

## How can thermoelectric coupling catalysis be applied to facilitate biomass conversion into value-added products and hydrogen?

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**Table S1** Key performance metrics of thermocatalysis, electrocatalysis, and thermoelectric catalysis: substrate types, reaction conditions, and product selectivity

| Performance metrics | Thermocatalysis | Electrocatalysis | Thermoelectric catalysis |
|---|---|---|---|
| Substrate | Mainly large polymers; also small molecules (low selectivity) | Small molecules | Large & small molecules |
| Typical temperature (°C) [a] | 100-250 | Room temperature | 25-100 |
| Applied potential (V vs. RHE) [a] | – | 1.2-1.8 (lower for noble metals via direct adsorption) | 0.6-1.2 |
| Major products | Furanics, sugars, levulinic acid | Formate, xylonic acid, 2,5-Furandicarboxylic acid | 2,5-Furandicarboxylic acid, formate, furans |
| Applicable to macromolecular biomass | Yes | No | Yes |
| Faradaic efficiency [a] | – | 60-95%[1-4] | > 90%[5, 6] |
| Product selectivity | Low | High | High |

[a] The reported values represent typical ranges summarized from the literature and serve as reference comparisons, exceptions may exist in individual studies.

**Table S2** General criteria distinguishing reversible vs. irreversible reconstruction under thermoelectric fields

| Descriptor category | Reversible/Adaptive surface evolution (strategy: engineer-controlled evolution) | Irreversible/Structural failure (strategy: preserve intrinsic lattice stability) | Assessment method |
|---|---|---|---|
| Driving principle | Field-regulated, shallow restructuring enabling optimized intermediate binding | Thermally accelerated disorder leading to permanent structural destabilization | - |
| Atomic coordination | Mild, recoverable change in metal-ligand coordination; surface-limited adjustments | Collapse or significant loss of coordination framework; bulk transformation | *Operando* EXAFS/XAS |
| Electronic configuration | Tunable electronic states (e.g., reversible valence modulation, controllable orbital occupancy) responsive to temperature | Uncontrolled charge redistribution; trapped high-valence species or electronic disorder | XPS, XAS edge shift, DOS analysis |
| Surface phase behavior | Transient surface ordering/local motif rearrangement; reversible upon cooling or OCV | Amorphization, grain boundary proliferation, dissolution-driven vacancy runaway | *Operando* Raman/XRD |
| Energy landscape | Moderate reduction in activation barrier/ΔG for key steps (e.g., ~0.3–0.7 eV tuning) without destabilizing lattice[7-9] | Loss of energetic selectivity window; drastic ΔG shifts (> 1.0 eV) leading to non-selective pathways[10] | DFT + kinetic analysis |
| Electrochemical signature | Minimal, reproducible hysteresis; stable slopes under cycling[11] | Progressive hysteresis growth; decay in charge-transfer characteristics[12] | LSV, Tafel, EIS |
| Chemical stability/Leaching | Minimal leaching (<0.1–0.3% /100 h); stable ligand or lattice integrity[13, 14] | Accelerated dissolution/ligand loss; irreversible composition drift[15] | ICP-MS/in situ UV-Vis |
| Operational stability | Maintains function under temperature fluctuations and industrial-level current stress | Degradation accelerated by Joule heating, bubble stress, or thermal gradients | MEA/flow cell tests |
| Design rules | Controlled, surface-confined, and reversible structural adaptation | Strong scaffold, inhibited lattice flexibility, robust ligation environment | Material selection + computational screening |

**Table S3** Representative design strategies linking challenges, engineering solutions, and performance benefits across different scales.

| Design Scale | Key Challenge | Engineering Strategy | Representative Catalyst | Performance Benefit / Mechanism | Ref. |
|---|---|---|---|---|---|
| Atomic Scale | Competition between organic/$OH^-$ adsorption | Heterointerface electronic modulation | $CeF_3$@$Ni_3N$ | Enhanced co-adsorption; lowered potential for MOR from 1.60 V (OER) to 1.38 V | 16 |
| | Sluggish reaction kinetics (high $E_a$) | Defect engineering (dual-cation vacancies) | High-entropy layered double hydroxides | Reduced ΔG for *OH-to-*OOH step from 1.09 eV to 0.52 eV | 17 |
| | CO poisoning of active sites | High-entropy alloy environment | $Pt_1$-NiCoMgBiSn | Modified d-band center (-2.22 to -2.73 eV); maintained durability for 180,000 s | 18 |
| | Thermal sintering of single atoms | Strong metal-support interaction | FeNi on $WC_x$ | Maintained atomic dispersion after annealing at 900 °C | 19 |
| Interfacial Scale | Low local reactant concentration | Local electric field enhancement | CuO@Co-MOF | Increased interfacial $OH^-$ concentration and facilitated organics transfer | 20 |
| | Diffusion barrier of bulky molecules | Disruption of H-bond network | $Ni(OH)_2$/$Cu(OH)_2$ | Weakened interfacial water network; enabled high current density of 1.3 A $cm^{-2}$ | 21 |
| | Product inhibition/Equilibrium limits | Interfacial Joule heating | COF-$SO_3H$ | Selective evaporation of product; conversion increased to 80.5% (breaking thermal limit) | 22 |
| | Bubble passivation at high currents | Ordered parallel channels | $Ni(OH)_2$ PNAs | Electrolyte flux increased by 4.4-fold (100 μm $s^{-1}$); halved bubble detachment time | 23 |
| Mesoscale | Thermal agglomeration of nanoparticles | Physical protective shell | Ni@C | Carbon shell prevented sintering; maintained high $Ni^0/Ni^{2+}$ ratio (43%) | 24 |
| | Structural instability/Leaching | Energetic anchoring via core-shell | Pd@Pd-P@Pt | Increased vacancy formation energy (+0.29 eV); retained 93.9% activity after 20,000 cycles | 25 |
| Dynamic Design | Intrinsic activity limitation | Lattice strain engineering | $Sr_2IrO_4$ | Downshifted d-band center *via* thermal expansion; overpotential reduced by 77 mV | 26 |
| | Electronic state activation | Thermal suppression of charge disproportionation | $Sr_3Fe_2O_7$ | OER activation energy (Q) reduced from 57.9 to 35.8 kJ $mol^{-1}$ | 27 |
| | High kinetic barrier for redox steps | Thermally triggered spin transition | $Ni_{0.67}Fe_{0.33}O_xH_y$ | Heat drove spin-flipping; activation energy reduced from 6.33 to 2.79 kJ $mol^{-1}$ | 28 |

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