Silver Alloys for the Oxygen Reduction Reaction in Alkaline Media

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1) Introduction

Currently the most widely used fuel cells are the proton exchange membrane FCs (PEMFC), which operate in acidic conditions and only platinum can provide high activity and stability.

Thus, switching to alkaline conditions implies:
- ✓ Enhanced ORR (oxygen reduction reaction) kinetics
- ✓ Milder conditions
- ✓ Use non-PGM (Pt-group metals)
- ✓ Inexpensive catalysts

Target: finding the activity of different metals covered by silver in order to be used as catalysts in an anion exchange membrane FC (AEMFC). Since these metals are usually *less expensive* than silver, it is important to understand if their electronic structure can affect the activity of silver.

2) Methodology

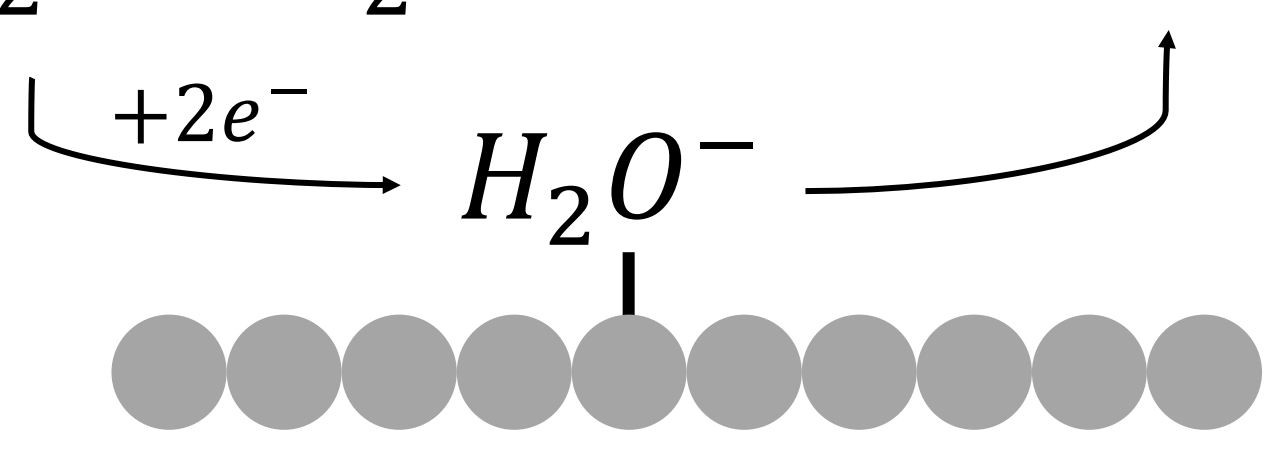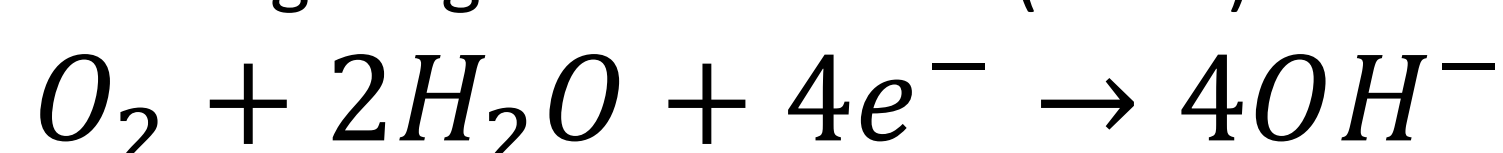i) Physical Vapor Deposition (PVD)

ii) Working electrode

Ag 3 nm
Pd, Au, Ti, V, or Ni 40 nm
Glassy carbon
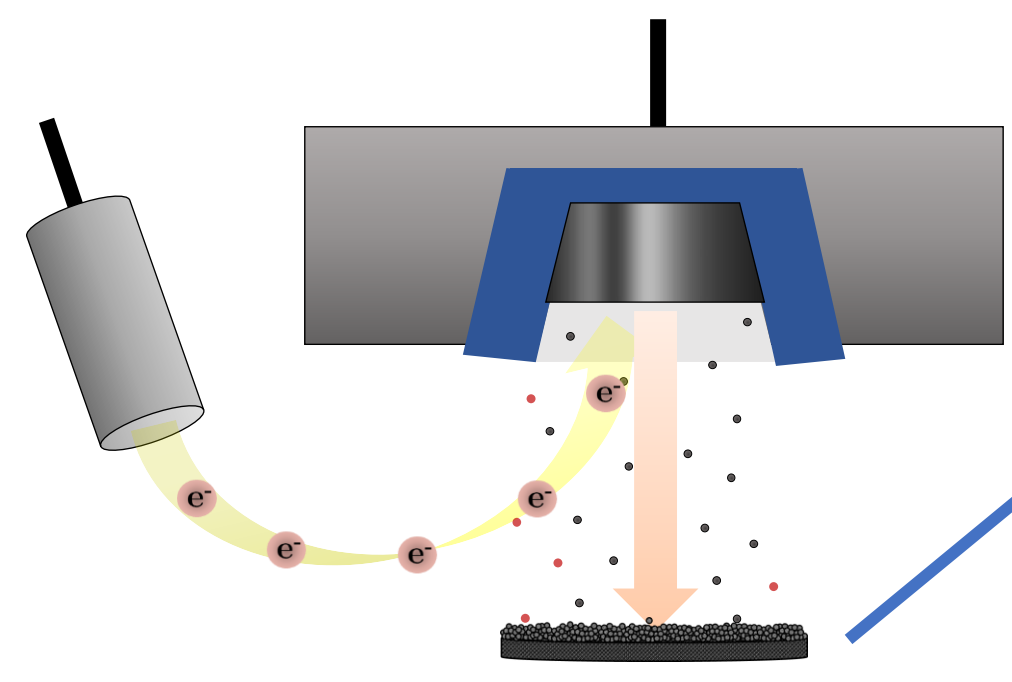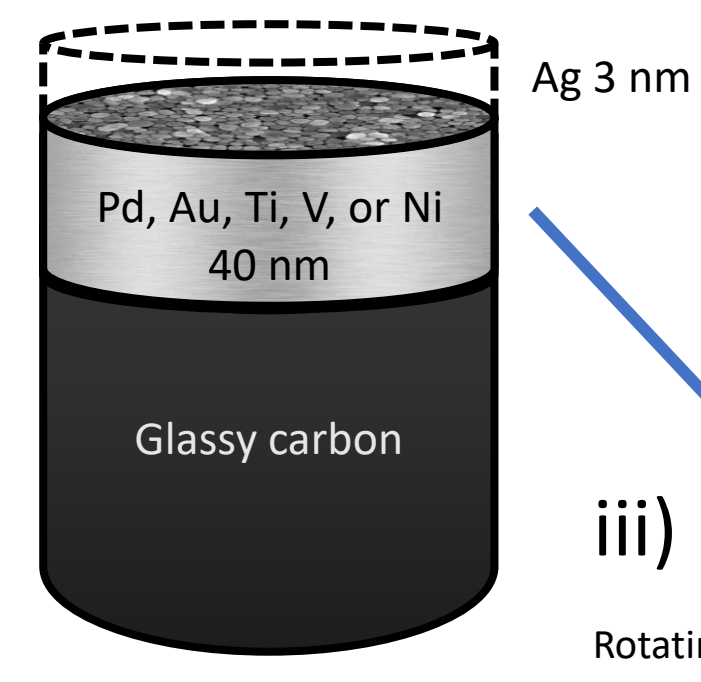
iii) RDE

Rotating Disk Electrode

iv) Cyclic Voltammetry (CV)

v) Rotating Ring Disk Electrode (RRDE)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
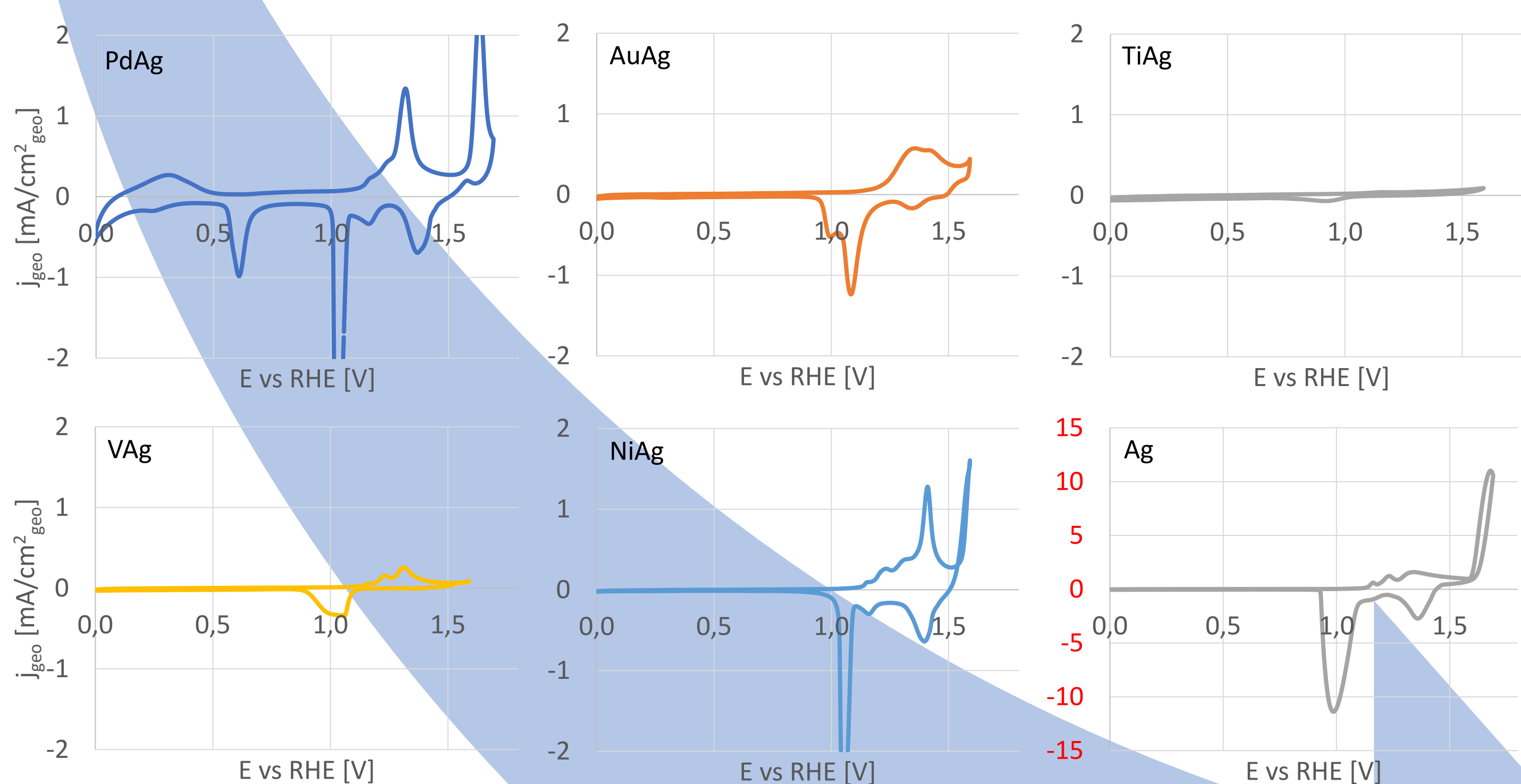$$\xrightarrow{+2e^-} H_2O^-$$

Ar

KOH 1M

vi) CV and discussion over activity of alloys
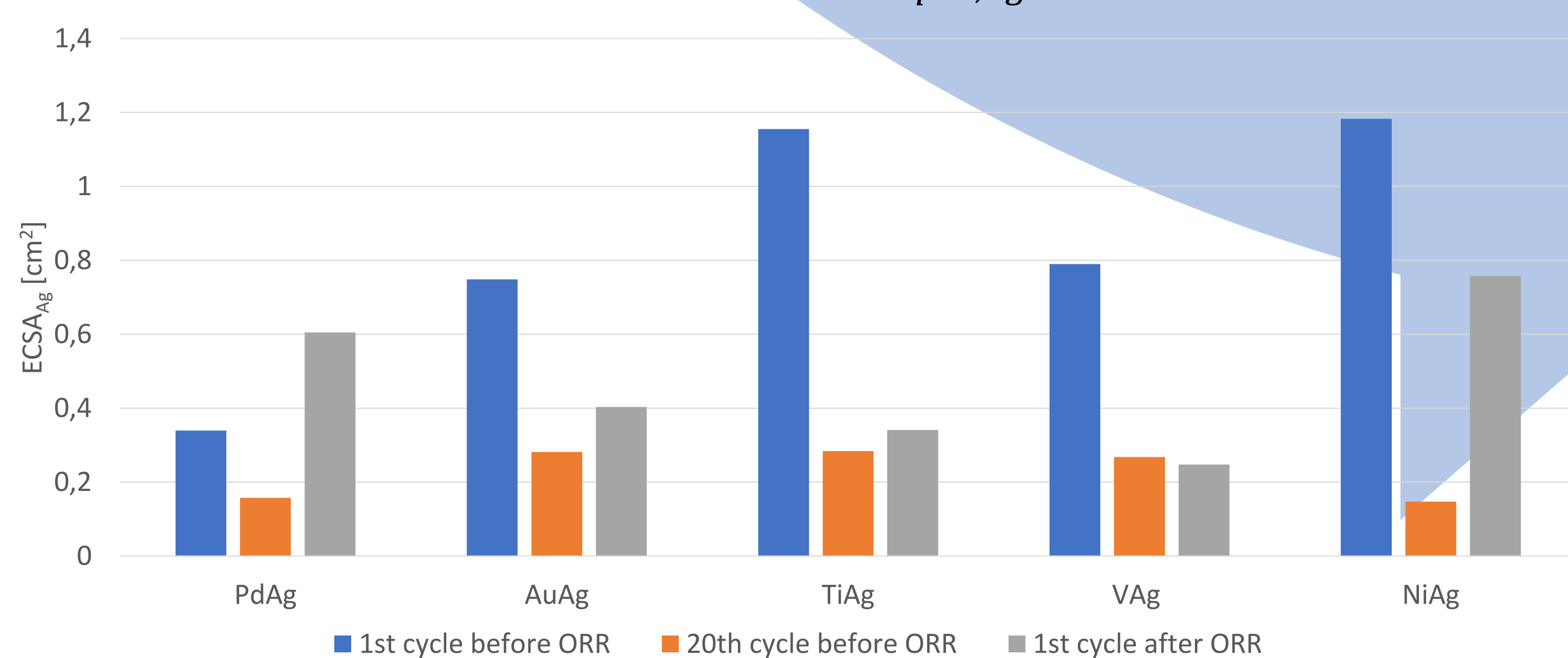
3) Results and Discussion

3.1) Cyclic Voltammetry (CV)

Potential is changed linearly with time and the generated current is measured on both cathodic and anodic scans.

The electrochemical surface area (ECSA) of silver can be obtained by the reduction peak of its oxide (AgO) at $1V_{RHE}$.

$$ECSA_{Ag} = \frac{Q_{AgO \rightarrow Ag}}{Q_{spec,Ag}}$$

3.2) ORR polarization curves

The current density is the main parameter to evaluate the efficiency of catalysts. It is the driving force since it provides the number of electrons flowing through the circuit per cm².

Geometric activity from the geometric area

Specific activity from the ECSA
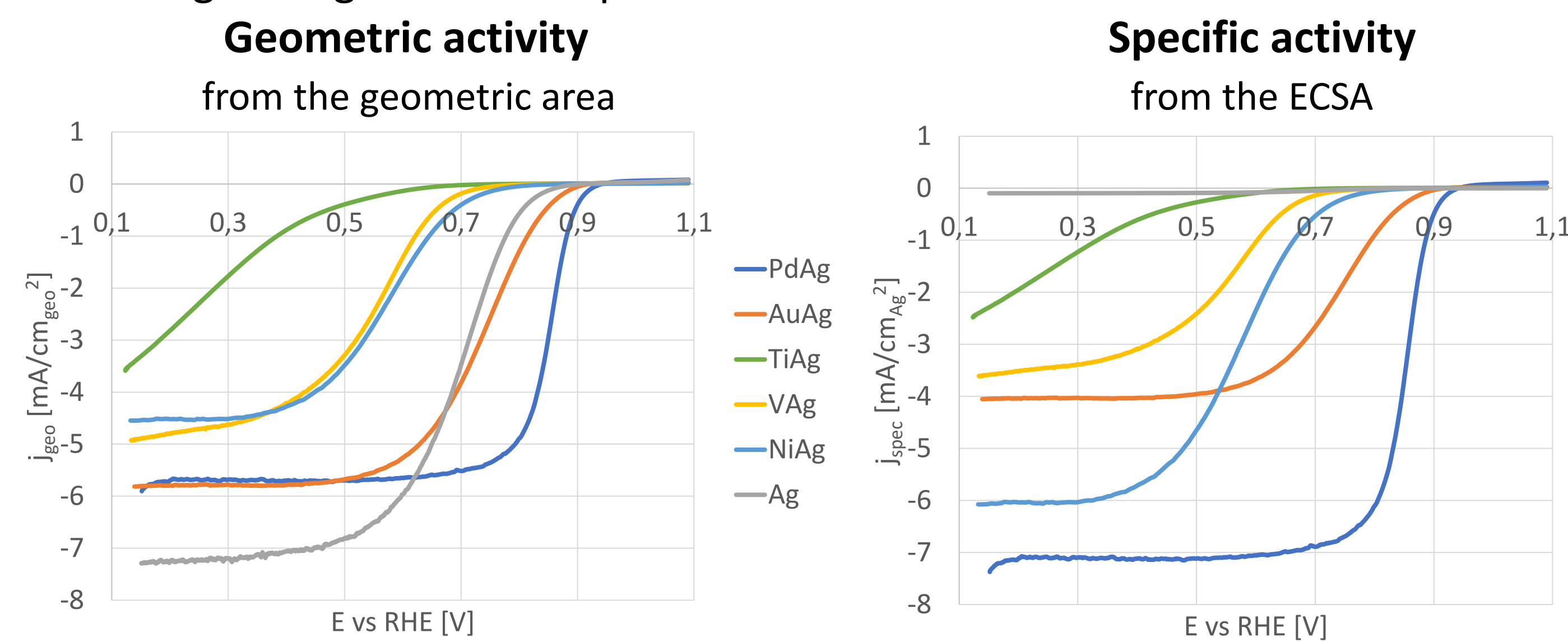
In the geometric current density:
- Silver is performing well in the mass transfer region (at low E).
- PdAg and AuAg exhibit the best activity in the kinetic region (at high E) and in the mixed region.
- TiAg is the least effective, followed by VAg and NiAg.

In the specific current density:
- PdAg is the most efficient catalyst, followed by AuAg.
- Pure silver is the least efficient, since it has many active sites.
- All catalysts exhibit different mass transport current densities due to different Ag ECSAs.

3.3) Hydrogen peroxide (H_2O_2) formation ($n_{e^-} < 4$)

Does the reaction go straight to OH⁻?
The electron transfer coefficient (n_{e^-}) can give us this information. It can be determined through the hydrogen peroxide formation on the ring electrode (N=0.25 is the collector efficiency):

$$n = 4\frac{I_d}{I_d + I_r/N}$$

And the percentage of H_2O_2 can be calculated from:

$$\%H_2O_2 = \frac{I_r/N}{I_d + I_r/N}$$

Sample	n from H₂O₂	% H₂O₂	E_onset [V]	E_1/2 [V]
PdAg	3.99	0.5	0.94	0.85
AuAg	3.99	0.4	0.92	0.74
TiAg	3.69	15.3	0.77	0.30
VAg	3.76	11.7	0.87	0.55
NiAg	3.71	14.4	0.88	0.58
Ag	3.97	1.2	0.91	0.70

3.4) X-ray Photoelectron Spectroscopy (XPS)

- Elemental composition analysis
- Surface sensitive (~3 nm)
- Qualitative and quantitative
- All of them have 60% Ag as-evaporated
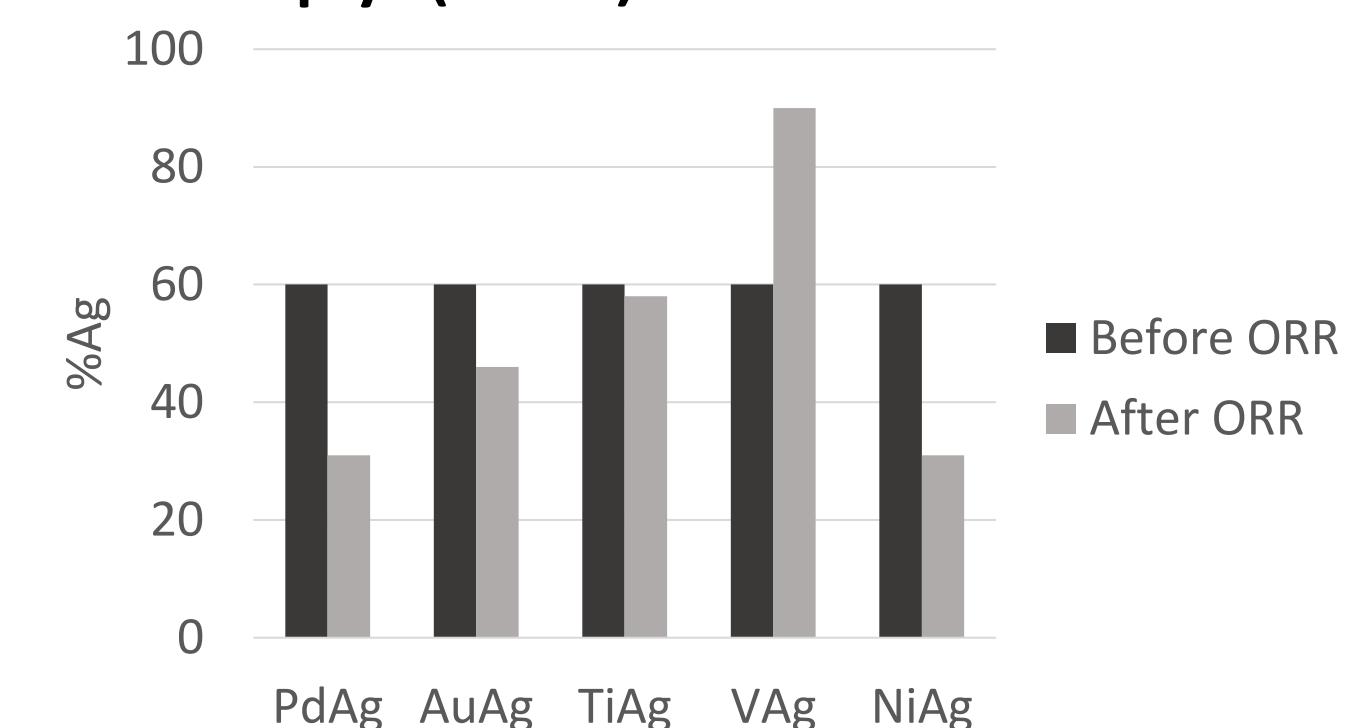
4) Conclusions

The combination between silver and different metals is not always successful: titanium, nickel and vanadium decrease the activity of silver through alloying.

However, good candidates for future research can be palladium and gold since they can provide very good durability and very high activity at potentials relevant for FCs.

Hypothesis: this behaviour can be attributed to the electronic structure of the alloying metal: Ti (d²) < V (d³) < Ni (d⁸) < Au (d¹⁰) = Pd (d¹⁰)

TRA105 Fuel Cell Systems