

# Direct conversion of sunlight into useful energy: a whole new world

Adélio Mendes

Light, from the Earth to the Stars  
Lisbon, July 2<sup>nd</sup>, 2015



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Faculdade de Engenharia

**FEUP**

Chemical Engineering Department

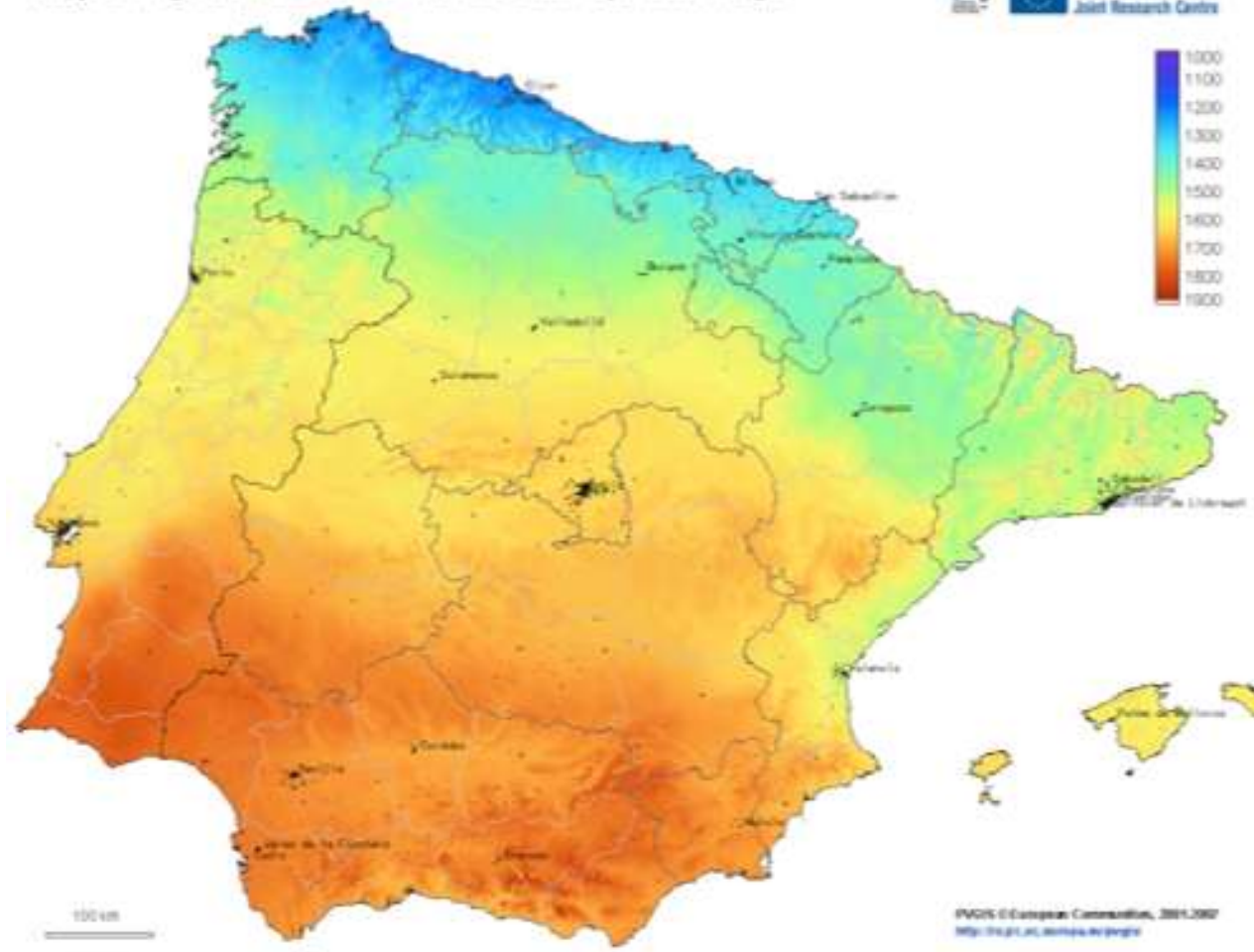


**Lepabe**

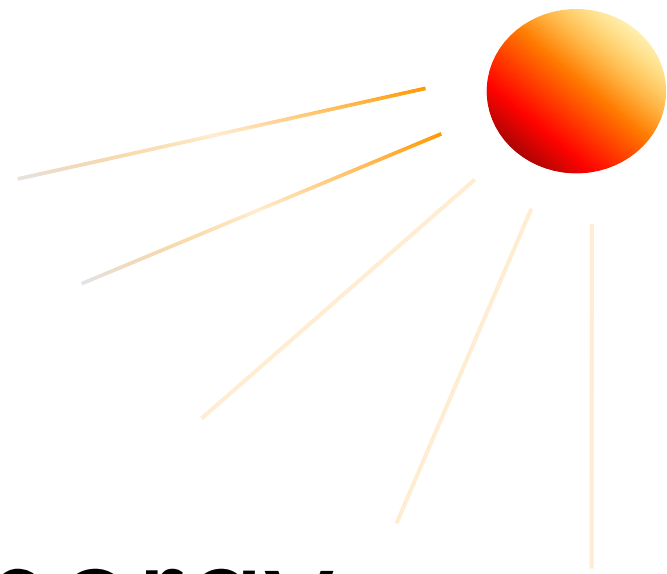
Laboratory for Process Engineering,  
Environment, Biotechnology and Energy

# The sun

Yearly sum of global irradiation on a horizontal surface - Spain and Portugal

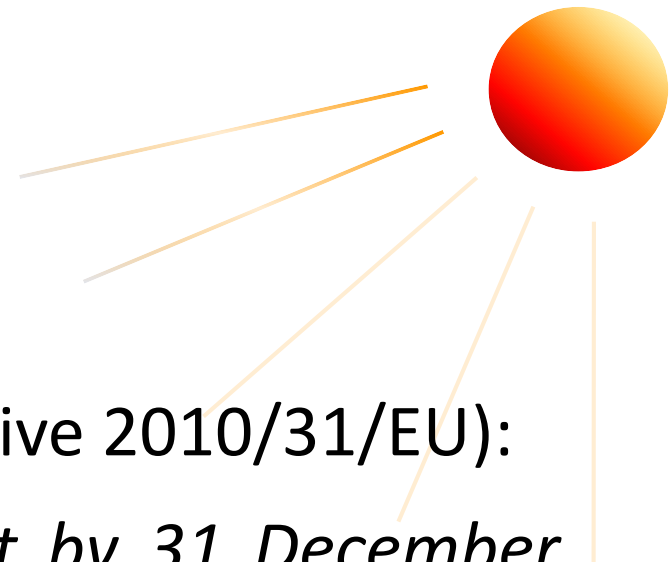


kWh·year<sup>-1</sup>



# Nearly zero-energy buildings

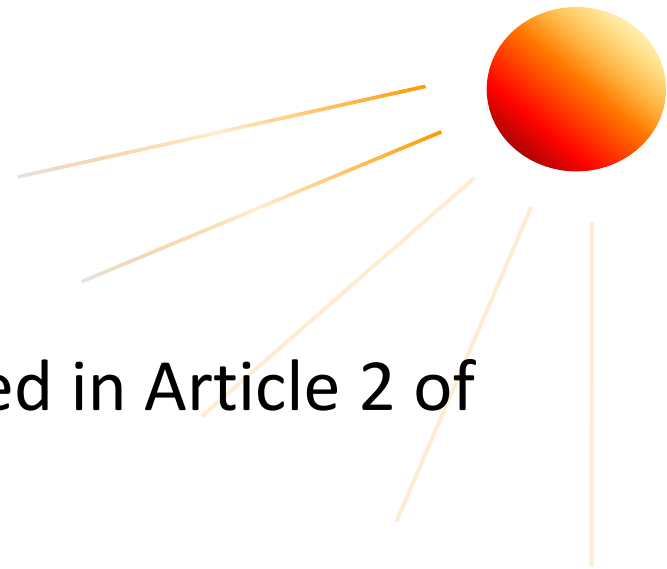
# Nearly zero-energy buildings



Nearly zero-energy buildings – (Directive 2010/31/EU):

*“Member States shall ensure that by 31 December 2020 all new buildings are nearly zero-energy buildings; and after 31 December 2018, new buildings occupied and owned by public authorities are nearly zero-energy buildings”.*

# Nearly zero-energy buildings



A nearly zero-energy building is defined in Article 2 of the EPBD recast as:

*“The nearly zero or very low amount of energy required should be covered to a **very significant extent by energy from renewable sources**, including energy from renewable sources **produced on-site or nearby**”.*

# Nearly zero-energy buildings

A great opportunity for my research? For my company?



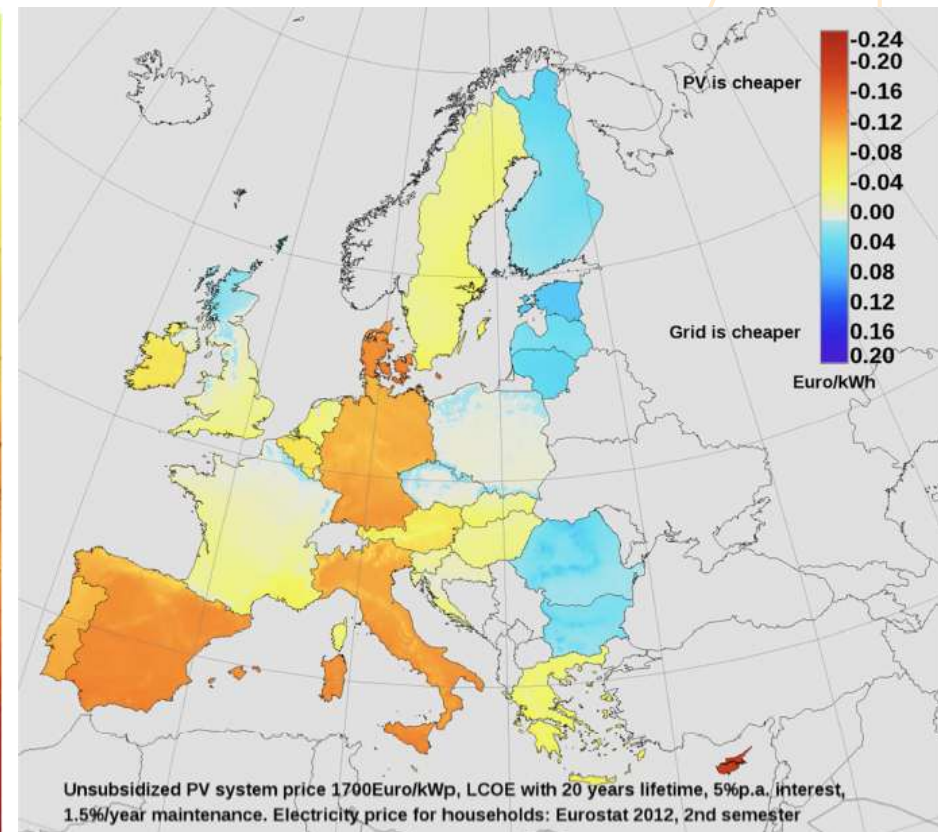
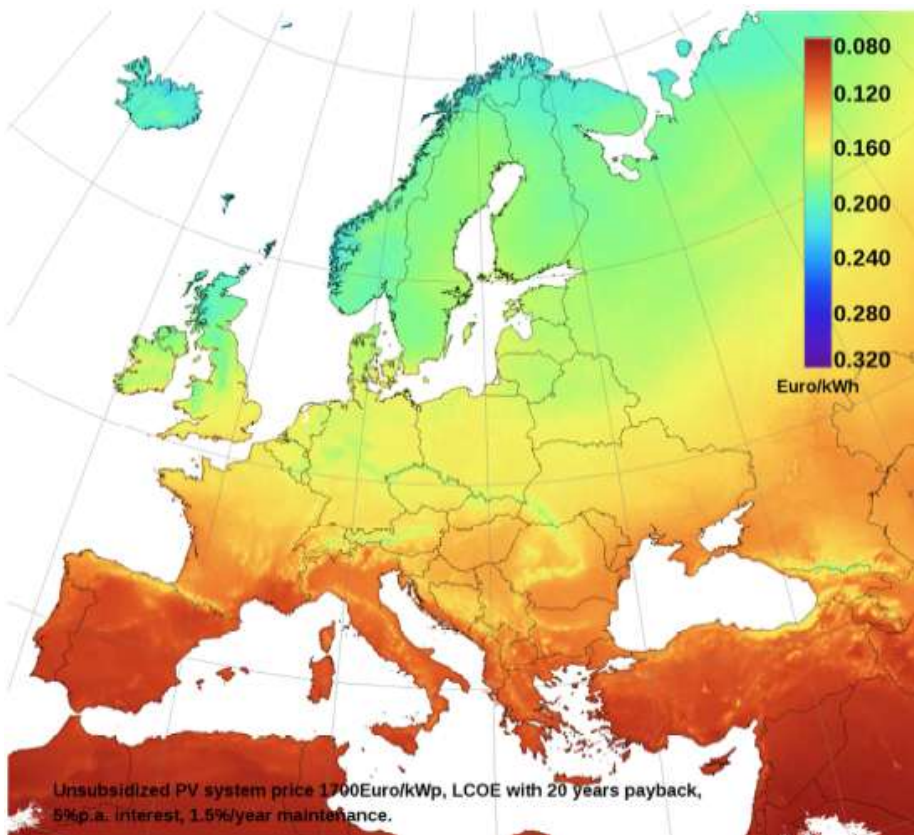


# Nearly zero-energy buildings

Levelled cost of electricity from photovoltaics:

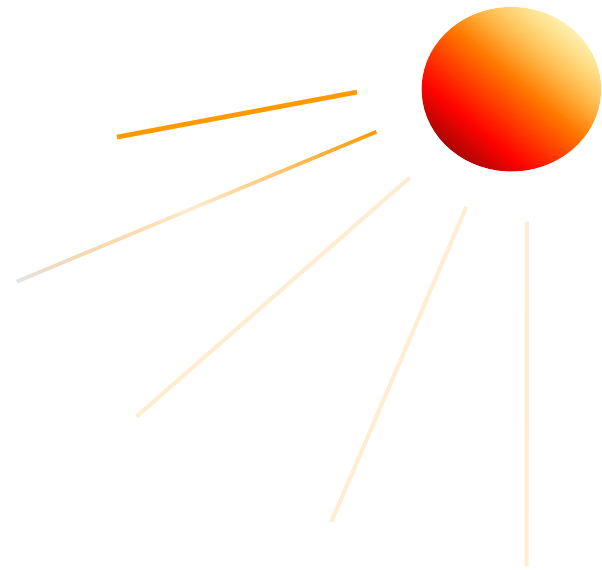
Photovoltaic electricity cost

Difference between the grid price and the PV electricity cost



Data from the EC of 2013

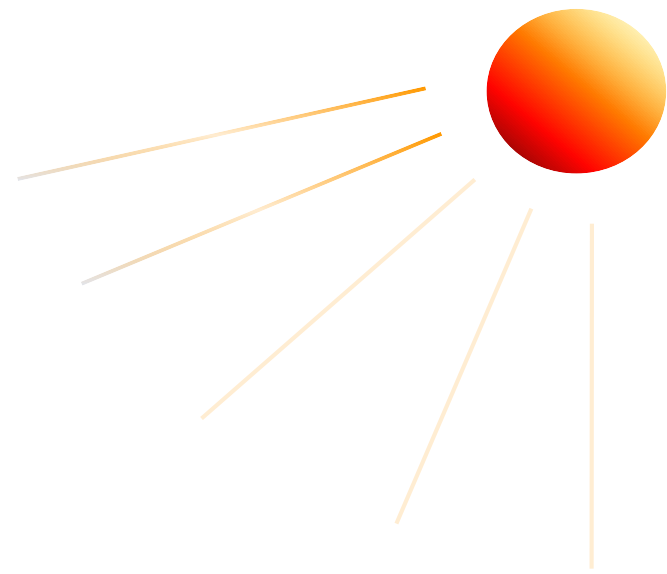
# Nearly zero-energy buildings



Local electricity storage is required because:

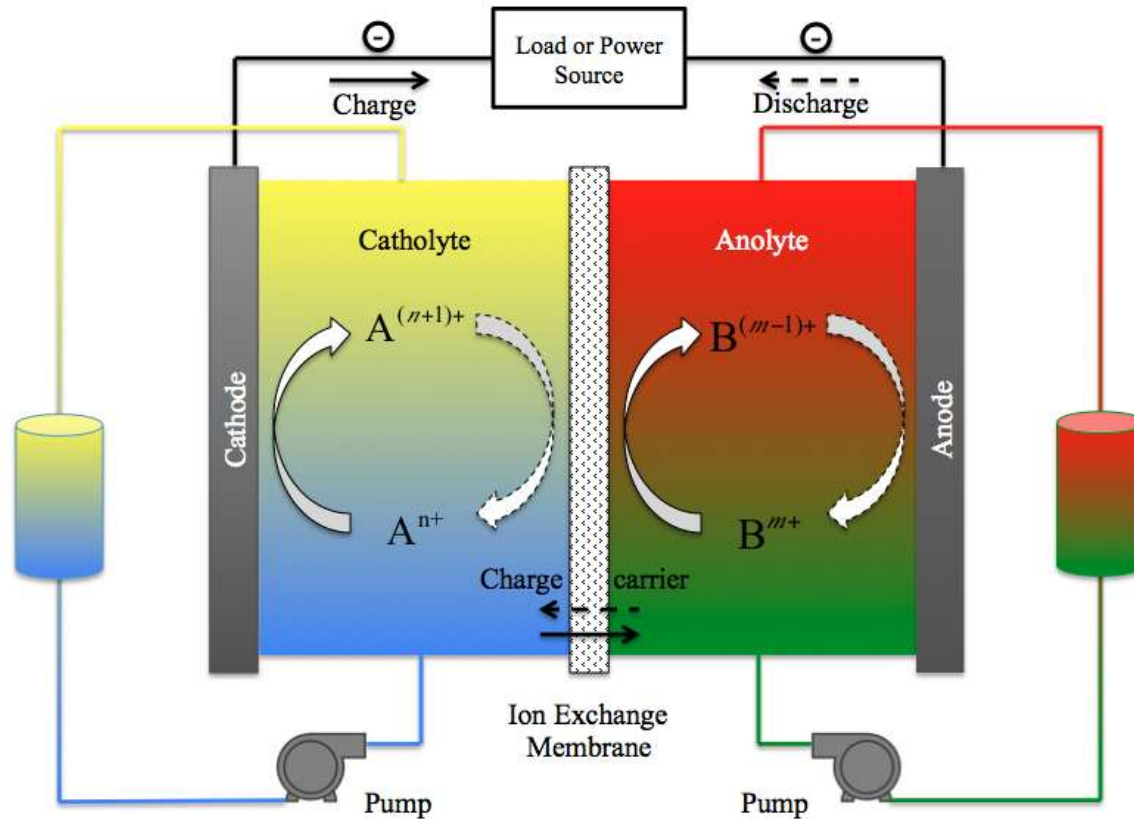
- ✓ Stabilizing the local (low potential) grid;
- ✓ Make the renewable electricity dispatchable;
- ✓ Make the production of renewable electricity more profitable
  - no feed-in tariffs are assumed.





# Redox flow battery

# Redox flow battery



## Charge

Positive (cathode):  $A^{n+} \rightarrow A^{(n+1)+} + e^{-}$

Negative (anode):  $B^{m+} + e^{-} \rightarrow B^{(m-1)}$

# Redox flow battery



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



Journal of Power Sources 160 (2006) 716–732



Review

## Redox flow cells for energy conversion

C. Ponce de León<sup>a,\*</sup>, A. Frías-Ferrer<sup>b</sup>, J. González-García<sup>b</sup>,  
D.A. Szánto<sup>c</sup>, F.C. Walsh<sup>a</sup>

### Charge

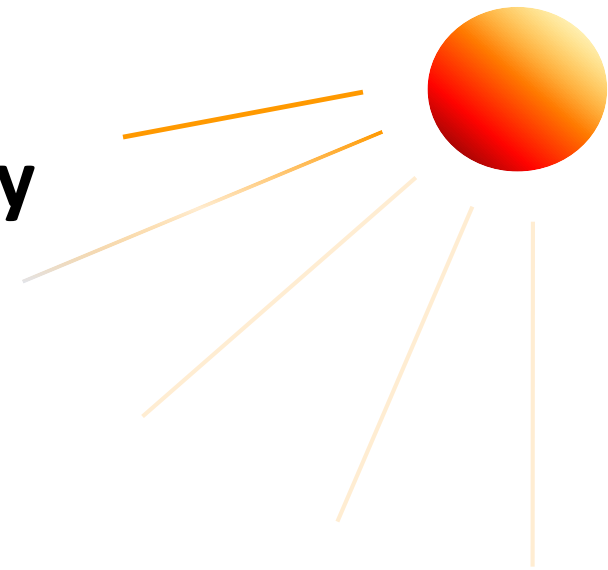
Positive (cathode):  $\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2\text{H}^+ + \text{e}^-$ ,  $E^0 = -0.99 \text{ V}_{\text{SHE}}$

Negative (anode):  $\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$ ,  $E^0 = -0.26 \text{ V}_{\text{SHE}}$

$2\text{VOSO}_4 + 2\text{H}_2\text{O} + \text{V}_2(\text{SO}_4)_3 \rightarrow 2(\text{VO}_2)_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 2\text{VSO}_4$ ,  $E^0 = -1.25 \text{ V}$

# Redox flow battery

## Concept and Efficiency



### Vanadium RFB

Specific energy	$\sim 30 \text{ Wh}\cdot\text{kg}^{-1}$ (compared Li-ion, $150 \text{ Wh}\cdot\text{kg}^{-1}$ , gasoline $\approx 12.5 \text{ kWh}\cdot\text{kg}^{-1}$ )
Energy density	$\sim 30 \text{ Wh}\cdot\text{L}^{-1}$
Charge/discharge efficiency	80 %
Time durability	20 years
Nominal cell voltage	1.25 V
Expected energy storage cost per cycle	3 ¢€·kWh <sup>-1</sup>

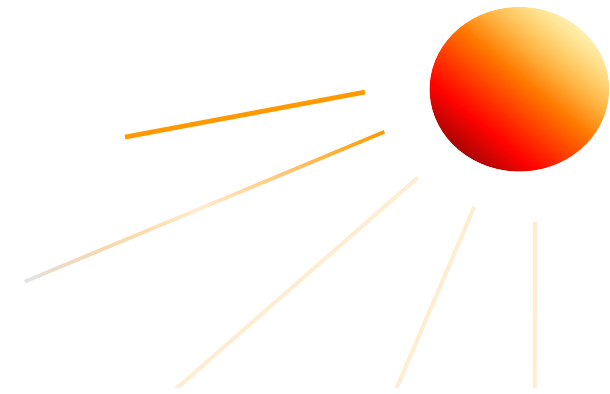
# Redox flow battery

200 kW all vanadium redox flow battery by Gildemeister

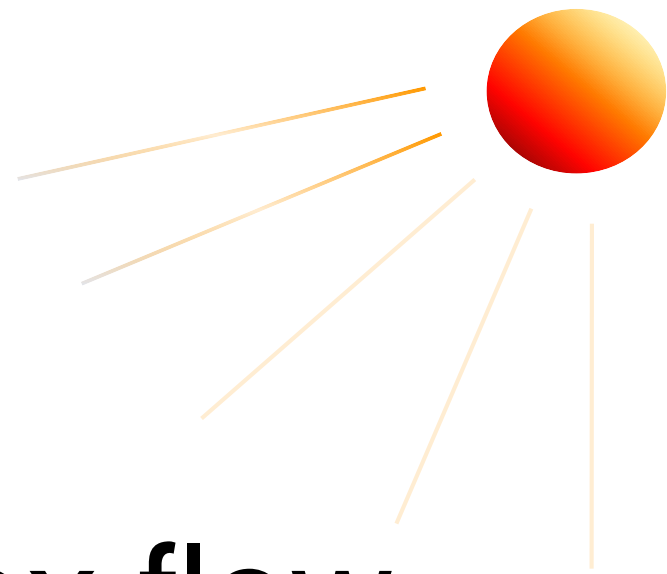


# Redox flow battery

Gildemeister – CellCube

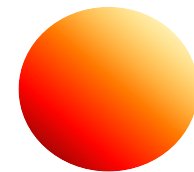






# Emerging redox flow battery

# Emerging redox flow battery technologies



9,10-anthraquinone-2,7-disulphonic acid (AQDS) – bromide acid redox flow battery:

- ✓ 99 % cyclic efficiency!
- ✓ Maximum power density:  $600 \text{ mW} \cdot \text{cm}^{-2}$ ;
- ✓ Current density:  $1.3 \text{ A} \cdot \text{cm}^{-2}$ ;
- ✓ Nominal cell voltage: ca. 0.8 V;
- ✓ Energy density:  $50 \text{ Wh} \cdot \text{L}^{-1}$ ;
- ✓ Cost: 70 % cheaper than vanadium

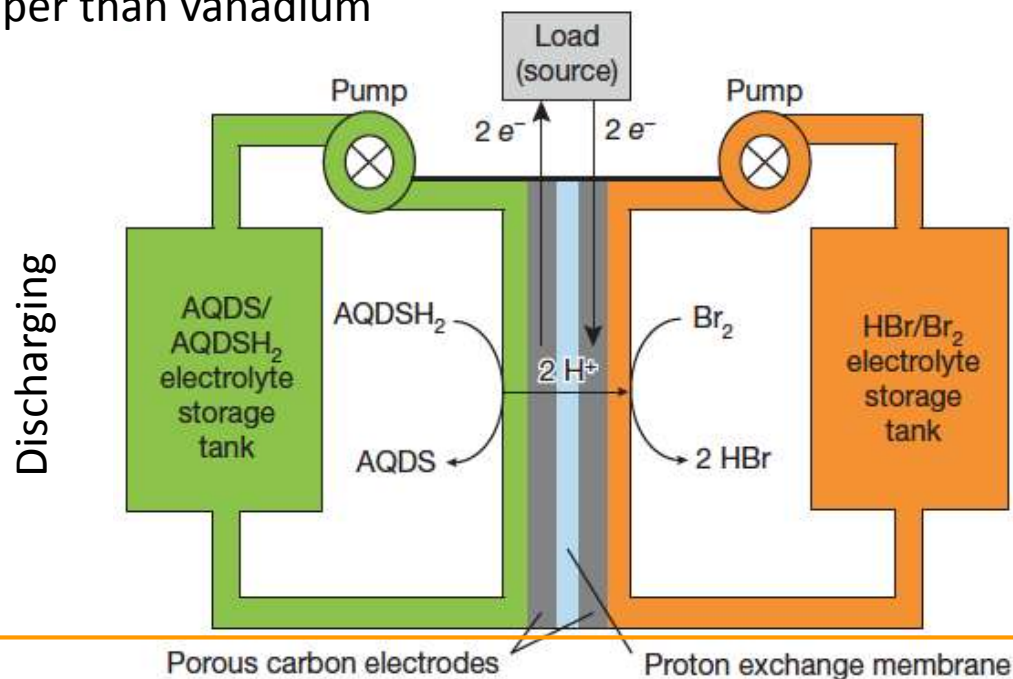
A metal-free organic–inorganic aqueous flow battery

Brian Huskinson, Michael P. Marshak, Changwon Suh, Süleyman Er, Michael R. Gerhardt, Cooper J. Galvin, Xudong Chen, Alán Aspuru-Guzik, Roy G. Gordon & Michael J. Aziz

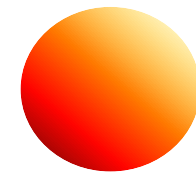
Affiliations | Contributions | Corresponding author

Nature 505, 195–198 (09 January 2014) | doi:10.1038/nature12909

2014

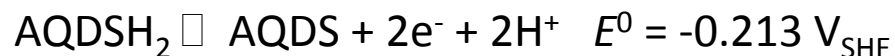
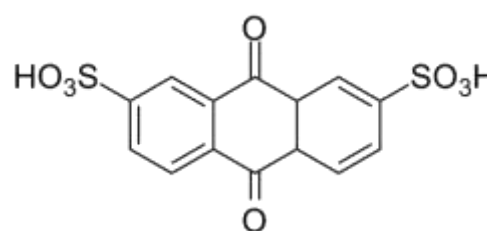
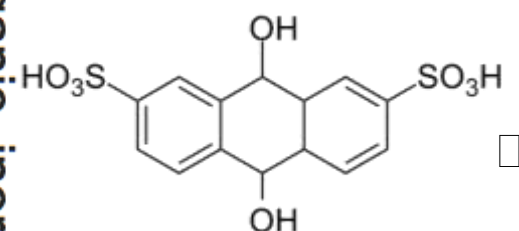


# Emerging redox flow battery technologies



Anthraquinone (9,10-anthraquinone-2,7-disulphonic acid - AQDS)

Discharge



$$\Delta V = 0.86 \text{ V}$$

## A metal-free organic-inorganic aqueous flow battery

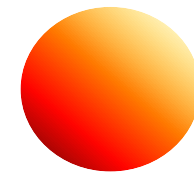
Brian Huskinson, Michael P. Marshak, Changwon Suh, Süleyman Er, Michael R. Gerhardt, Cooper J. Galvin, Xudong Chen, Alán Aspuru-Guzik, Roy G. Gordon & Michael J. Aziz

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# Emerging redox flow battery technologies

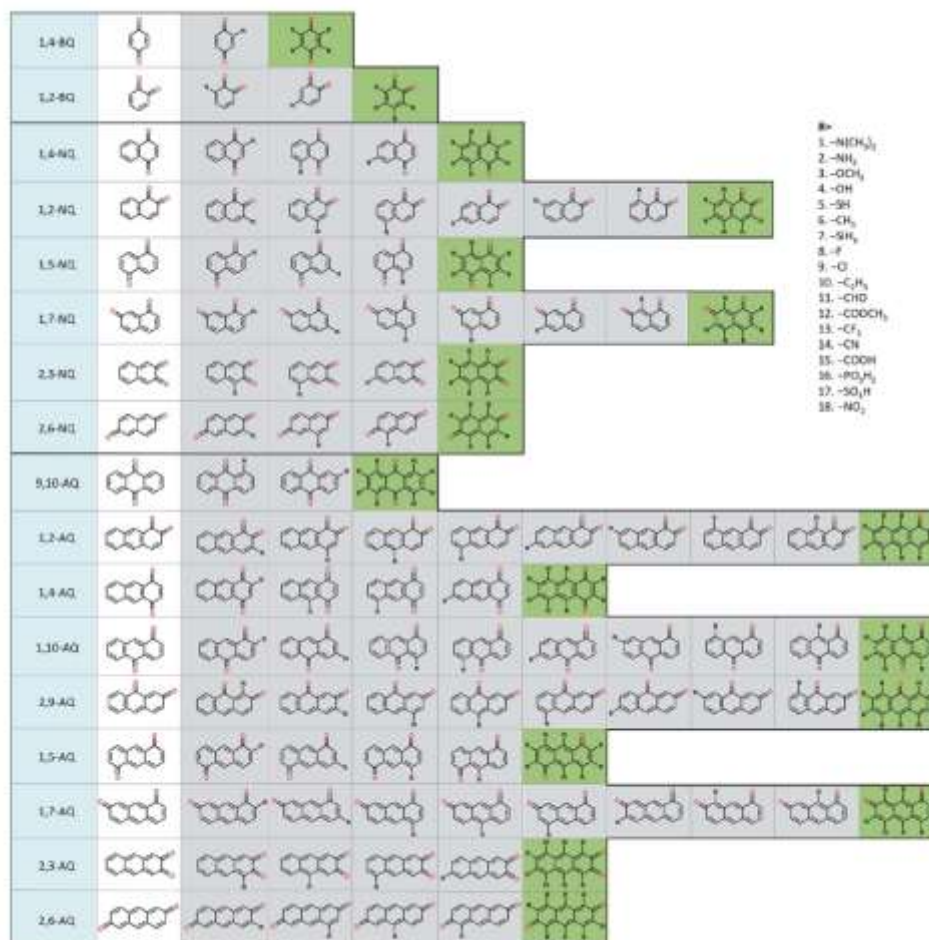


## Computational design of molecules for an all-quinone redox flow battery†

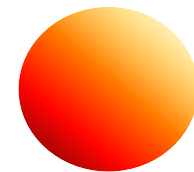
Cite this: Chem. Sci., 2015, 6, 1885



Süleyman Er,<sup>‡ab</sup> Changwon Suh,<sup>‡c</sup> Michael P. Marshak<sup>a</sup> and Alan Aspuru-Guzik<sup>\*a</sup>



# Emerging redox flow battery technologies



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## Computational design of molecules for an all-quinone redox flow battery†

Süleyman Er,<sup>a,b</sup> Changwon Suh,<sup>a,b</sup> Michael P. Marshak<sup>a</sup> and Alan Aspuru-Guzik<sup>a,\*</sup>

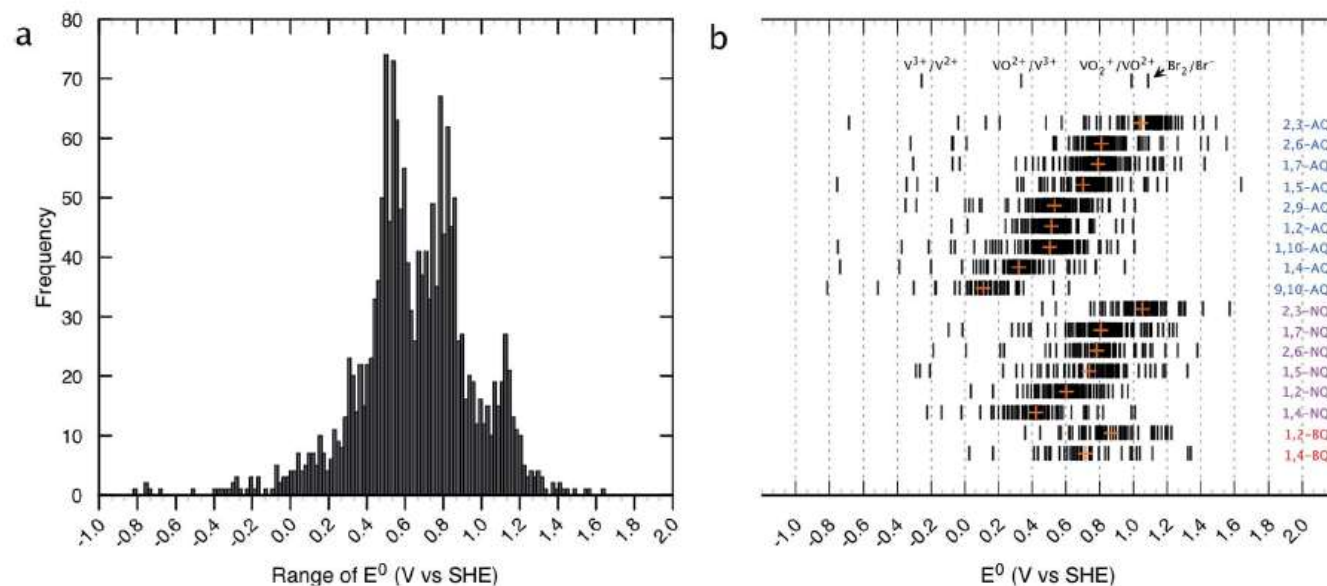


Fig. 2 Distribution of HT screened quinone/hydroquinone redox couples. (a) A histogram of theoretically predicted  $E^0$  (V vs. SHE). Number of bins and width of the histogram are 130 and 0.1 V, respectively. (b)  $E^0$  windows for the different classes of quinones. The orange crosses show the mean values of  $E^0$  for each class. Redox potentials of the conventional inorganic AFB redox couples are noted for comparison.<sup>43</sup>

Chemical  
Science

EDGE ARTICLE



Cite this: Chem. Sci., 2015, 6, 885

2015



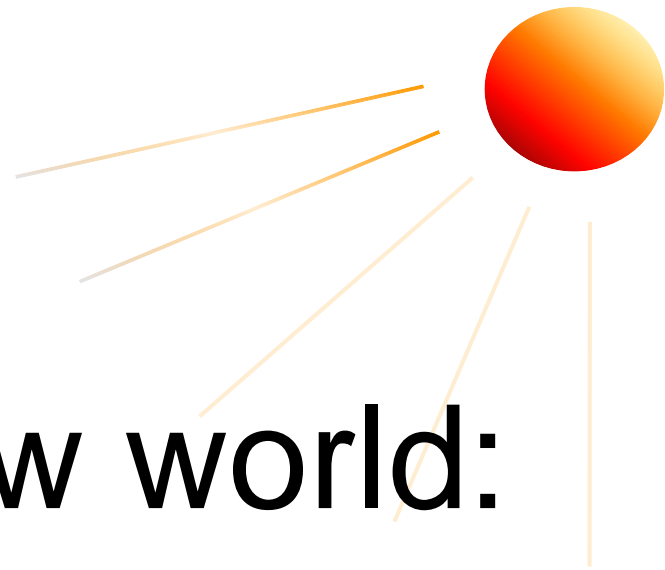
Moving beyond the obvious



## Moving beyond the obvious

**Would be it possible to convert directly  
the sunlight into storable energy?**





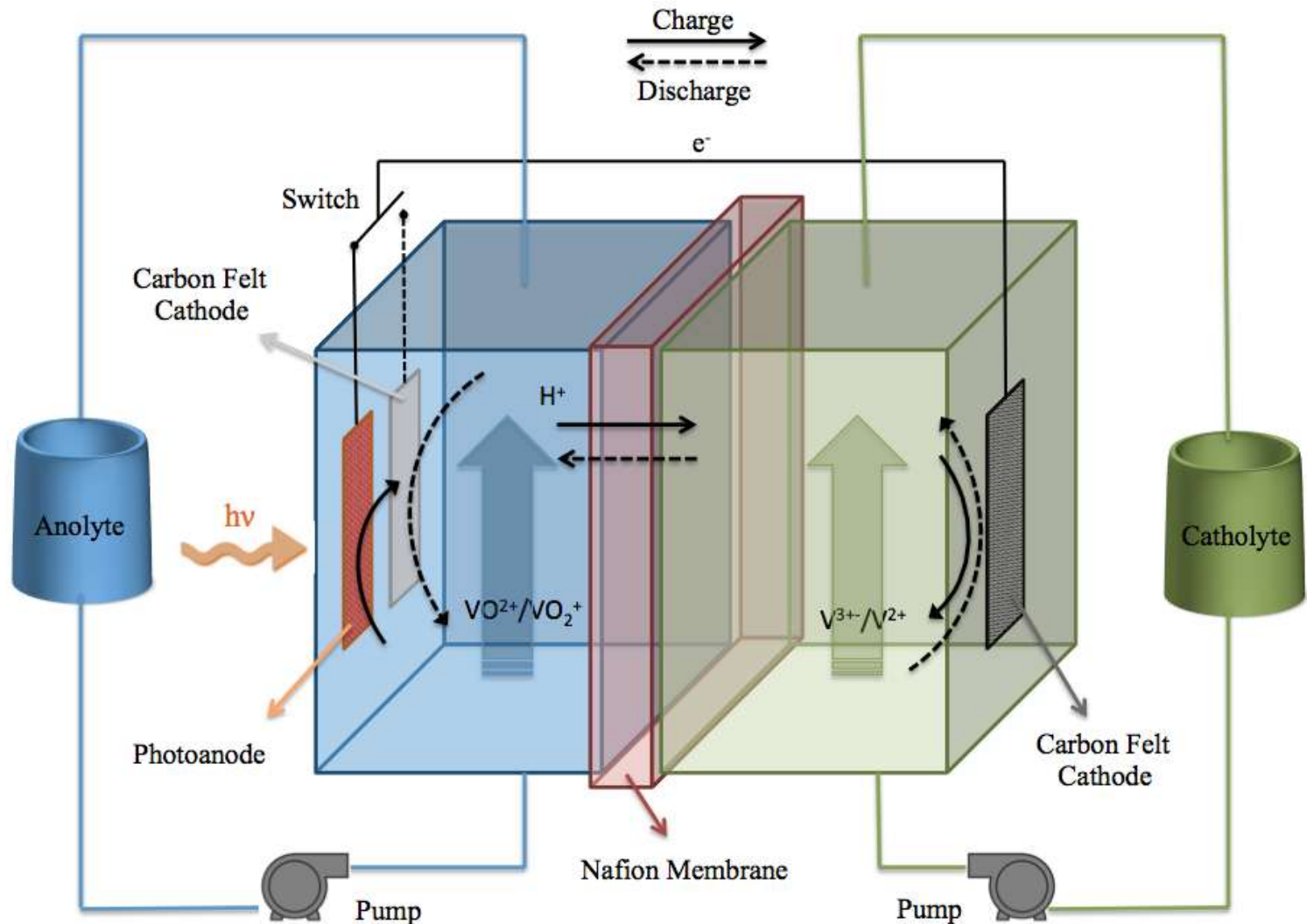
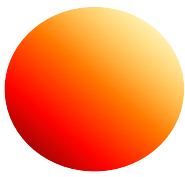
A completely new world:

**Solar chargeable redox  
flow battery**

# Moving beyond the obvious

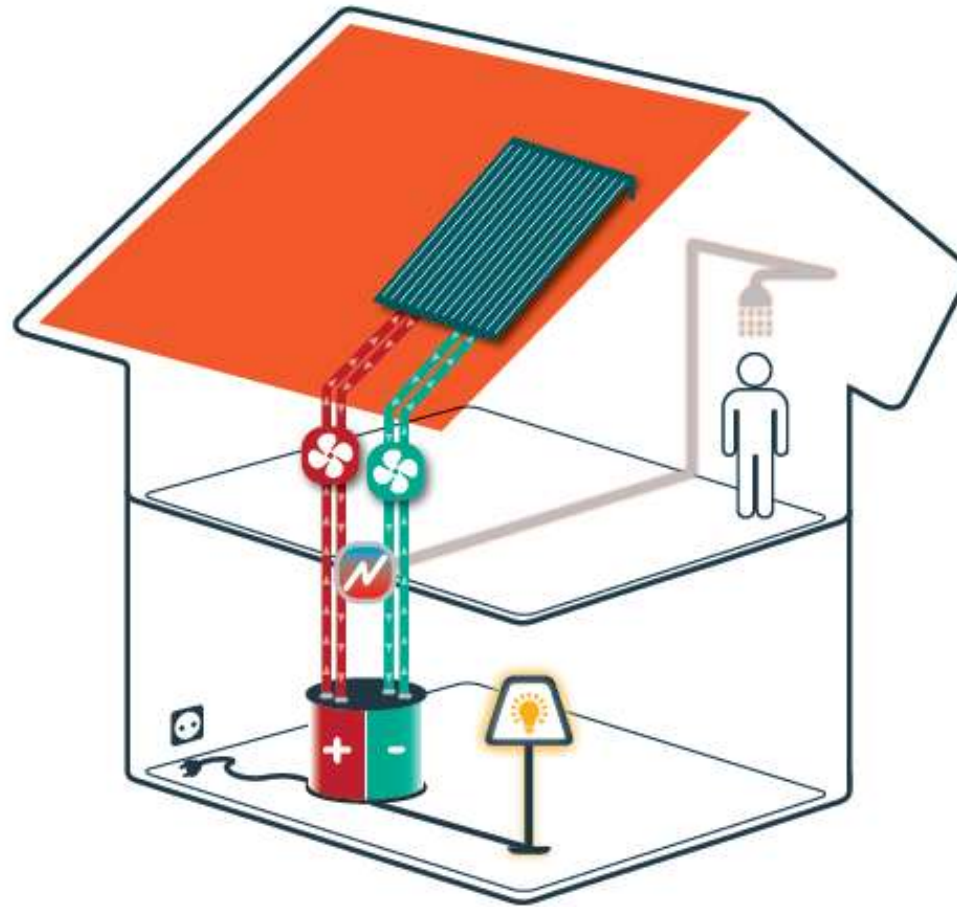


# Solar chargeable redox flow battery - concept



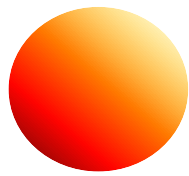
# Solar chargeable redox flow battery - concept

## The concept - cogeneration



**Sunlight** -> storable electrochemical energy and heat

# Solar chargeable redox flow battery - concept



## Expected figures

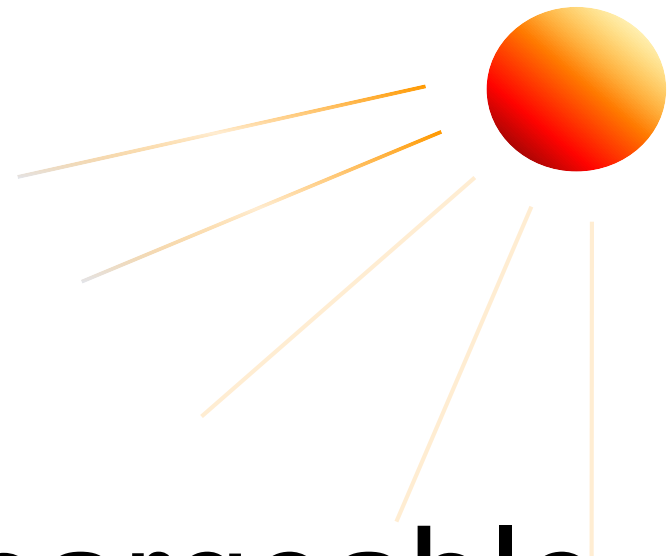
Overall energy efficiency	~80 %
Electricity storage cost per cycle	3 ¢€/kWh
Time durability	20 years
Nominal cell voltage	1.3 V

## Solar rechargeable redox flow battery

Specific power (assumed $\eta = 10 \%$ )	100 Wp·m <sup>-2</sup>
Specific energy (assumed 1.6 MWh·year <sup>-1</sup> ·m <sup>-2</sup> )	4.4 kWh·day <sup>-1</sup> ·m <sup>-2</sup>
Volume of electrolyte produced per day (assumed 30 Wh·kg <sup>-1</sup> )	29 L·day <sup>-1</sup> ·m <sup>-2</sup>
Typical electricity house - consumption per day	9 kWh -> 300 L -> <b>20 m<sup>2</sup></b>
Heat production	61 kWh·day <sup>-1</sup> *

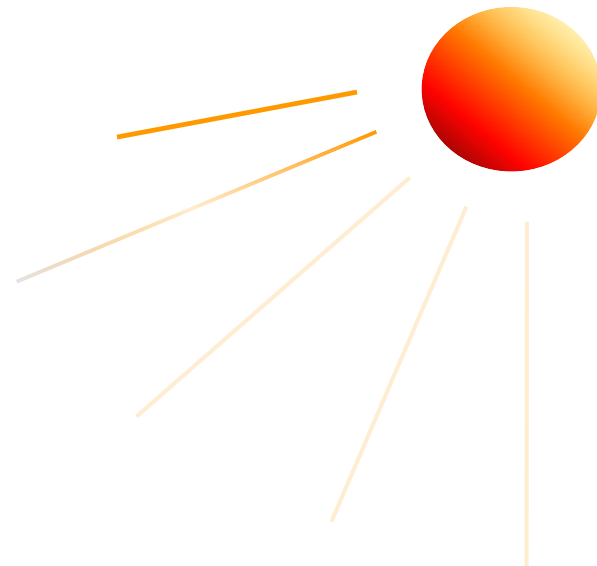
\*Enough for heating 960 L of water from 5 °C to 60 °C assuming  $\eta = 70 \%$





# Vanadium solar chargeable redox flow battery - experimentation

# Redox flow battery



## Chosen redox system

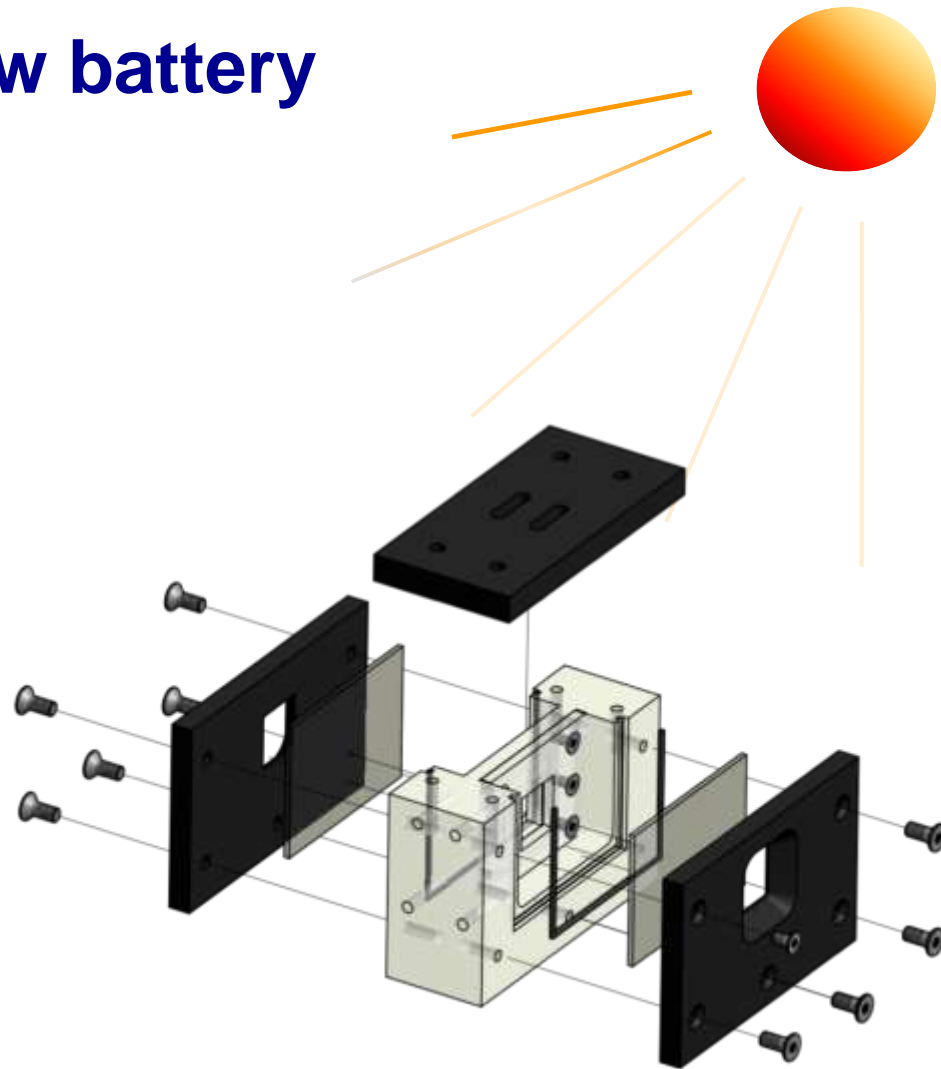
### Charge

Positive (cathode):  $V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-$ ,  $E^0 = -0.34 V_{SHE}$

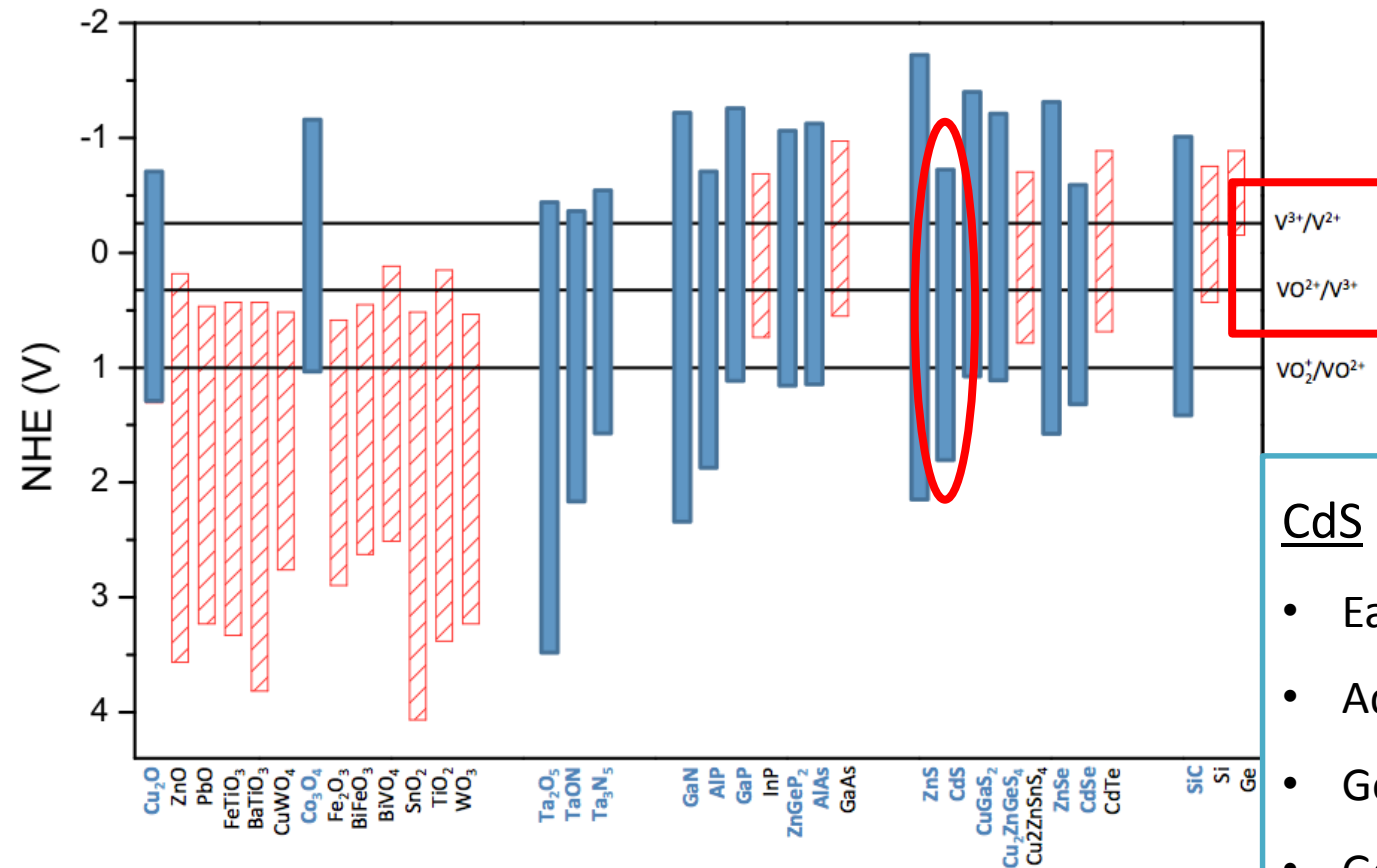
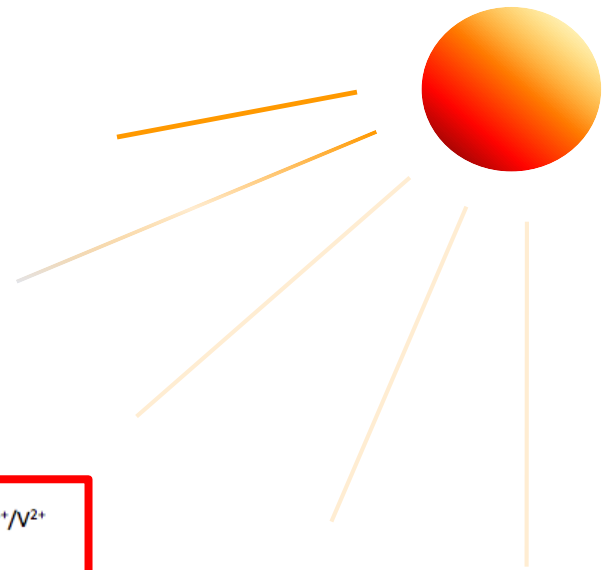
Negative (anode):  $V^{3+} + e^- \rightarrow V^{2+}$ ,  $E^0 = -0.26 V_{SHE}$

$V_2(SO_4)_3 + H_2O \rightarrow VOSO_4 + H_2SO_4 + VSO_4$ ,  $E^0 = -0.60 V$

# Solar chargeable redox flow battery



# Solar chargeable redox flow battery



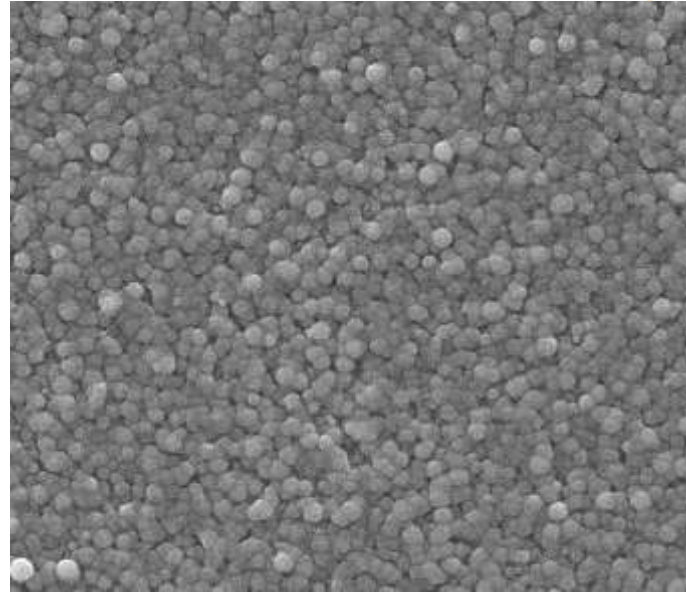
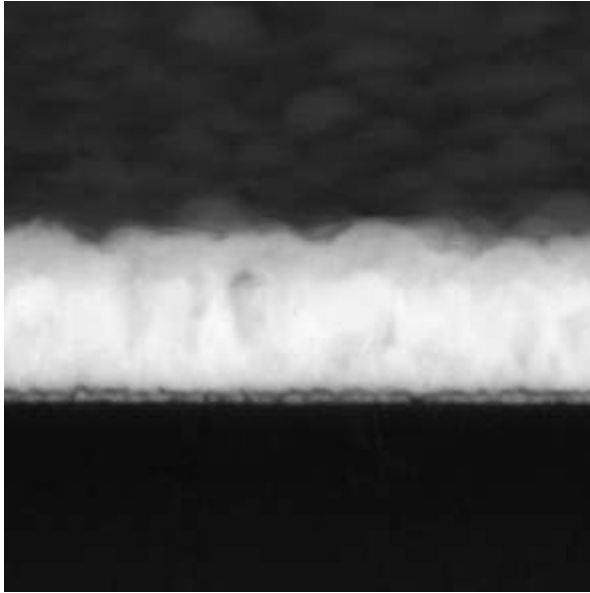
## CdS

- Easy to prepare
- Adequate band gap
- Good light absorption
- Good electrical conductivity

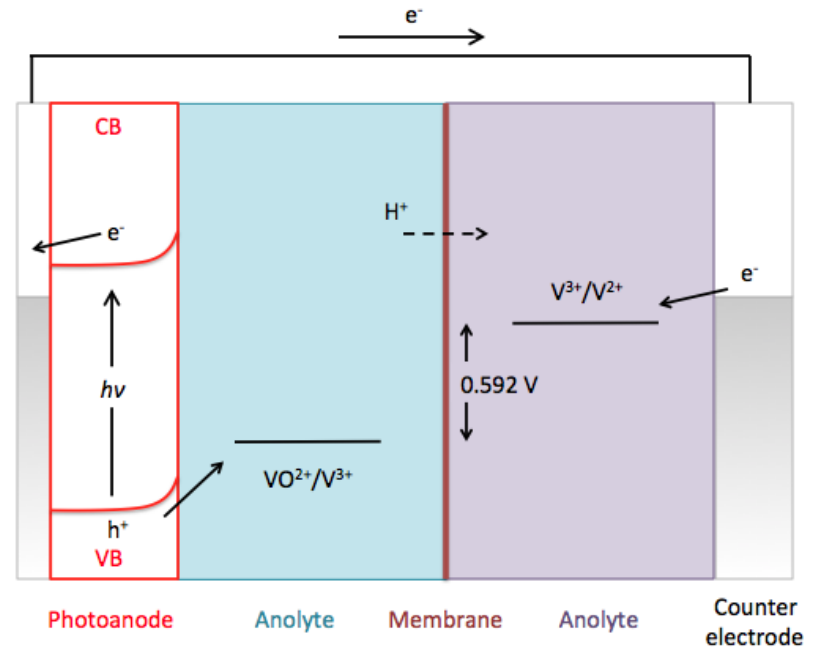
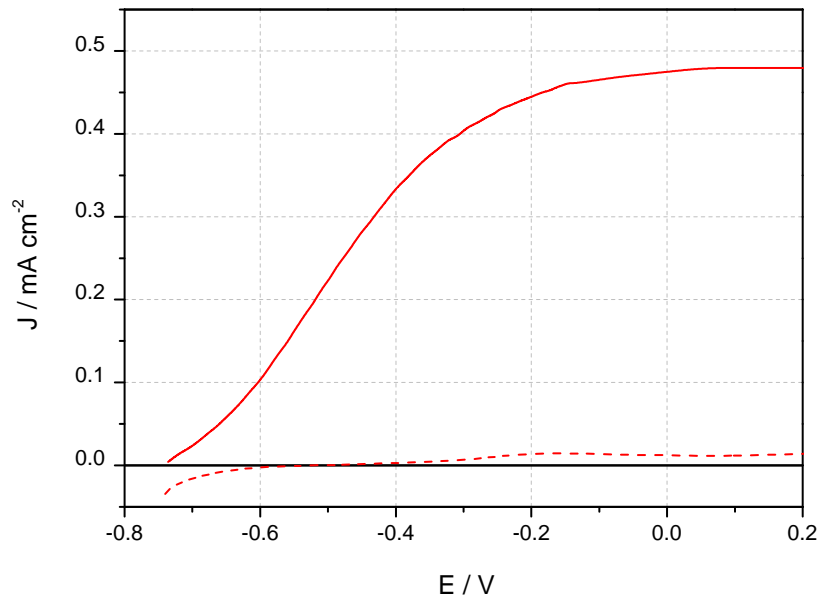
Band edge positions for selected semiconductors at pH 0, together with vanadium redox potentials.

# Solar chargeable redox flow battery

CdS photoelectrode



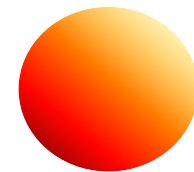
# Solar chargeable redox flow battery



1.5 AM light and dark conditions (in  $0.2 \text{ M V}^{3+} / 2 \text{ M H}_2\text{SO}_4$  electrolyte) of a CdS photoanode



# Solar chargeable redox flow battery

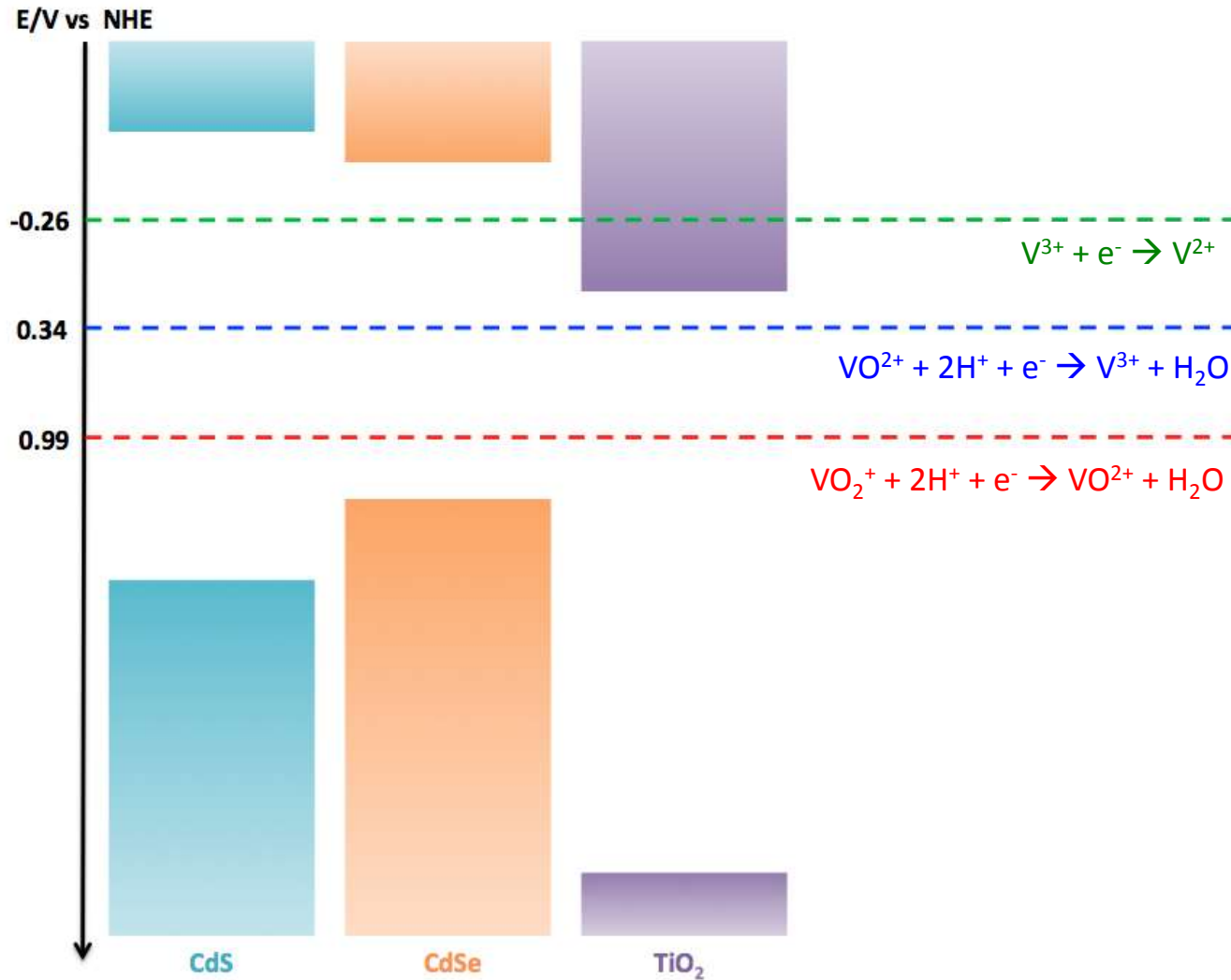


CdS photoelectrode with a CdSe protective layer

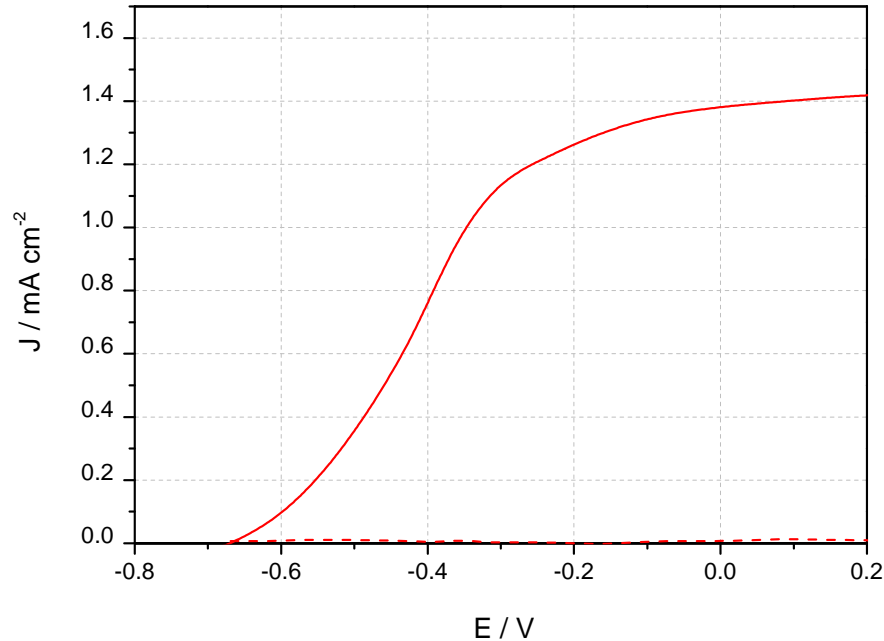
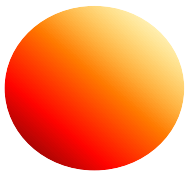
Sample ID	Anode/Cathode	Configuration	$J$ at 0 V (mA/cm <sup>2</sup> )	$J/J_0$ after 5 min at 0 V (%)
1	Anode	Bare CdS	0.47	46
<b>2</b>	<b>Anode</b>	<b>CdS/200 nm CdSe</b>	<b>1.40</b>	<b>86</b>
3	Anode	CdS/200 nm CdSe (back illumination)	0.66	81
4	Anode	TiO <sub>2</sub> (paste)/CdS/200 nm CdSe	0.12	63
5	Cathode	CdS/200 nm CdSe/100 nm TiO <sub>2</sub> (ALD)	-1.90	47
6	Anode	CdS/200 nm CdSe/5 nm TiO <sub>2</sub> (ALD)	0.40	26

# Solar chargeable redox flow battery

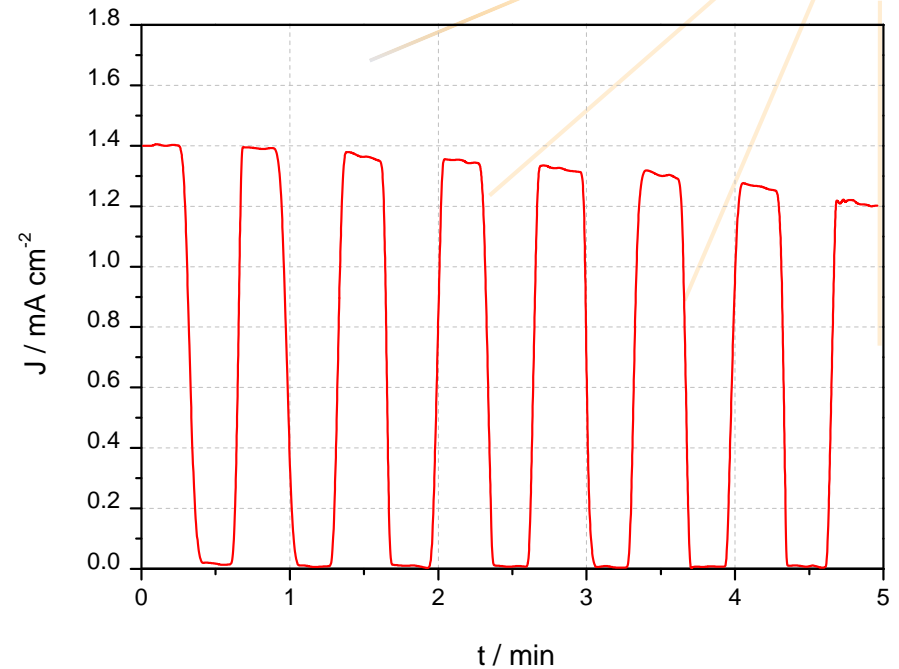
CdS photoelectrode with a CdSe protective layer



# Solar chargeable redox flow battery



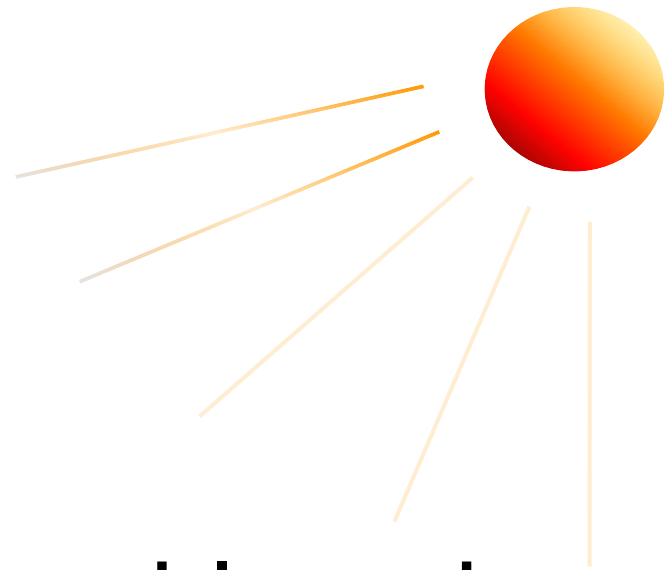
I-V curve of a Cd/CdSe photoelectrode sample



Stability of a Cd/CdSe sample

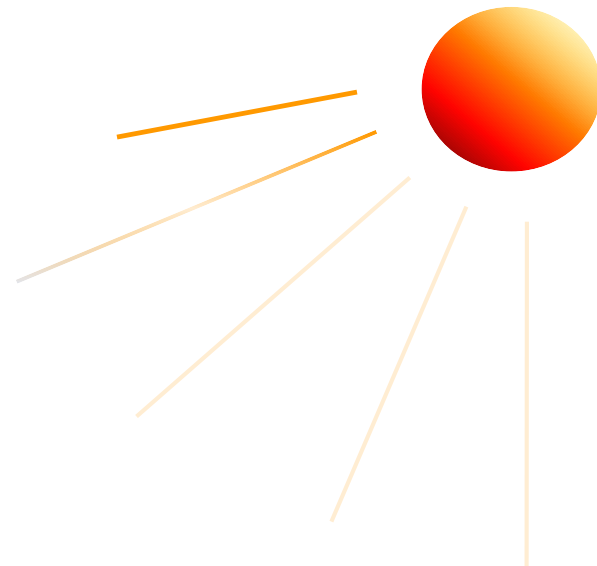
## CdS / CdSe configuration

- ✓ Better light absorption in the visible range
- ✓ Higher photocurrents
- ✓ Improved stability



All vanadium solar chargeable redox  
flow battery – tandem arrangement

# Redox flow battery



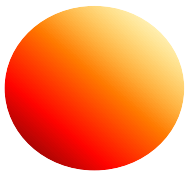
## Charge

Positive (cathode):  $\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2\text{H}^+ + \text{e}^-$ ,  $E^0 = -0.99 \text{ V}_{\text{SHE}}$

Negative (anode):  $\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$ ,  $E^0 = -0.26 \text{ V}_{\text{SHE}}$

$2\text{VOSO}_4 + 2\text{H}_2\text{O} + \text{V}_2(\text{SO}_4)_3 \rightarrow 2(\text{VO}_2)_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 2\text{VSO}_4$ ,  $E^0 = -1.25 \text{ V}$

# Solar chargeable redox flow battery

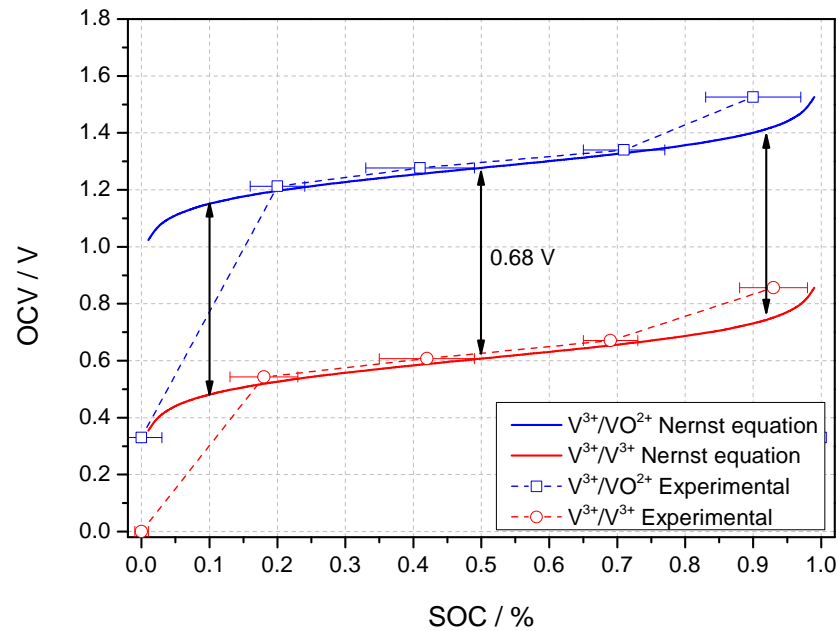
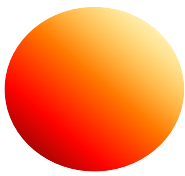


Dye sensitized solar cells (DSC) :

- ✓ Considered organic PV type.
- ✓ Maximum energy efficiency: 12 %.
- + Low cost and high efficiency harvesting diffuse light.
- + Very aesthetic for BIPV.
- + Uses abundant and non toxic materials.
- Moderate efficiencies.
- Not yet commercial.

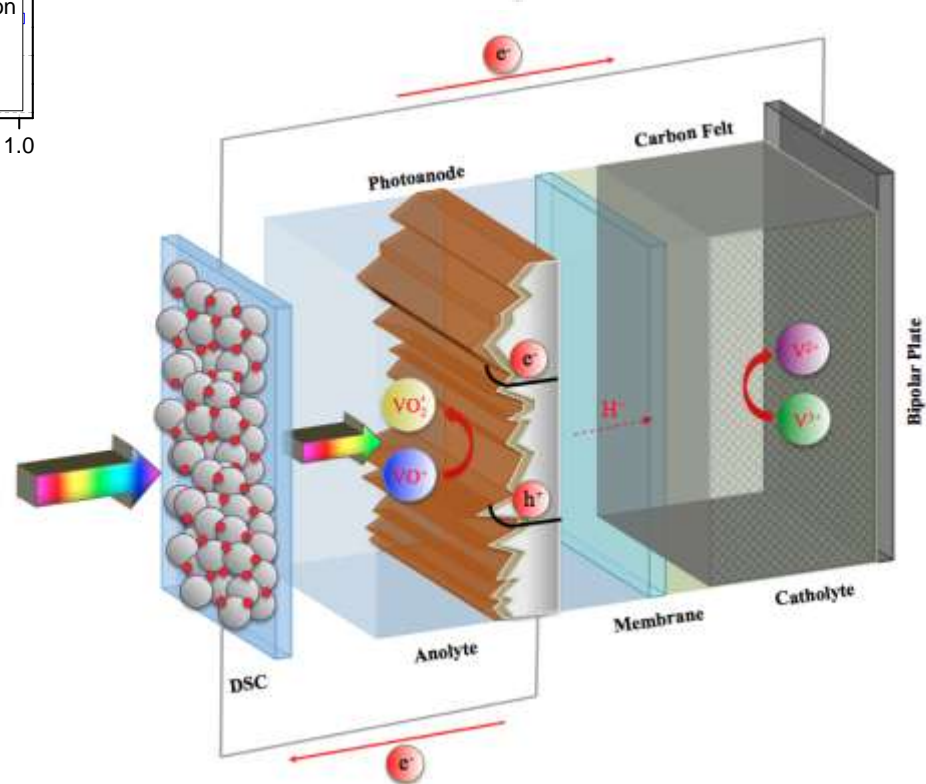


# Solar chargeable redox flow battery

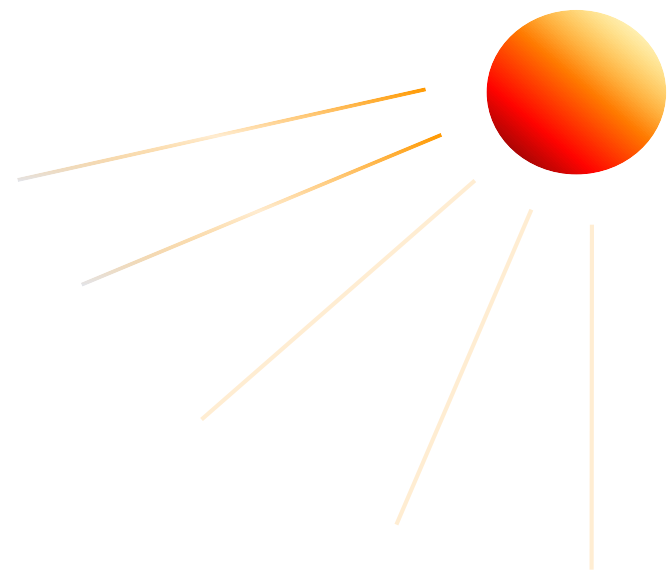


0.68 V extra to charge a standard all vanadium redox flow battery

Tandem Configuration

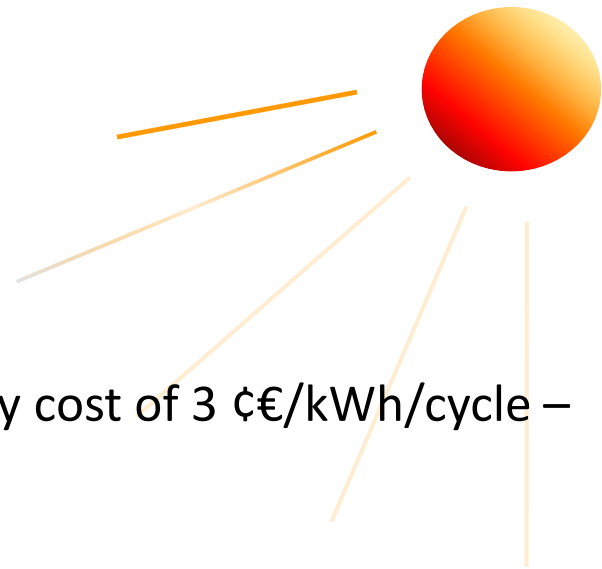






# Conclusions

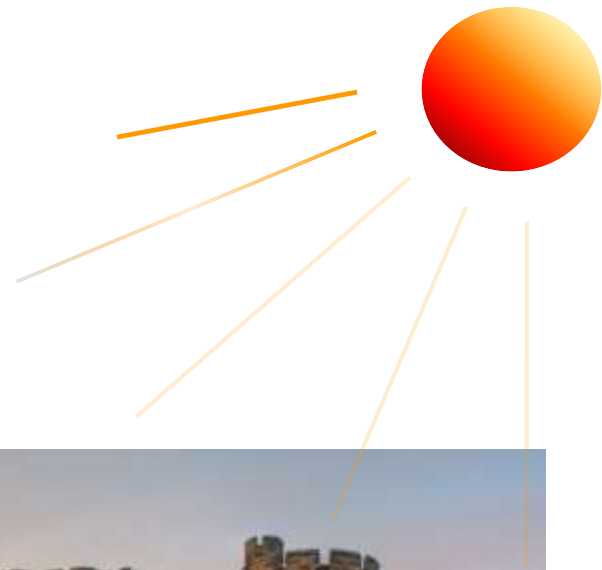
# Conclusions & outlook



- ✓ Redox flow batteries will soon have a storage electricity cost of 3 ¢€/kWh/cycle – the lowest local storage cost technology;
- ✓ Photoelectrochemical cells are better used to store sunlight energy into RFB electrolytes!
- ✓ Tandem arrangements of PEC + DSC proved to charge completely a all vanadium battery;
- ✓ New are more exciting systems are around the corner and soon they will be reported.

# A new world

**My home is my castle:  
I need sunlight but no grid!**



# Acknowledgements

João Azevedo

José Nogueira

Tânia Lopes

Luísa Andrade

Marta Boaventura

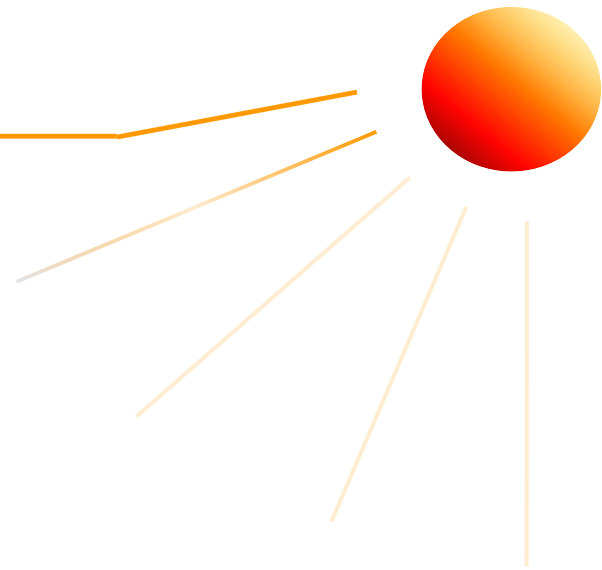
Verena Stockhausen

Jorge Pinto

André Monteiro

and the whole research team.





**Questions are welcome**

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